Supporting Information

Explanation of "Silver Effects" in Gold(I)-Catalyzed Hydroalkoxylation of Alkynes

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Supporting information

1. General information

General information about NMR spectra

- NMR spectra immediately follow experimental description and are presented in such a way as to allow clear observation of all essential features. The areas not containing essential information were cut off. The parts of spectra are separated by a double line. In rare cases, small parts of spectra may be inserted (put over) a bigger part. Vertical scaling within the parts of a given spectrum might differ in order to improve the quality of presentation. Horizontal scaling is constant for parallel fragments within each double line bordered area. In all cases the solvent and the number of experiment are indicated on the spectra in the left corner. In most cases the date when an experiment was performed is also given on the spectra on the right corner. Selected assignments are given on the spectra near the corresponding signals. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker Avance II 400, at 299.3 K using standard 5 mm NMR tubes.

- Proton chemical shifts are calibrated to the residual proton resonance of the solvent: $CDCl_3$ (δH 7.25), CD_2Cl_2 (δH 5.32), CD_3OD (δH 3.30). The corresponding solvent resonance is always marked on the spectra. It is not given only if the corresponding area was cut out.

- Phosphorus chemical shifts are not calibrated and given as is, but the scale is constant for all experiments in a given solvent. Residual proton resonance observed on our Bruker Avance II 400 spectrometer was as follows: $CDCl_3$ (δH 7.27), CD_2Cl_2 (δH 5.35), MeOD (δH 3.32). Therefore, all phosphorus resonances given in this paper are expected to be wrong (exaggerated) by +0.02 ppm for $CDCl_3$ and CD_2Cl_2, +0.02 for MeOD.

General information about experimental conditions

- All experiments were routinely performed at room temperature and without inert atmosphere (under open air).
- Most experiments were performed simply in NMR tubes. Most ^{1}H spectra were accumulated in 32 scans (acquisition time 2:14 min), ^{31}P NMR in 128 scans (acquisition time 3:41 min). In kinetic experiments ^{1}H spectra were accumulated most often in 8 or 16 scans (acquisition times 32 sec, 1:07 min).
- Times correspond to the middle of spectrum acquisition periods with an accuracy of ±1 sec.

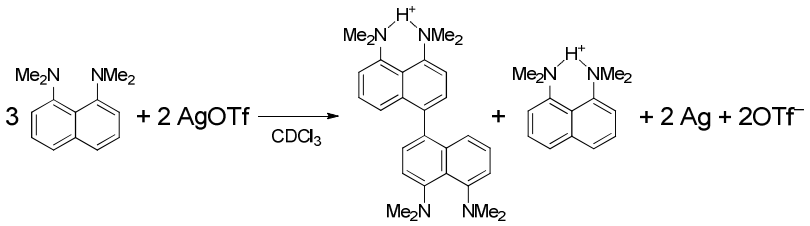
Miscellaneous general information

All deuterated solvents used in the reactions were used as received. All solvents used in the reactions were purified before use. Dry Et_2O, THF, were distilled from sodium and benzophenone, whereas dry CH_2Cl_2, DMF, methanol, ethyl acetate, benzene, toluene and triethylamine were distilled from CaH_2. Distilled petroleum ether with a boiling range of 40–60 °C was used. All commercially available compounds (Acros, Aldrich, Fluka, Merck) were used without purification (unless indicated). $Ph_3PAuNCMe^+$ SbF_6^- (**1**) and *L2*AuNCMe$^+$ SbF_6^- (**2**, *L2* = 2-(di-*tert*-butylphosphino)biphenyl) were synthesized by known methods.[1] Alcohols **S1**, **S4**, **S5**, and 6-phenylhexyn-5-ol-1 were synthesized by literature methods.[2]

2. Synthesis and properties of argento vinyl gold species

Initially, we applied the same conditions that were previously used for the successful synthesis of diaurated species in our laboratory. This implies the use of proton sponge (PrSp) as a base. However, we found that PrSp is incompatible with AgOTf, as it causes fast reduction of AgOTf and formation of silver as a black precipitate. Therefore, the synthesis of argento vinyl gold is unavoidably accompanied by this undesired redox side process. Use of the redox stable base *t*Bu_2Py instead of PrSp led to successful results.

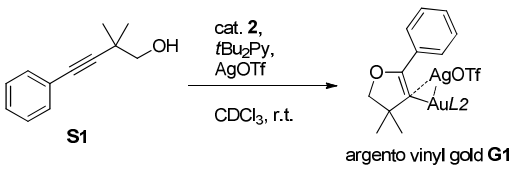
2226. Instant reduction of AgOTf by PrSp.



To a suspension of AgOTf (1.79 mg) in $CDCl_3$ (0.55 mL) was added PrSp (2.62 mg). A black precipitate immediately formed. The identity of monoprotonated diprotonsponge salt and reaction stoichiometry was confirmed by NMR. This salt converts to the known free base by treatment of the reaction mixture with K_2CO_3.

2.1. Experiments at room temperature

2209. Preparation of an enriched sample of argento vinyl gold **G1**. Characterization of argento vinyl gold by NMR in situ under conditions of fast and slow silver exchange either at room or at low temperature.



S1 argento vinyl gold **G1**

Complex **2** (33.4 mg, 43.3 µmol) and AgOTf (12.86 mg, 50.0 µmol) were dissolved in THF-*d8* (73 mg). In another vial, 2,2-dimethyl-4-phenylbutyn-3-ol-1 (**S1**) (8.71 mg, 50 µmol) and tBu$_2$Py (12.3 mg, 64 µmol) were dissolved in $CDCl_3$ (0.5 mL). This solution was added to the solution containing silver and gold. Additional $CDCl_3$ (ca. 0.2 mL) was used for complete transfer. A slightly exothermic reaction occurred and a white crystalline precipitate quickly appeared (pure tBu$_2$PyH$^+$ SbF$_6^-$). The mixture was left to stay for 2–3 min and then the solution was filtered using a Pasteur pipette with a piece of cotton to transfer the filtrate into an NMR tube. Additional $CDCl_3$ (ca. 0.2 mL) was used for complete transfer. A small random amount of CF_3CO_2Me was added to the content to enable quantitative determination of OTf$^-$ and silver using a combination of ^{1}H and ^{19}F NMR spectra. NMR analysis indicated complete formation of argento vinyl gold species **G1** as a single organometallic product. The total quantity of OTf$^-$ was established to be 1.2 equiv with regard to gold. Also the remaining amount of 2,2-dimethyl-4-phenylbutyn-3-ol-1 was estimated to be 0.12 equiv. The amount of enol ether product was found to be just 0.02 equiv. This means, that formation of argento vinyl gold species occurred very cleanly, almost free of competitive hydroalkoxylation. Since alcohol, silver and base were still available in the mixture, an additional amount of complex **2** (2.91 mg, 3.77 µmol, 0.087 equiv) was added to convert the residual starting materials to argento vinyl gold species. Then the reaction mixture was filtered though celite and an NMR spectrum was recorded to establish an Au:Ag ratio of 1:1.11, which is close to the stoichiometric 1:1. Then freshly powdered $NaHCO_3$ (5 mg) was added and the reaction mixture was shaken for a brief period and filtered through celite. An NMR spectrum confirmed complete neutralization of residual tBu$_2$PyH$^+$. After this, the solution was evaporated till dryness. Attempts were made to obtain crystalline product by recrystallization from various solvent systems (CH_2Cl_2/pentane, CH_2Cl_2/benzene, CH_2Cl_2/Et_2O, MeOH, MeOH/ Et_2O) but all attempts failed to deliver any crystalline material. The final solution was evaporated, the residue was evaporated one time with $CDCl_3$ and a final NMR spectrum was recorded to find that argento vinyl gold survived all crystallization attempts with only minor decomposition (max 10%). It was further characterized in solution by ^{1}H, ^{31}P, ^{19}F, ^{13}C, HH-COSY, HMBC, HSQC, DEPT spectra.

The following spectra (Figures S1 and S2) show the presence of impurities tBu$_2$Py (0.29 equiv) and enol ether (0.1 equiv) with regard to argento vinyl gold. Other impurities can be disregarded (<4%).

Signals of tBu$_2$Py and enol ether were verified separately. Signals of tBu$_2$Py: ^{1}H NMR: 7.49 t, 7.07 d, 1.34 s. ^{13}C NMR: 167.4, 135.9, 115.2, 37.6, 30.1. Signals of enol ether: ^{1}H NMR: 7.53 d, 7.24–7.34 m, 4.14 s, 1.21 s; ^{13}C NMR: 154.1, 131.2, 128.20, 128.15, 125.0, 107.1, 82.6, 43.6, 27.8.

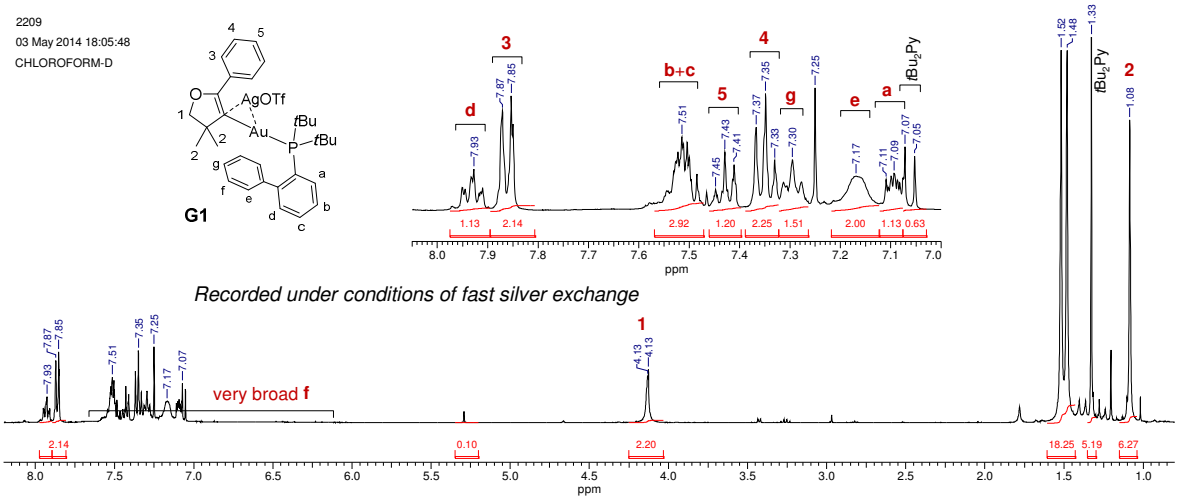


Figure S1. ^{1}H NMR spectrum of **G1** in $CDCl_3$.

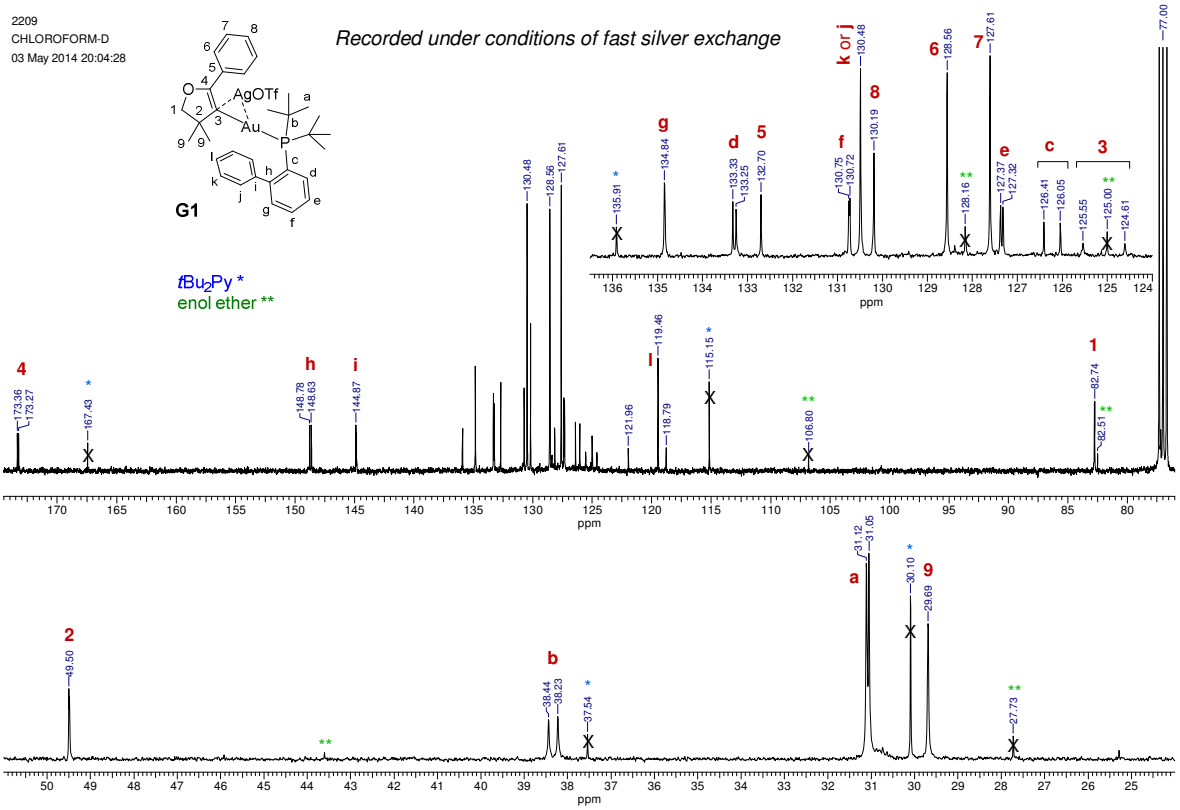


Figure S2. ^{13}C NMR spectrum of **G1** in $CDCl_3$.

Argento vinyl gold **G1**. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.91-7.95 (m, 1H), 7.86 (d, *J*=7.1 Hz, 2H), 7.48-7.54 (m, 2H), 7.43 (t, *J*=7.3 Hz, 1H), 7.35 (t, *J*=7.3 Hz, 2H), 7.30 (t, *J*=7.3 Hz, 1H), 7.17 (br, 2H), 7.07-7.11 (m, 1H), ~6-8 (br, 2H, Ar), 4.13 (s, 2H), 1.50 (d, *J*=15.2 Hz, 18H), 1.08 (s, 6H). **^{13}C NMR** ($CDCl_3$): one signal responsible for 2 CH of the phenyl ring of the ligand is missing because of line broadening: δ = 173.3 (d, *J*=9.1 Hz), 148.7 (d, *J*=14.9 Hz), 144.8 (d, *J*=5.8 Hz), 134.8, 133.3 (d, *J*=7.4 Hz), 132.7, 130.7 (d, *J*=2.5 Hz), 130.5, 130.2, 128.6, 127.6, 127.3 (d, *J*=5.8 Hz), 126.2 (d, *J*=36.5 Hz), 125.1 (d, *J*=93.7 Hz), 115.6-125.1 (q,

J=319.3 Hz, OTf), 119.5, 82.7 (d, *J*=3.3 Hz), 49.5 (d, *J*=1.7 Hz), 38.3 (d, *J*=21.6 Hz), 31.1 (*J*=6.6 Hz), 29.7. **^{31}P NMR** ($CDCl_3$): δ = 65.81. **^{19}F NMR** ($CDCl_3$): –77.57.

The aforementioned spectra (Figures S1 and S2) were recorded under conditions of fast silver exchange, which is caused by the residual AgOTf in solution. The occurrence of the silver exchange is confirmed by observation of split spectra of **G1**, that were obtained under conditions excluding any AgOTf at room temperature or simply at low temperature (e.g. –50 °C). The split spectra directly reveal the unsymmetrical structure of the **G1** molecule. Every time when a fresh AgOTf (as a solution in minimum THF) was added to the solution initially showing a split spectrum, the spectrum is simplified indicating resumption of the fast silver exchange. The ^{31}P resonance recorded in the absence of the residual AgOTf is identical to the resonance in the presence of AgOTf.

The most reliable method to exclude AgOTf and achieve a split spectrum of **G1** is the treatment of the solution by portions of PrSp under NMR control until all the residual AgOTf is gone (the reduction of AgOTf by PrSp takes place instantly). This moment is evident by the persisting signal of residual free PrSp at 2.8 ppm. The excess of PrSp will also reduce the silver at **G1**, but much slower.

In the presence of CaH_2 which is routinely used in our practice to simply create anhydrous conditions in situ, the spectrum of **G1** also becomes split. Presumably, CaH_2 destroyed the residual free AgOTf in solution (this is suggested by the darkening of the suspension). The best spectrum recorded under these conditions is shown below (Figure S3). **G1** is unreactive towards CaH_2. Assignments were confirmed by HH-COSY. Note, that the aromatic protons **e** and **f** appear as pairs of slightly broad signals (doublets: **e**, **e'**; triplets: **f**, **f'**). However, treatment with CaH_2 to remove silver is not a reliable method. It seems the reduction under heterogeneous conditions can remove only sufficiently low amount of silver likely due to limitations of the surface capacity. Therefore, the split spectrum of **G1** was not always reproduced.

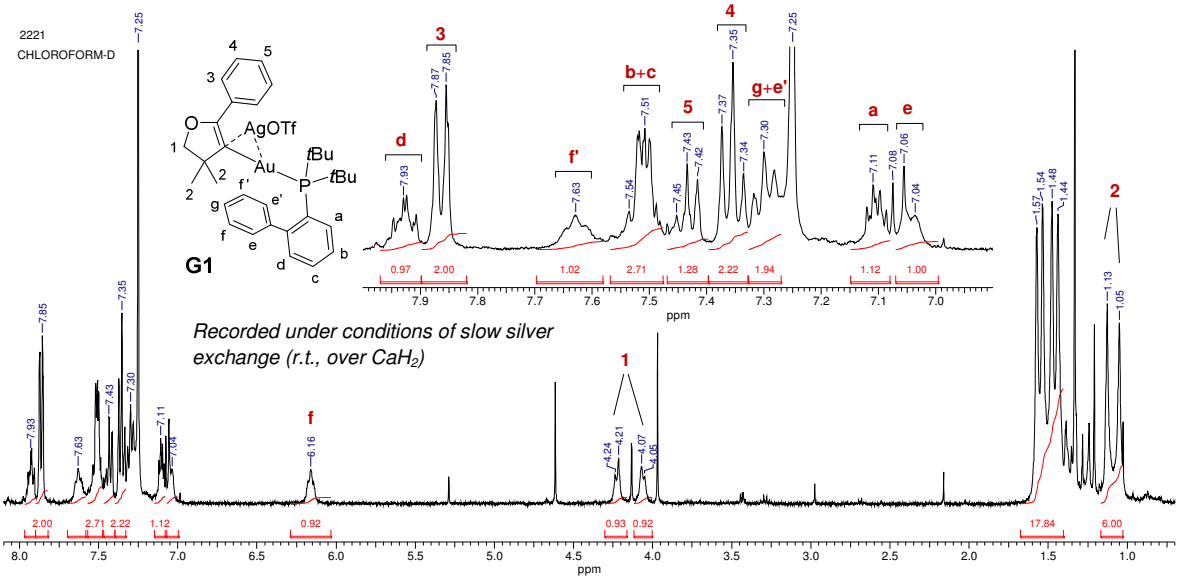


Figure S3. ^{1}H NMR spectrum of **G1** in $CDCl_3$ in the presence of CaH_2.

The following ^{13}C spectrum was recorded on 600 MHz instrument at –20 °C (Figure S4).

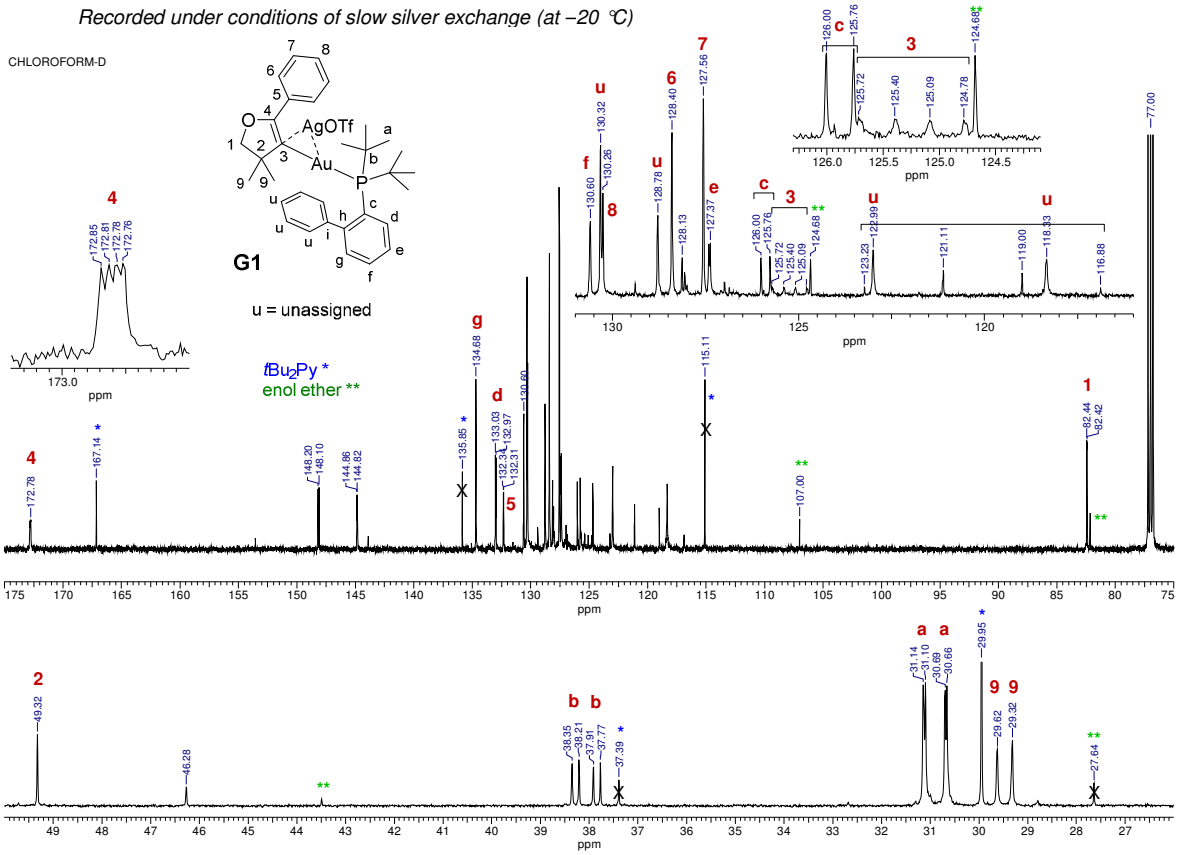


Figure S4. ^{13}C NMR spectrum of **G1** in $CDCl_3$ at –20 °C.

Analysis of ^{13}C NMR spectrum revealed the following notable differences in peak multiplicity in ^{13}C spectra of **G1** recorded at r.t. and at –20 °C (corresponding to the conditions of fast and slow Ag exchange), Table S1:

Table S1. Relevant peaks in ^{13}C spectra of **G1**.

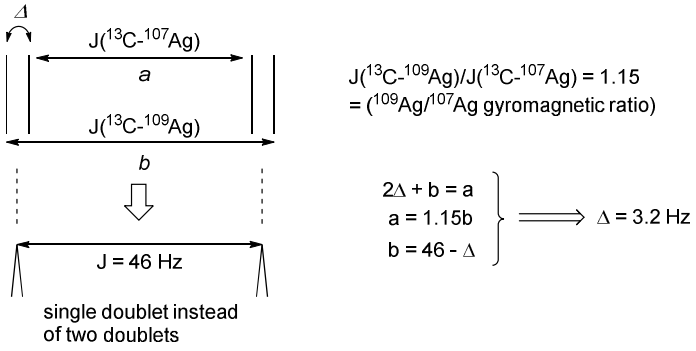
^{13}C assignment (see structure on Figure S4)	At r.t. (fast silver exchange)	At –20 °C (slow silver exchange)
C-3	125.1 (d, J_P = 93.7 Hz)	125.3 (dd, J_P = 95.1, J_{Ag} = 46 Hz)
C-4	173.3 (d, J_P=9.1 Hz)	172.3 (dd, J_P = 9, J_{Ag} = 4 Hz)
C-5	132.7 (s)	132.3 (d, J = 3.5 Hz)
C-9	29.7 (one singlet)	Two singlets: 29.6, 29.3
C-a	One doublet	Two doublets
C-b	One doublet	Two doublets

Discussion of differences in ^{13}C NMR:

1. Two new signals appeared in the ^{13}C spectrum –20 °C, attributable to **G1** but the assignments within the structure were not made.

2. The coupling of Ag was not confirmed by C{Ag} experiments. The assignment of Ag coupling is made from comparison of multiplicity in 13C spectra recorded at r.t. and at –20 °C, knowing the P coupling from the room temperature spectrum.

3. Carbon peaks C-3 and C-4 being doublets due to C–P coupling at r.t. increased the multiplicity at –20 °C, revealing the coupling with Ag. Theoretically, the signals due to coupling to Ag should be doubly doubled due to couplings to ^{109}Ag and ^{107}Ag (yielding overall 2 dd). However, the *J*(C–Ag) appears to be not large, and, for the largest coupling J_{Ag} = 46 Hz in our situation (peak at 125.3 ppm, C-3), the theoretical difference of 3.2 Hz between the doublet components may be calculated. Due to slightly broadened peaks this difference is not resolved into a double line, thus only a single common coupling is observed due to both ^{109}Ag and ^{107}Ag:

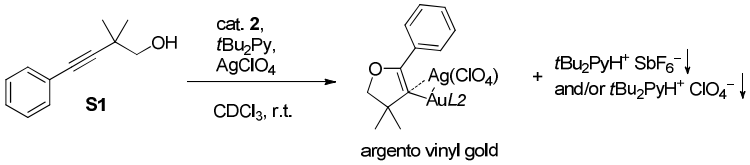


4. Carbon peaks C-1 and C-2 being doublets due to C–P coupling at r.t. did not increase the multiplicity at –20 °C, giving no coupling with Ag.

5. Carbon peak C-5 being a singlet at r.t has become a doublet. It is likely due to Ag coupling. But the P coupling cannot be excluded. So, the coupling remained unassigned.

Formation of argento vinyl gold with various counterions at silver (OAc^-,ClO_4^-)

2238. With $AgClO_4$



Complex **2** (1.91 mg, 2.50 µmol) and $AgClO_4$ (0.52 mg, 2.51 µmol) were dissolved in THF-*d8* (2 drops). In another vial, 2,2-dimethyl-4-phenylbutyn-3-ol-1 (**S1**) (0.50 mg, 2.87 µmol) and *t*Bu_2Py (0.63 mg, 3.3 µmol) were dissolved in $CDCl_3$ (0.5 mL). This solution was added to the solution containing silver and gold. Additional $CDCl_3$ (ca. 0.1 mL) was used for complete transfer. A white crystalline precipitate quickly appeared (*t*Bu_2PyH^+ SbF_6^- and/or *t*Bu_2PyH^+ ClO_4^-). A ^1H NMR spectrum after 5 min indicated comlete formation of argento vinyl gold as a single organogold product (Spectrum Figure S5). There are only very

minor changes in comparison with the spectrum of **G1** triflate. The most notable: CH_2O is shifted from 4.13 to 4.16 ppm, P is shifted from 65.81 to 66.11 ppm.

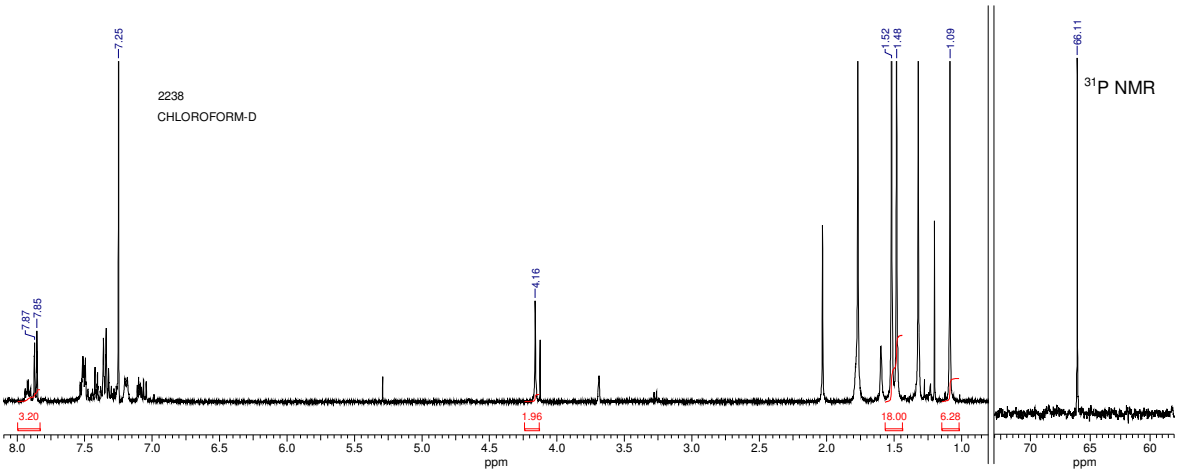
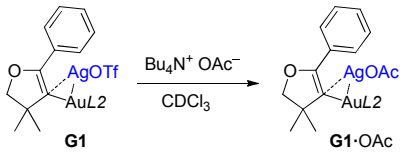


Figure S5. ^{1}H and ^{31}P NMR spectra for experiment 2238.

2259. Titration of argento vinyl gold **G1** triflate with OAc^- to probe covalent binding of OTf^- and OAc^- to silver



To a solution of enriched argento vinyl gold triflate **G1** (ca. 2.4 µmol), containing $PhCH_2CH_2Ph$ (ca. 1.1 equiv to **G1**) as internal standard, in $CDCl_3$ (0.55 mL) was added CaH_2 and a blank NMR spectrum was recorded. Then $n Bu_4N^+$ OAc^- (random amounts, 6 times) was added to the solution. ^{1}H, ^{31}P, ^{19}F NMR spectra were recorded after each addition. The ratio of the components was determined by NMR. At all ratios argento vinyl gold exhibited a single set of averaged signals due to fast ligand exchange. Selected chemical shift values are given in Table S2. (minor background protodeauration occurred with liberation of *L2*AuOAc, δP = 55.38). Based on the changes in chemical shifts upon addition of $n Bu_4N^+$ OAc^- it is concluded that the equivalence point is reached after 1 equiv of OAc^-. This experiment also suggests that OTf^- must be bound to silver before being substituted by OAc^-.

Table S2. Titration of argento vinyl gold **G1** triflate with OAc^-.

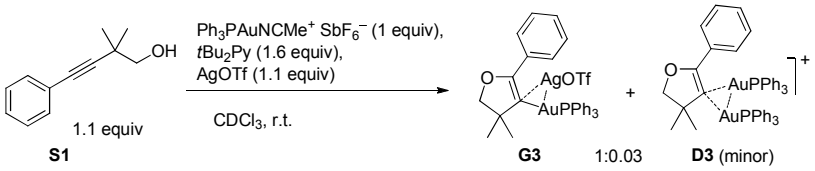
2259						
ΣOAc, equiv	δP	δAr	δAr	δCH2O	δCH3	δF
0	65.84	7.86	6.17	4.21, 4.08	broad	-77.58
0.09	65.83	7.86	6.17	4.22, 4.07	1.13, 1.05	
0.34	65.67	7.89	6.27	4.20, 4.06	1.14, 1.04	-77.77
0.61	65.32	7.93	br	4.18, 4.01	1.17, 1.01	-77.94
1.2	64.48	8.02	6.55	4.13, 3.94	overlap	-78.27
1.6	64.42	8.02	6.52	4.13, 3.93	overlap	-78.29
2.8	64.42	8.02	6.51	4.13, 3.92	overlap	-78.29

Argento vinyl gold **G1** acetate. **^{31}P NMR** ($CDCl_3$): δ = 64.42.

*L2*AuOAc. **^{31}P NMR** ($CDCl_3$): δ = 55.38.

Formation of argento vinyl gold in situ

2225. Formation of argento vinyl gold **G3** in situ



Complex **1** (2.05 mg, 2.79 µmol) and AgOTf (0.84 mg, 3.27 µmol) were dissolved in THF-*d8* (2 drops). In another vial, 2,2-dimethyl-4-phenylbutyn-3-ol-1 (**S1**) (0.56 mg, 3.2 µmol) and *t*Bu_2Py (0.86 mg, 4.5 µmol) were dissolved in $CDCl_3$ (0.5 mL). This solution was added to the solution containing silver and gold. Additional $CDCl_3$ (ca. 0.1 mL) was used for complete transfer. A white crystalline precipitate quickly appeared (pure *t*Bu_2PyH^+ SbF_6^-). The reaction mixture was transferred into an NMR tube and a small random amount of CF_3CO_2Me was added. Examination by NMR indicated complete consumption of the starting alcohol and formation of argento vinyl gold as a major organogold product and diaurated species as a minor (molar ratio argento vinyl gold/diaurated=1:0.03), Figure S6.

Note: it was possible to obtain a split ^{1}H spectrum of **G3** at –60 ℃.

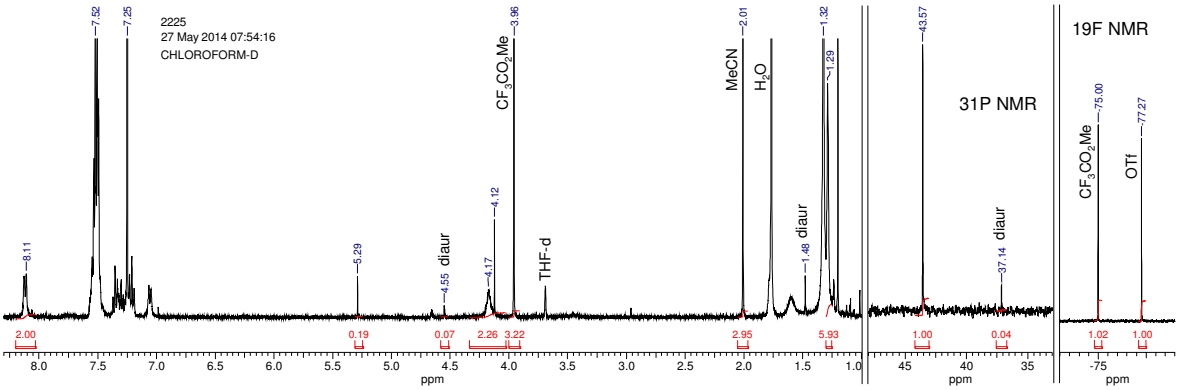
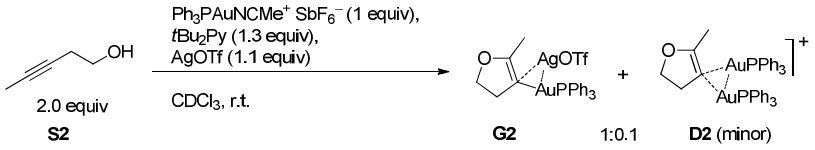


Figure S6. ^{1}H, ^{31}P and ^{19}F NMR spectra for experiment 2225.

Argento vinyl gold **G3**. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.11 (d, 2H), 7.19-7.57 (m), 4.17 (br s, 2H), 1.29 (s, 6H). **^{31}P NMR** ($CDCl_3$): δ = 43.57.

2227. Formation of argento vinyl gold **G2** in situ



Complex **1** (1.77 mg, 2.40 µmol) and AgOTf (0.68 mg, 2.64 µmol) were dissolved in THF-*d8* (2 drops). In another vial, pentyn-3-ol-1 (**S2**) (0.41 mg, 4.9 µmol) and *t*Bu_2Py (0.61 mg, 3.2 µmol) were dissolved in $CDCl_3$ (0.5 mL). This solution was added to the solution containing silver and gold. Additional $CDCl_3$ (ca. 0.1 mL) was used for complete transfer. A white crystalline precipitate quickly appeared (pure *t*Bu_2PyH^+ SbF_6^-). The reaction mixture was transferred into an NMR tube and a small random amount of CF_3CO_2Me was added. Examination by NMR indicated incomplete consumption of the starting alcohol

and formation of argento vinyl gold as a major organogold product and diaurated species as a minor (molar ratio argento vinyl gold/diaurated=1:0.1), Figure S7.

In another experiment, using pentyn-3-ol-1 (1.5 equiv), AgOTf (1.6 equiv), tBu$_2$Py (1.4 equiv) and catalyst **1** (1 equiv) in $CDCl_3$, argento vinyl gold was obtained exclusively, without any diaurated species.

Note: ^{1}H spectrum of **G2** broadens but does not split into separate signals at –60 ℃ even in the presence of PrSp.

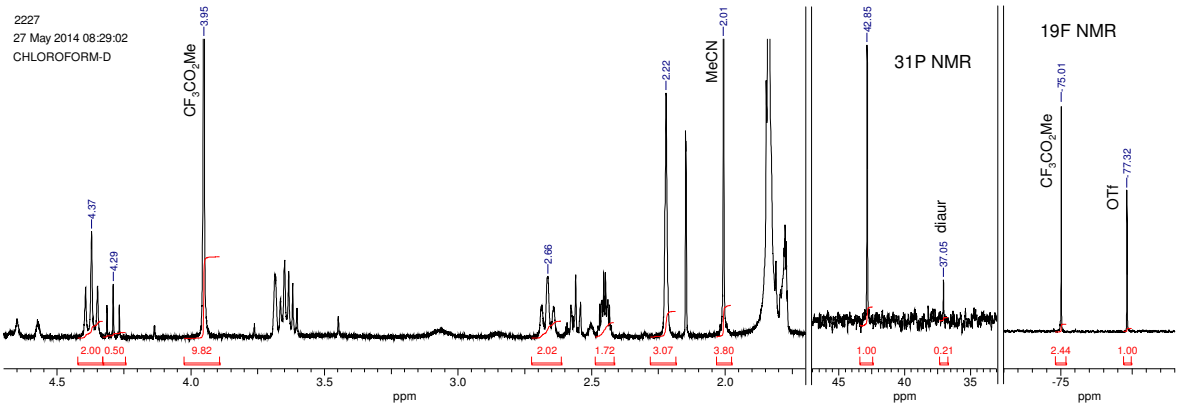


Figure S7. ^{1}H, ^{31}P and ^{19}F NMR spectra for experiment 2227.

Argento vinyl gold **G2**. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.48-7.53 (m, 15H), 4.37 (t, 2H), 2.66 (t, 2H), 2.22 (s, 3H). **^{31}P NMR** ($CDCl_3$): δ = 42.85.

2295. Formation of argento vinyl gold **G4** in situ

Complex **2** (7.15 mg, 9.26 µmol) and AgOTf (3.35 mg, 13.0 µmol) were dissolved in THF-*d8* (2 drops). In another vial, pentyn-3-ol-1 (**S2**) (1.21 mg, 14.4 µmol) and tBu$_2$Py (3.51 mg, 18.4 µmol) were dissolved in $CDCl_3$ (0.5 mL). This solution was added to the solution containing silver and gold. Additional $CDCl_3$ (ca. 0.1 mL) was used for complete transfer. A white crystalline precipitate quickly appeared (pure tBu$_2$PyH$^+$ SbF_6^-). The reaction mixture was filtrered using a Pasteur pipette with a piece of cotton to transfer the filtrate into an NMR tube. A small random amount of CF_3CO_2Me was added. Examination by NMR indicated complete formation of argento vinyl gold as a single organogold product (Figure S8). However, it substantially decomposed upon evaporation of volatiles in vacuo and subsequent crystallization attempts, giving a dark precipitate.

Note: it was possible to obtain a split ^{1}H spectrum of **G4** at room temperature after treatment of the solution with PrSp for complete disappearance of free AgOTf. The ^{31}P resonance recorded in the absence of the residual AgOTf is identical to the resonance in the presence of AgOTf.

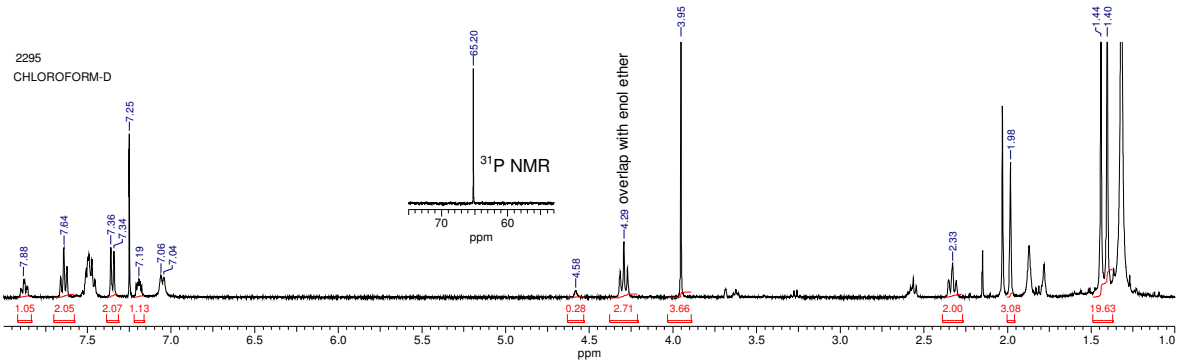
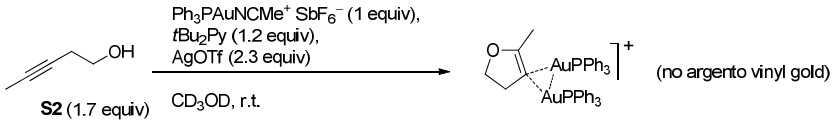


Figure S8. ^{1}H and ^{31}P NMR spectra for experiment 2295.

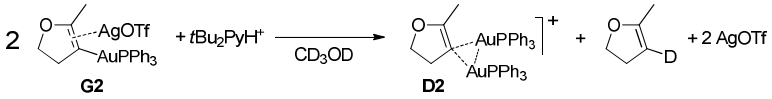
Argento vinyl gold **G4**. **^{1}H NMR** (400 MHz, $CDCl_3$) conditions of fast silver exchange, selected signals: δ = 7.88 (m, 1H), 7.64 (t, 2H), …, 4.29 (t, 2H), 2.33 (t, 2H), 1.98 (s, 3H), 1.42 (d, 18H). **^{31}P NMR** ($CDCl_3$): δ = 65.20.

2295. Formation of diaurated species **D2** instead of argento vinyl gold **G2** in methanol



No argento vinyl gold was detected by NMR. For spectral data, see ref.[2]

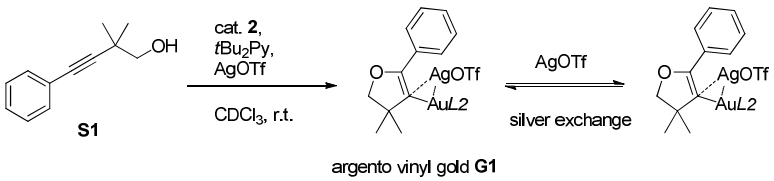
2271. Complete transformation of argento vinyl gold **G2** to diaurated species **D2** in methanol



A reaction mixture containing argento vinyl gold **G2** in solution and tBu$_2$PyH$^+$ as a precipitate was prepared in $CDCl_3$ as described in N2227. Ca. 80% of the solvent was removed in vacuo below room temperature and the residue was dissolved in CD_3OD. NMR analysis indicated complete disappearance of the starting argento vinyl gold and formation of diaurated species **D2** as a single organogold product.

2.1. Experiments at low temperature

2341. Spectrum of **G1** at low temperature. Evidence of the silver exchange. Fast silver exchange upon addition of extra AgOTf.



argento vinyl gold **G1**

Complex **2** (2.61 mg, 3.38 µmol) and AgOTf (0.93 mg, 3.62 µmol) were dissolved in THF-*d8* (2 drops). In another vial, 2,2-dimethyl-4-phenylbutyn-3-ol-1 (**S1**) (0.60 mg, 3.44 µmol) and tBu$_2$Py (1.13 mg, 6.11 µmol) were dissolved in $CDCl_3$ (0.45 mL). This solution was added to the solution containing silver and gold. Additional $CDCl_3$ (ca. 0.1 mL) was used for complete transfer. A white crystalline precipitate quickly appeared (tBu$_2$PyH$^+$ SbF$_6^-$). The clear supernatant solution was taken using a Pasteur pipette and cotton. An ^{1}H NMR spectrum at 20 ℃ after 5 min indicated comlete formation of argento vinyl gold as a single organogold product (Spectrum Figure S9, a). ^{1}H NMR spectra of this solution were then recorded at –50, –20, 0, 10, and 15 ℃. After that, the contents of the NMR tube were poured into a solution of AgOTf (1.32 mg) in THF-*d8* (1 drop). An ^{1}H NMR spectrum of the resulting mixture was recorded at 15 ℃. The spectra at 20, –50, –20, and 15 ℃ and also the last spectrum with extra silver at 15 ℃ are given below.

The initial spectrum at 20 ℃ shows a single set of signals of **G1** undergoing fast silver exchange due to the presence of residual AgOTf in solution (Spectrum a). At –50 ℃ the spectrum becomes more complicated, revealing the unsymmetrical structure of **G1** (Spectrum b). Upon heating up till 15 ℃, the spectrum remains well resolved, but only minor changes occur (the most notable one is the shift of the triplet at 5.81 to 6.12 ppm), (Spectra c, d). When a fresh portion of AgOTf was added, the spectrum (at the same temperature) indicates fast silver exchange, proving the origin of the phenomenon being the silver exchange (Spectrum e).

The resolved spectrum at 15 ℃ is in sharp contrast to the fast exchange situation initially observed at 20 ℃ (compare spectra a and d). This change could not happen only due to the 5 ℃ temperature difference. We suppose the residual AgOTf that remained in solution at 20 ℃ simply precipitated upon cooling and did not return in solution upon heating. Crystalline AgOTf is almost insoluble in $CDCl_3$. Logically, when fresh AgOTf was added as a solution in a minimum amount of THF, the spectrum (at the same temperature) indicated the fast exchange again (some silver remained in solution, being unable to precipitate quantitatively very fast).

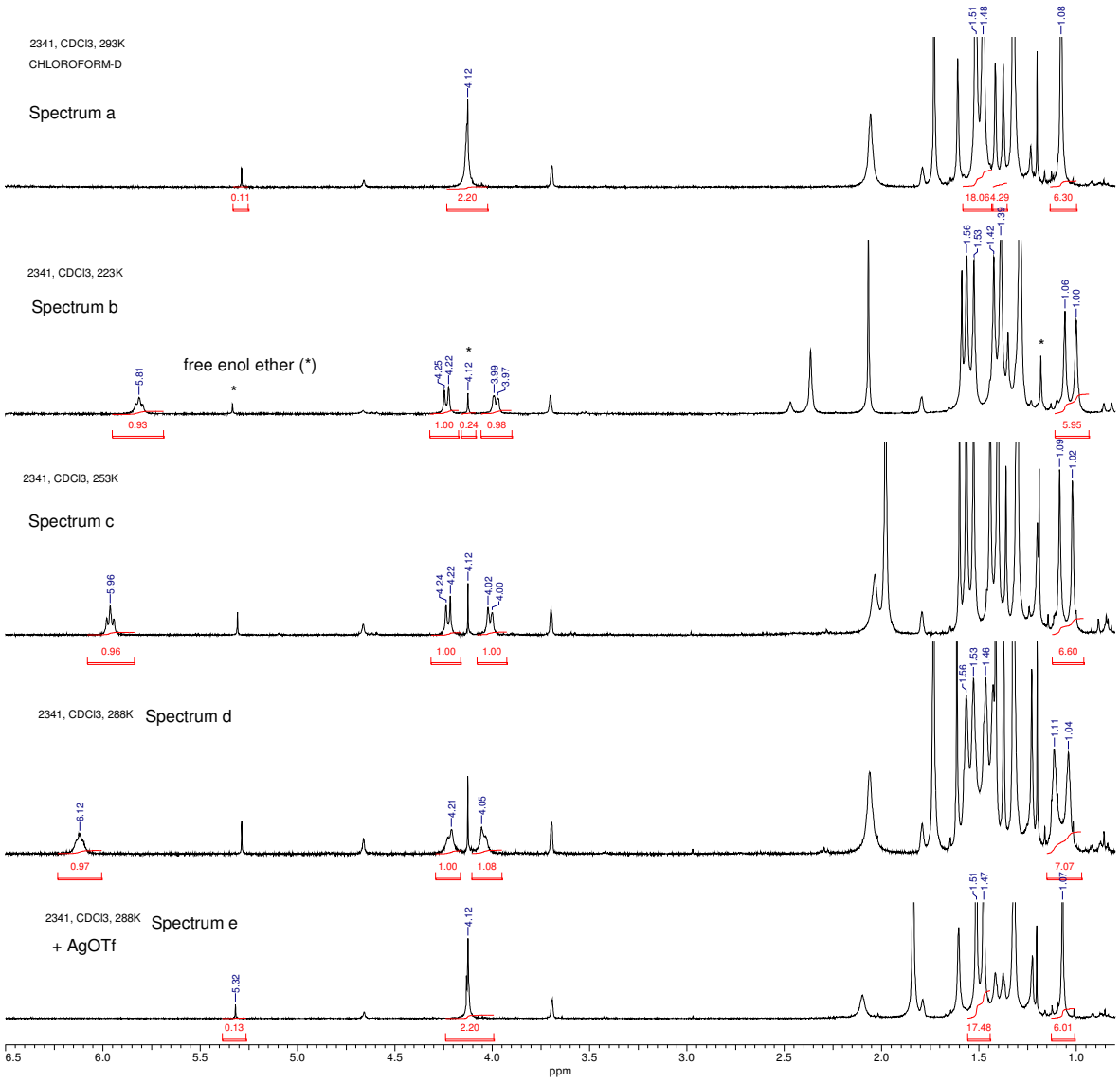
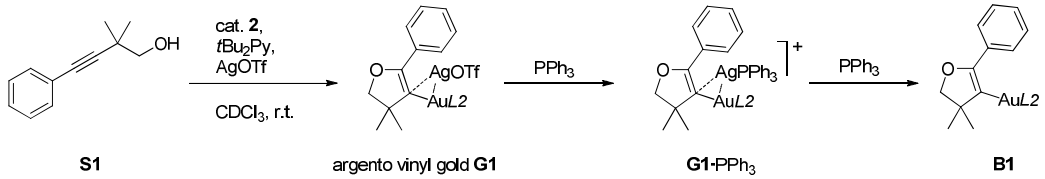


Figure S9. ^{1}H NMR spectruma of **G1** at various temperatures.

2344. Titration of **G1** with PPh_3 at –40 ℃



Complex **2** (2.61 mg, 3.38 µmol) and AgOTf (0.93 mg, 3.62 µmol) were dissolved in THF-*d8* (2 drops). In another vial, 2,2-dimethyl-4-phenylbutyn-3-ol-1 (**S1**) (0.60 mg, 3.44 µmol) and tBu$_2$Py (1.13 mg, 6.11 µmol) were dissolved in $CDCl_3$ (0.45 mL). This solution was added to the solution containing silver and gold. Additional $CDCl_3$ (ca. 0.1 mL) was used for complete transfer. A white crystalline precipitate quickly appeared (tBu$_2$PyH$^+$ SbF_6^-). The clear supernatant solution was taken using a Pasteur pipette and cotton. An ^{1}H NMR spectrum at –40 ℃ after 8 min indicated comlete formation of argento vinyl gold as a single organogold product. Then small random amounts of PPh_3 were added and NMR spectra were recorded after each addition. They revealed formation of a 1:1 adduct of **G1**/PPh_3. When no free **G1** was left,

G1·PPh_3 reacted further with PPh_3 to yield **B1** as the final product. The ratio of the reaction mixture components was determined from the NMR spectra. The 1:1 **G1**/PPh_3 ratio was confirmed by ^{31}P NMR spectrum at –60 ℃ (see below), and integration of ^{1}H, ^{31}P NMR spectra taking into account the material balance of the system in PPh_3, Ag, Au and R. The accuracy of this analysis is not very high, but enough to exclude formation of a 1:2 **G1**/PPh_3 complex.

Table S3. NMR titration of **G1** with PPh_3 at –40 ℃.

2344

			eq to starting **G1**									
MeCN/H2O	ΣAlk 0.8-1.7	ΣAr	PPh3	**G1**	**G1***PPh3	LAuPPh3	vinylAu	enol	ΣR	ΣAu	ΣCH2	Figure S10
6.27	39.81	23.04	0	1	0		0	0.167	1.167		2.36	
6.09	39.81	27.45	0.29	0.81	0.15	0.09	0	0.2	1.16	1.05	2.3	
6.15	39.81	37.75	0.98	0.3	0.52	0.18	0	0.3	1.12	1	2.29	**Spectrum a**
6.18	39.81	55.79	2.18	0	0.42	0.4	0.18	0.5	1.1	1	2.31	**Spectrum b**
6.17	39.81	68.66	3.04	0	0.14	0.42	0.443	0.54	1.123	1.003	2.28	

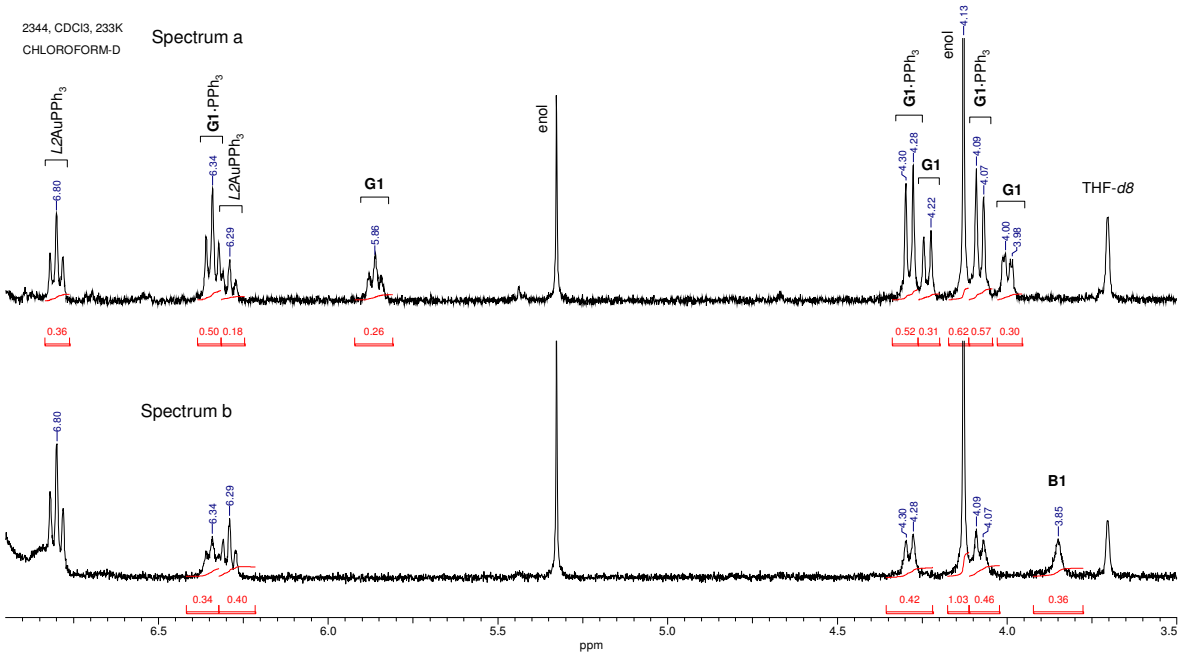
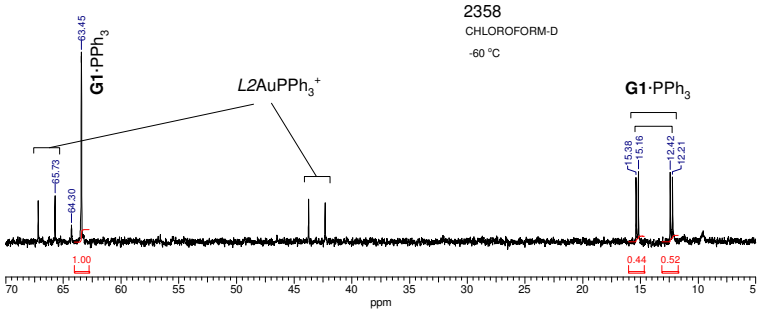


Figure S10. ^{1}H spectra for experiment 2344.

A ^{31}P NMR spectrum of **G1**·PPh_3 at –60 ℃ recorded in another experiment.

G1·PPh_3. ^{31}P NMR ($CDCl_3$ at –60 ℃): δ = 63.46 (d, $^{1}J(^{31}P–^{107,109}Ag)$=4.4 Hz,), 13.79 (two d, $^{1}J(^{31}P–^{109}Ag)$=641 Hz, $^{1}J(^{31}P–^{107}Ag)$=555 Hz):

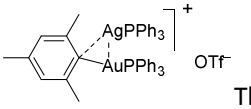


This spectrum shows one doublet of *L2* (63.45 ppm) and two doublets (centered at 13.79 ppm) of PPh_3 coupled to the two silver isotopes (^{109}Ag, ^{107}Ag). The $^{1}J(^{31}P–^{109}Ag)/^{1}J(^{31}P–^{107}Ag)$ = 1.15 ratio is equal to the

^{109}Ag/^{107}Ag gyromagnetic ratio. Integration of the ^{31}P spectrum confirms the 1:1 **G1**/PPh_3 ratio in **G1**·PPh_3. Because of the very small coupling constant, the signal at 63.45 appears as one doublet instead of two doublets.

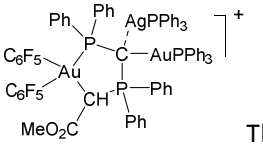
Trying to find further evidence to confirm the structure of **G1**·PPh_3 in solution we appealed to the low temperature ^{31}P NMR spectral data in the literature, that are available rather scarcely. It is known that the magnitude of $^1J(^{31}P–^{109,\,107}Ag)$ is characteristic of the number of coordinated ligands, decreasing with increasing the coordination number.[3] For example, the coupling constant $^1J(^{31}P–^{107}Ag)$ in $[(Ph_3P)_nAg]^+$ for n = 1, 2, 3, 4 is correspondingly 755, 507, 319, 224 Hz at –40 ℃.[4] A tetracoordinate complex having two phosphorus ligands and a 1,10-phenanthroline ligand at silver had $^1J(^{31}P–^{109}Ag)$=422 Hz, $^1J(^{31}P–^{107}Ag)$=368 Hz.[5]

To the best of our knowledge, only a single example of compound being the closest analog to our **G1**·PPh_3 species was characterized by low temperature ^{31}P NMR spectrum.[6] This is a mesitylene complex:



This complex has the following resonance of $AgPPh_3$: ^{31}P NMR ($CDCl_3$ at –55 ℃): δ = 11.2 (two d, $^1J(^{31}P–^{109}Ag)$=473 Hz, $^1J(^{31}P–^{107}Ag)$=416 Hz).

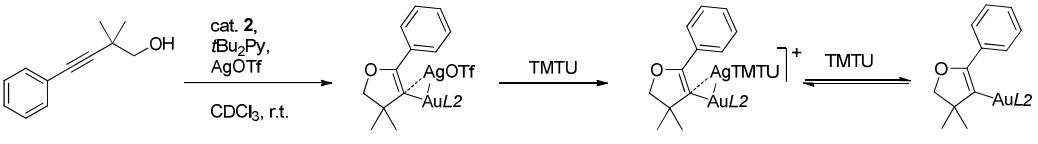
Another example of a mixed Au/Ag compound is:



This complex has the following resonance of $AgPPh_3$: ^{31}P NMR ($CDCl_3$): δ = 11.8 (two d, $^1J(^{31}P–^{109}Ag)$=629 Hz, $^1J(^{31}P–^{107}Ag)$=544 Hz).[7]

These data are consistent with our observation of $^1J(^{31}P–^{109}Ag)$=641 Hz, $^1J(^{31}P–^{107}Ag)$=555 Hz, indicating that the silver atom is bound to a single PPh_3 in **G1**·PPh_3.

2345. Titration of **G1** with TMTU at –40 ℃



S1 argento vinyl gold **G1** **G1**·TMTU **B1**

Similarly as was described in N 2344, NMR titration **G1** with TMTU was performed at –40 ℃. Before the equivalence point the system exhibited a set of 2 dublets for the CH_2O moiety common for **G1** and **G1**·TMTU mixture. This indicates that the silver exchange is slow at this temperature, but the TMTU exchange at silver at **G1** is still fast. Beyond the equivalence point the system exhibited a single broad singlet for the CH_2O moiety. This suggests partial liberation of free **B1** and fast exchange of $AgTMTU^+$ at **B1**.

Table S4. Titration of **G1** with TMTU at –40 ℃.

2345

ΣAlk 0.8-1.7	ΣAr	eq to st **G1** TMTU	Σ**G1**	G1*TMTU	LAuTMTU	vinylAu	enol	ΣR	Figure S11
39.02	22.68	0	1	0	0	0	0.16	1.16	
39.02	21.3	0.83	0.76		0.127		0.3	1.06	**Spectrum a**
39.02	21.1	1.45	0.65				0.37	1.02	**Spectrum b**

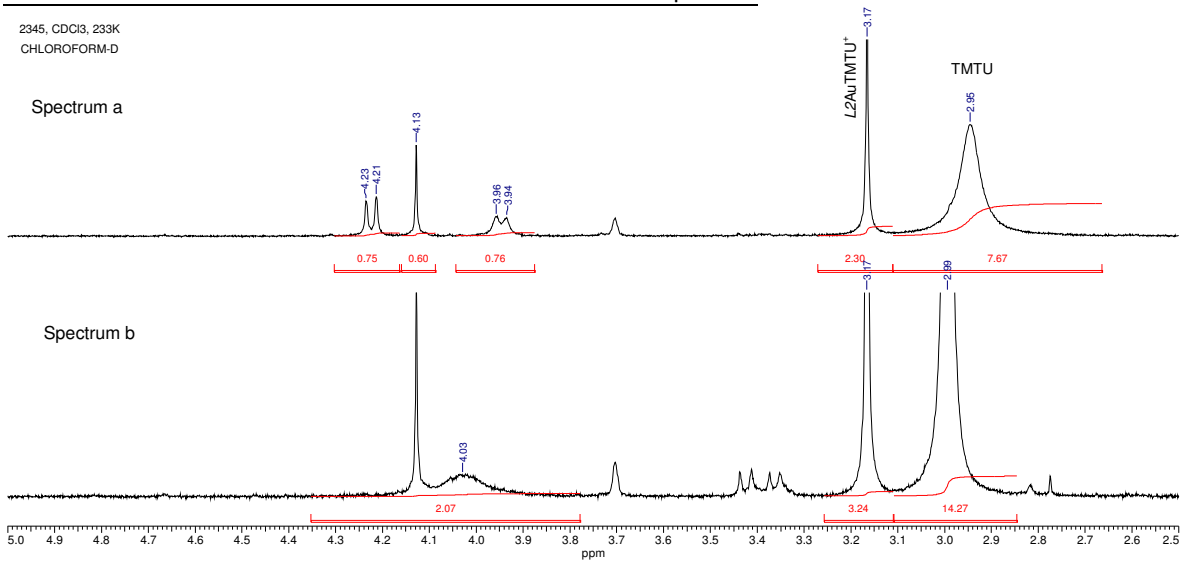
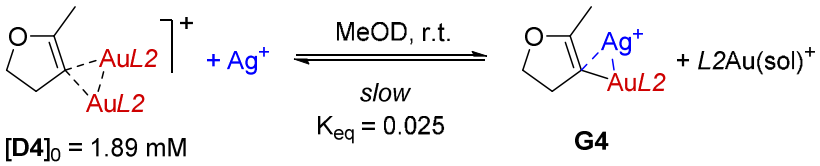


Figure S11. ^{1}H NMR spectra for experiment 2345.

3. Reactivity of silver toward diaurated species

2290-2294. Kinetics of reaction of **D4** with $AgClO_4$ in MeOD. Determination of equilibrium constant



Stock solution A. Diaurated species **D4** (11.49 mg, 8.77 µmol) and mesitylene (4.02 mg, 33.4 µmol) were dissolved in a minimum of CD_2Cl_2 (2 drops) and diluted with CD_3OD (1.22 mL) in a vial.

Stock solution B. $AgClO_4$ (55.16 mg, 266 µmol) and $PhCH_2CH_2Ph$ (7.95 mg, 43.6 µmol) were dissolved in CD_3OD (1.00 mL) in a vial.

An aliquot of solution A (0.15 mL, containing 1.02 µmol of **D4**) was combined with an aliquot of stock solution B (0.04, 0.08, 0.16, 0.32, 0.16 mL for experiments 2290, 2291, 2292, 2293, 2294 correspondingly) and diluted with CD_3OD (till 0.54 mL) all in one syringe. For experiment N2294, complex **2** (1.69 mg, 2.19 µmol) was introduced as a solution in CD_3OD (0.3 mL). Since $AgClO_4$ can not be traced by NMR, the amount of silver in the reaction mixtures was determined from the CH_2 peak of $PhCH_2CH_2Ph$. The molar ratio $Ag/PhCH_2CH_2Ph$ 6.10:1 was determined from the masses of $AgClO_4$ and $PhCH_2CH_2Ph$. The amounts of all components were determined from NMR spectra (the CH_2O, CH_3 and *t*Bu peaks from **D4** and **G4** were used for the integration). The choice varies depending on overlaps, because the spectrum of **G4** changes depending on the amount of Ag). The results are given in Table S5.

Table S5. Determination of chemical kinetics. Amounts of **D4**, **G4**, LAu^+, sum R are given in equiv relative to the starting amount of **D4**.

2290												
D4	1.89 mM											
AgClO4	10.6 equiv											
abs. time	time, h		Mes	**D4**	**G4**	MeOD	PhCH2CH2Ph	sum R	δCH3	LAu	K_{eq}
18:43:50	0		10.63	1	0			1			
18:56:06	0.204		10.63	0.985	0.01	65.63	6.93	0.995	1.96		
20:07:19	1.39		10.63	0.923	0.084	65.54	6.97	1.007			
22:05:03	3.35		10.63	0.82	0.146	65.27	6.94	0.966			
23:42:14	4.97		10.63	0.78	0.174	65.62	6.94	0.954	1.96	0.314	0.007
43:30:00	24.77		10.63	0.583	0.184	64.95	7.17	0.767		0.823	**0.025**

2291											
D4	1.89 mM										
AgClO4	20.7 eq										
abs. time	time, h	δP	Mes	**D4**	**G4**	MeOD	PhCH2CH2Ph	sum R	δCH3	LAu	K_{eq}
18:45:29	0		10.63	1	0			1			
18:58:26	0.216		10.63	0.967	0.026	64.75	13.58	0.993	1.98		
20:09:40	1.40		10.63	0.85	0.154	64.85	13.66	1.004	1.98		
22:07:27	3.37		10.63	0.717	0.253	65.1	13.64	0.97			
23:45:25	5.00		10.63	0.657	0.284	65.2	13.67	0.941	1.98	0.479	0.010
43:23:00	24.63	65.42	10.63	0.467	0.297	64.52	14.1	0.764	1.98	0.97	**0.030**
	add AgOTf	65.54							2.05		

2292										
D4	1.89 mM									
AgClO4	40.6 eq									
abs. time	time, h		Mes	**D4**	**G4**	MeOD	PhCH2CH2Ph	sum R	LAu	K_{eq}
18:47:40	0		10.63	1	0			1		
19:00:56	0.221		10.63	0.92	0.058	64.82	26.64	0.978	0.111	
19:28:27	0.680		10.63	0.798	0.138	64.54	26.65	0.936	0.194	
20:12:03	1.41		10.63	0.669	0.259	64.87	26.7	0.928	0.278	
21:09:45	2.37		10.63	0.576	0.369	65.03	26.64	0.945	0.374	
22:09:54	3.37		10.63	0.505	0.414	64.72	26.61	0.919	0.432	0.009
23:47:53	5.00		10.63	0.43	0.453	65.1	26.77	0.883	0.736	0.019

2293	
D4	1.89 mM

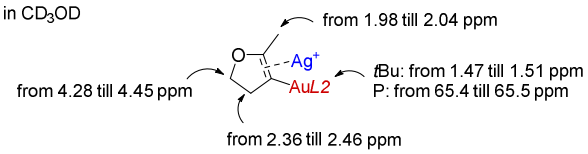
AgClO4	82.9 eq									
abs. time	time, h	Mes	**D4**	**G4**	MeOD	PhCH2CH2Ph	sum R	δCH3	LAu	K_{eq}
18:49:45	0	10.63	1	0			1			
19:03:36	0.231	10.63	0.833	0.136	65.88	54.39	0.969	2.04		
19:25:13	0.591	10.63	0.646	0.255	65.92	54.23	0.901			
20:14:38	1.41	10.63	0.425	0.467	65.63	54.2	0.892			
21:12:11	2.37	10.63	0.301	0.546	65.64	54.13	0.847	2.04	0.948	0.021
22:12:49	3.38	10.63	0.278	0.574	65.89	54.41	0.852		1.01	**0.025**
23:50:30	5.01	10.63	0.256	0.567	65.85	54.52	0.823	2.04	1.05	**0.028**

2294										
D4	1.89 mM									
AgClO4	41.3 eq									
cat. **2**	2.06 eq									
abs. time	time, h	Mes	**D4**	**G4**	MeOD	PhCH2CH2Ph	sum R	δCH3	LAu	K_{eq}
19:12:30	0	10.63	1	0			1			
19:21:35	0.151	10.63	0.905		66.59	27.11	0.905			
20:16:54	1.07	10.63	0.78	0.185	66.93	27.27	0.965			
22:15:19	3.05	10.63	0.644	0.218	67.41	27.5	0.862		2.62	**0.022**
23:52:45	4.67	10.63	0.626	0.211	66.79	27.23	0.837		2.71	**0.022**

Analysis of results

1. Minor protodeauration was noted as a side reaction.

2. The chemical shift of diaurated species keeps constant in all experiments. However, going from 10 equiv till 80 equiv Ag^+ in solution the chemical shift of argento vinyl gold changes as exemplified in the picture below:



Changes of chemical shifts in the presence of 10 till 80 equiv Ag^+

The chemical shift (^{1}H NMR) of argento vinyl gold keeps constant within each one of the experiments. It means, it is constant at a constant amount of Ag^+.

Since the system always arrived at the constant value of the equilibrium constant in the presence of various amounts of silver, these changes in chemical shift are not likely due to formation of any new complex like $RAuAg_2^{2+}$. Most likely they are associated with change in kinetics of silver exchange at argento vinyl gold. If there was significant accumulation of any organosilver-gold component in the system, it would influence the fraction of argento vinyl gold and the title equilibrium constant could not be established.

3. The equilibrium constant was determined by measuring the actual ratio *[**G4**][LAu(Sol)$^+$]/([**D4**][Ag$^+$])* that slowly approached the equilibrium ratio as reaction progressed. It is seen from the Table that the equilibrium is reached after 24 h in experiments 2290 and 2291 (10 and 20 equiv Ag^+). The equilibrium is almost reached after 5 h in experiment N 2292 (40 equiv Ag^+). In experiments 2293 (80 equiv Ag^+) and 2294 (40 equiv Ag^+ + additional 2.06 equiv LAu^+ at start) the equilibrium is reached within 5 h. The average value of K = 0.025 is accepted.

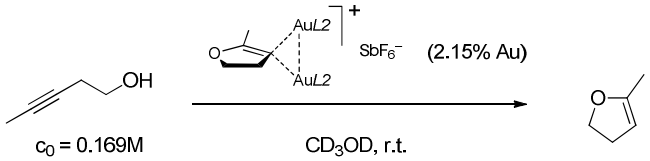
4. Kinetics of catalytic reactions (catalysis by diaurated species)

Stock solution A. Diaurated species **D4** (5.97 mg, 4.56 µmol) and mesitylene (4.64 mg, 38.67 µmol) were dissolved in CD_3OD (till 2.5 mL) in an analytical flask.

Stock solution B. *t*Bu_2PyH^+ OTf^- (0.97 mg, 2.84 µmol) was dissolved in CD_3OD (till 1.0 mL) in an analytical flask.

These solutions were used fresh in the next experiments 1312–1317 performed in a single day.

1312

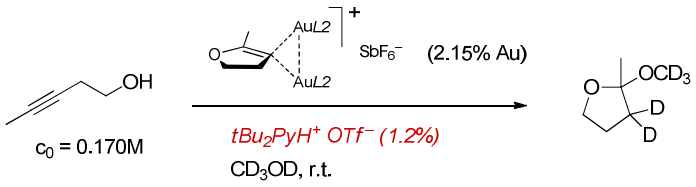


3-Pentynol-1 (7.70 mg, 92.0 µmol) was weighted into a vial. Stock **solution A** (0.54 mL, containing 0.985 µmol diaurated species **D4**, 2.15% mol gold) was taken in a glass syringe and diluted with CD_3OD till 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in Table S6 below.

Table S6. Determination of chemical kinetics in exp 1312.

1312								
c(sub)	0.169M							
cat diaur	2.15% Au	2.28% Au by NMR						
abs. time	time		Mes	Substr	Enol	diaur	Mes	sum R
19:52:09	0			1	0			1
20:11:32	0.323			0.991	0.009	0.0115		1
21:10:42	1.31			0.96	0.041	0.0114		1.001
22:05:18	2.22			0.931	0.06			0.991

1313

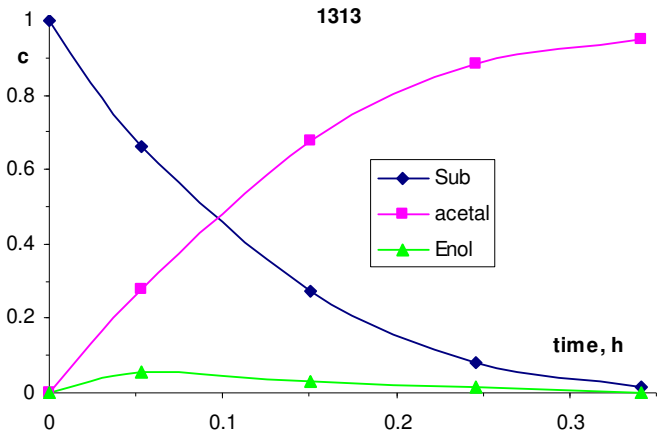


3-Pentynol-1 (7.71 mg, 91.7 µmol) was weighted into a vial. *t*Bu_2PyH^+ OTf^- (0.39 mg, 1.14 µmol, 1.2%) was weighted in another vial and diluted by **Stock solution A** (0.54 mL, contains 0.985 µmol diaurated species **D4**, 2.15% mol gold), the solution was taken in a glass syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table S7 and Diagram below.

Table S7. Determination of chemical kinetics in exp 1313.

1313								
c(sub)	0.170M							
cat diaur	2.15% Au							
tBu_2PyH^+	1.20%							
abs. time	time, h		Mes	Substr	Enol	acetal	MeOD	Mes	sum R

20:20:53	0			1	0	0			1
20:24:06	0.0536		2.61	0.662	0.054	0.28	7.35	8.24	0.996
20:29:54	0.150		2.61	0.271	0.032	0.678	7.35	8.16	0.981
20:35:40	0.246		2.62	0.0805	0.014	0.883	7.35	8.24	0.9775
20:41:22	0.341	**Spectrum**	2.61	0.0155	0	0.951		8.22	0.9665



As can be seen in the Spectrum below (Figure S12), diaurated species successfully survived till the end of the reaction:

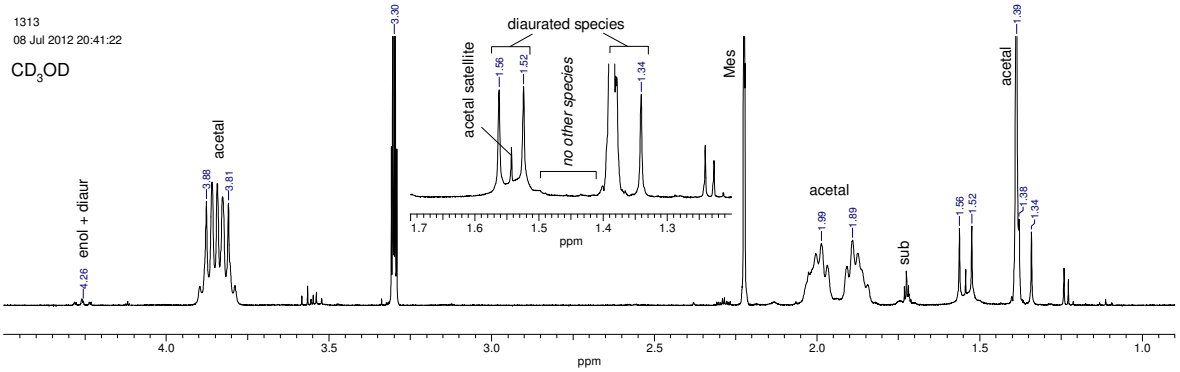
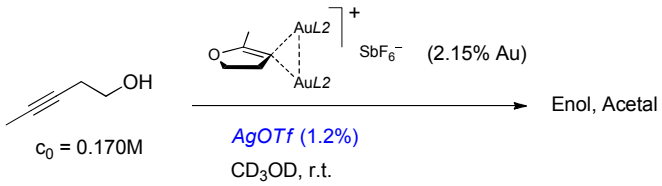


Figure S12. ^{1}H NMR spectrum at 0.341 h of experiment 1313.

1314



3-Pentynol-1 (7.71 mg, 91.7 µmol) was weighted into a vial. AgOTf (0.28 mg, 1.09 µmol, 1.2%) was weighted in another vial and diluted by **Stock solution A** (0.54 mL, contains 0.985 µmol diaurated species **D4**, 2.15% mol gold), the solution was taken in a glass syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table S8 and Diagram below.

Table S8. Determination of chemical kinetics in exp 1314.

1314	
c(sub)	0.170M
cat diaur	2.15% Au

AgOTf	1.20%									
abs. time	time, h		Mes	Substr	Enol	acetal	MeOD	diaur	Mes	sum R
21:11:59	0			1	0	0				1
21:15:10	0.053	Spectrum a	2.55	1	0	0	7.21	0.0112	8.02	1
21:20:56	0.149			1	0	0				1
21:31:12	0.320			1	0	0				1
22:57:42	1.76	Spectrum b	2.56	0.873	0.021	0.107	7.21		8.07	1.001
23:59:52	2.80		2.57	0.464	0.016	0.504	7.21		8.1	0.984

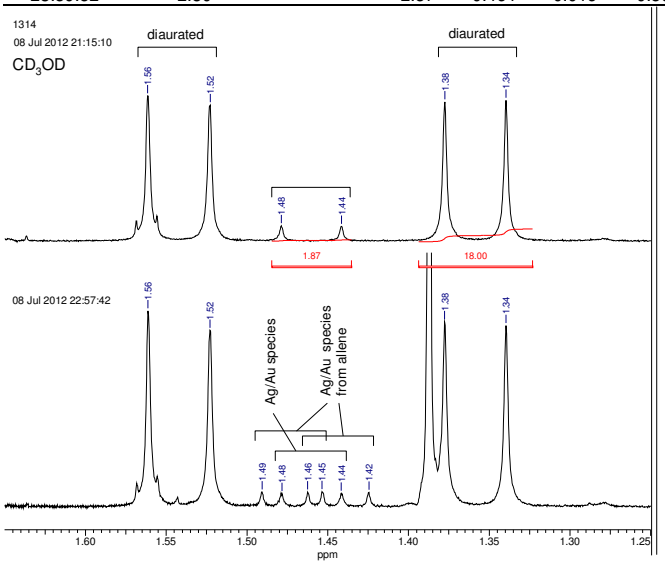


Figure S13. Spectra for experiment 1314 (the sample contained 0.2% allene impurity, see more details in section 4.2).

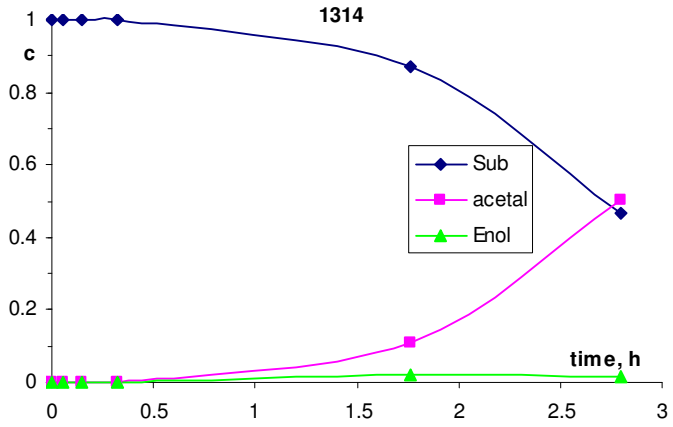
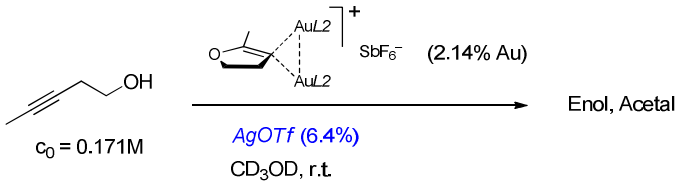


Figure S14. Diagram for experiment 1314.

1315



Completely the same experiment as 1314, except for using 1.52 mg, 5.91 µmol, 6.4% of AgOTf.

Table S9. Determination of chemical kinetics in exp 1315.

1315

c(sub)	0.171M								
cat diaur	2.14% Au								
AgOTf	6.40%								
abs. time	time, h	Mes	Substr	Enol	acetal	MeOD	diaur	Mes	sum R
21:42:29	0		1	0	0				1
21:45:42	0.054	2.52	1	0	0	7.2		7.96	1
21:51:24	0.149	2.52	1	0	0	7.2		7.93	1
22:15:52	0.556	2.52	0.982	0.006	0.011	7.2		7.96	0.999
23:01:16	1.31	2.52	0.909	0.006	0.085	7.2		7.94	1
00:03:16	2.35	2.52	0.717	0.006	0.271	7.2		7.96	0.994

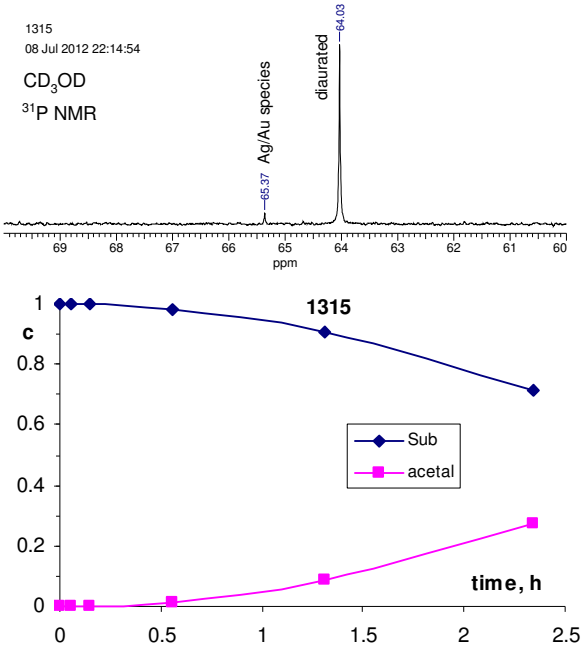


Figure S15. Diagram for experiment 1315.

A combined diagram of experiments 1312–1315 is given below (Figure S16), showing the effects of acid (tBu$_2$PyH$^+$ OTf$^-$) and silver (AgOTf) additives on the reaction. Note, that reaction is stronger accelerated in the presence of less silver.

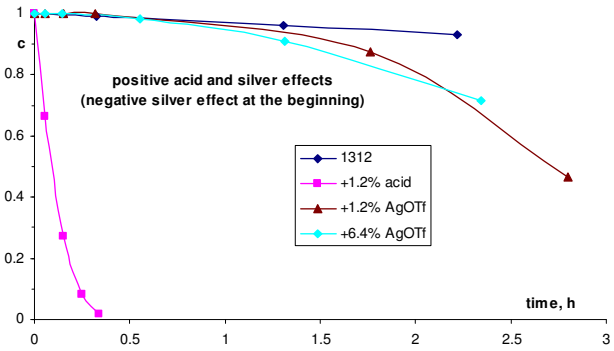


Figure S16. Diagram for experiments 1312–1315.

The negative silver effect on the beginning of the reaction is better seen on the diagram below (Figure S17), showing the first 1 h period:

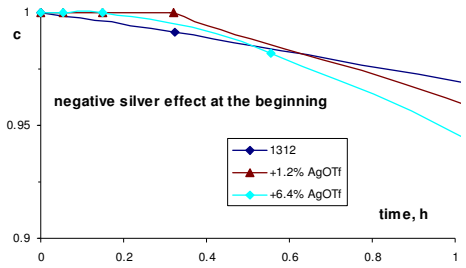
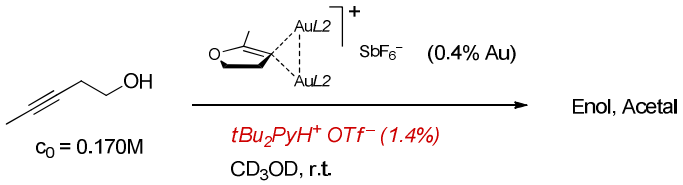


Figure S17. Diagram for experiments 1312, 1314, 1315 (the first hour).

1316



3-Pentynol-1 (7.70 mg, 91.6 µmol) was weighted into a vial. Stock **solution A** (0.10 mL, contains 0.182 µmol diaurated species **D4**, 0.4% mol gold) was taken in a glass syringe and diluted with **solution B** (0.44 mL, contains 1.25 µmol tBu$_2$PyH$^+$ OTf$^-$, 1.36% mol) and then with CD_3OD till 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table below.

Table S10. Determination of chemical kinetics in exp 1316.

1316									
c(sub)	0.170M								
cat diaur	0.4%Au								
tBu$_2$PyH$^+$	1.36%								
abs. time	time	Mes	Substr	Enol	acetal	MeOD	diaur	Mes	sum R
22:24:38	0		1	0	0				1
22:27:48	0.053	0.51	0.86	0.022	0.114	7.44		1.67	0.996
22:33:34	0.149	0.51	0.626	0.0205	0.344	7.44		1.66	0.9905
22:43:50	0.320	0.51	0.308	0.0145	0.664	7.44		1.66	0.9865
22:54:06	0.491	0.51	0.118	0.0075	0.844	7.44		1.66	0.9695

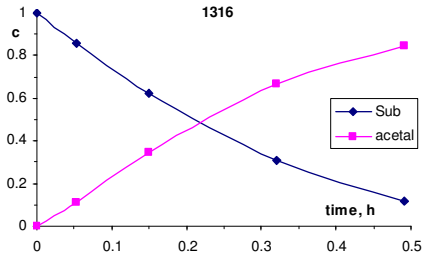
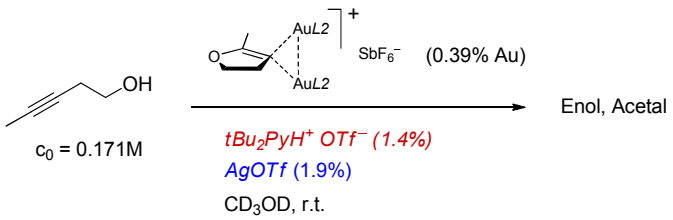


Figure S18. Diagram for experiment 1316.

1317



3-Pentynol-1 (7.75 mg, 92.2 µmol) was weighted into a vial. Stock **solution A** (0.10 mL, contains 0.182 µmol diaurated species **D4**, 0.4% mol gold) was taken in a glass syringe and diluted with **solution B** (0.44 mL, contains 1.25 µmol tBu$_2$PyH$^+$ OTf$^-$, 1.36% mol), additionally containing AgOTf (0.44 mg, 1.71 µmol, 1.86%) and then with CD_3OD till 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in Table S11 below.

Table S11. Determination of chemical kinetics in exp 1317.

1317									
c(sub)	0.171M								
cat diaur	0.39%Au								
tBu$_2$PyH$^+$	1.36%								
AgOTf	1.86%								
abs. time	time, h	Mes	Substr	Enol	acetal	MeOD	diaur	Mes	sum R
23:03:45	0		1	0	0				1
23:06:48	0.051	0.5	0.99	0	0.01	7.2		1.61	1
23:12:34	0.147	0.49	0.984	0	0.018	7.2		1.59	1.002
23:18:22	0.244	0.5	0.979	0	0.0225	7.2		1.61	1.0015
00:06:46	1.05	0.49	0.936	0	0.06	7.2		1.62	0.996
01:17:28	2.23	0.5	0.852	0	0.149	7.2		1.6	1.001

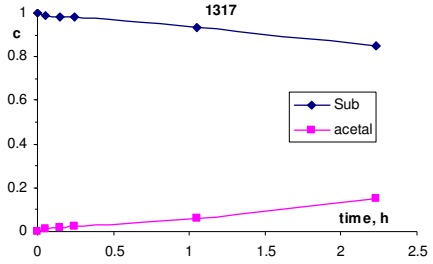


Figure S19. Diagram for experiment 1317.

A combined Diagram of experiments 1315, 1316, 1317 is shown below (Figure S20), showing acid and silver effects. Note, how the AgOTf additive retards the reaction in the presence of acid. The overall effect of both additives is positive in comparison to the reaction without any additives, but the acid additive alone works better than acid + silver together:

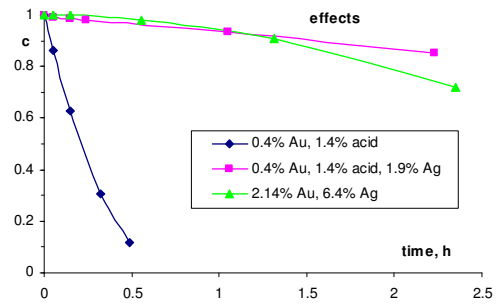


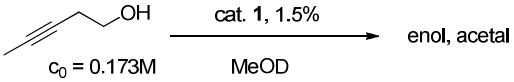
Figure S20. Diagram for experiments 1315, 1316, 1317.

5. Kinetics of catalytic reactions (conventional gold catalysts)

5.1. Series with 3-pentynol-1 and catalyst 1

Stock solution A. Catalyst **1** (13.05 mg, 17.73 µmol) and mesitylene (5.08 mg, 42.2 µmol) were dissolved in CD_3OD (till 2.5 mL) in an analytical flask. This solution was used fresh in experiments 1253–1261 performed in a single day.

1255



3-Pentynol-1 (7.85 mg, 93.3 µmol) was weighted into a vial. Stock **solution A** (0.20 mL, contains 1.42 µmol catalyst, 1.5% mol) was taken in a glass syringe and diluted with fresh CD_3OD till 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table and Diagram below. In this experiment complete formation of diaurated species was observed.

Table S12. Determination of chemical kinetics in exp 1255.

1255									
MeOD									
sub	0.173M								
cat **1**	1.50%								
abs time	time, min	Mes 6.75	Substr	Acetal	Enol	Diaur	MeOD	Mes 2.22	sum R
21:36:44	0		*1*	*0*	*0*	*0*			1
21:39:52	3.13	1.06	*0.84*	*0.148*	*0.0045*	*0.0075*	6.82	3.4	1
21:49:10	12.43	1.07	*0.4315*	*0.5345*	*0.003*	*0.0075*	6.82	3.43	0.9765
22:00:00	23.27	1.07	*0.134*	*0.8145*	*0.0015*	*0.007*	6.82	3.4	0.957
22:10:44	34	1.07	*0.0085*	*0.938*	*0*	*0.0075*	6.82	3.43	0.954
22:22:42	45.97	1.07	*0*	*0.9435*	*0*	*0.006*	6.82	3.42	0.9495

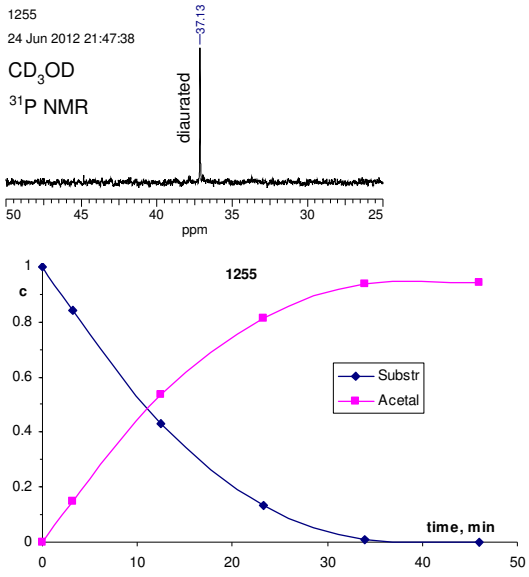
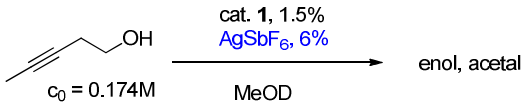


Figure S21. Diagram for experiment 1255.

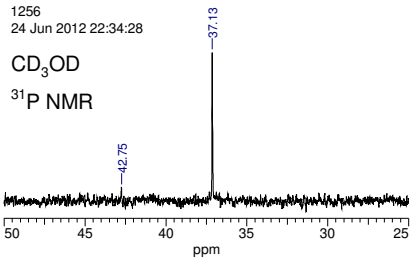
1256



3-Pentynol-1 (7.91 mg, 94.0 µmol) was weighted into a vial. Stock **solution A** (0.20 mL, contains 1.42 µmol catalyst, 1.5% mol) was taken in a glass syringe and diluted with a solution of $AgSbF_6$ (~2.0 mg, 5.8 µmol, 6% mol) in CD_3OD (0.34 mL, beforehand prepared in another vial) directly in the syringe, so that the total volume of 0.54 mL is established. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. In this experiment complete formation of diaurated species was observed as a sole organogold intermediate and no products with silver could be detected.

Table S13. Determination of chemical kinetics in exp 1256.

1256									
MeOD									
sub	0.174M								
cat **1**	1.50%								
$AgSbF_6$	6%								
abs time	time, min	Mes 6.75	Substr	Acetal	Enol	Diaur	MeOD	Mes 2.22	sum R
22:23:40	0		*1*	*0*	*0*	0			1
22:26:42	3.03	1.07	*0.8365*	*0.149*	*0.0035*	0.007	6.72	3.39	0.996
22:36:00	12.33	1.07	*0.4255*	*0.5375*	*0.003*	0.0075	6.72	3.44	0.9735
22:42:20	18.67	1.07	*0.2305*	*0.72*	*0.0015*	0.007	6.72	3.47	0.959
22:53:10	29.5	1.07	*0.035*	*0.9055*	*0*	0.0065	6.72	3.47	0.947



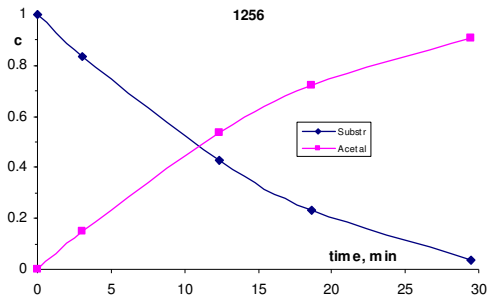
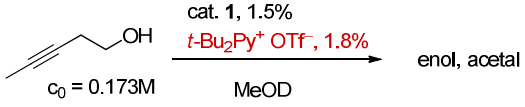


Figure S22. Diagram for experiment 1256.

1257



3-Pentynol-1 (7.85 mg, 93.3 µmol) was weighted into a vial. Stock **solution A** (0.20 mL, contains 1.42 µmol catalyst, 1.5% mol) was taken in a glass syringe and diluted with a solution of $t\text{Bu}_2\text{PyH}^+$ OTf^- (0.58

mg, 1.7 µmol, 1.8% mol) in CD_3OD (0.34 mL, beforehand prepared in another vial) directly in the syringe, so that the total volume of 0.54 mL is established. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. In this experiment complete formation of diaurated species was observed as a sole organogold intermediate.

Table S14. Determination of chemical kinetics in exp 1257.

1257									
MeOD									
sub	0.173M								
cat **1**	1.50%								
*t*Bu$_2$PyH$^+$	1.80%								
abs time	time, min	Mes 6.75	Substr	Acetal	Enol	Diaur	MeOD	Mes 2.22	sum R
22:55:13	0		*1*	*0*	*0*	0			1
22:58:24	3.18	1.05	*0.833*	*0.1535*	*0.004*	0.0075	6.77	3.39	0.998
23:07:44	12.52	1.05	*0.423*	*0.533*	*0.0025*	0.007	6.77	3.43	0.9655
23:14:04	18.85	1.06	*0.2295*	*0.719*	*0.0015*	0.007	6.77	3.39	0.957
23:23:28	28.25	1.06	*0.053*	*0.887*	*0*	0.007	6.77	3.41	0.947

A combined disappearance of the substrate diagram for experiments 1255–1257 is given below (Figure S23). As can be seen, there is no appreciable silver or acid effect observed:

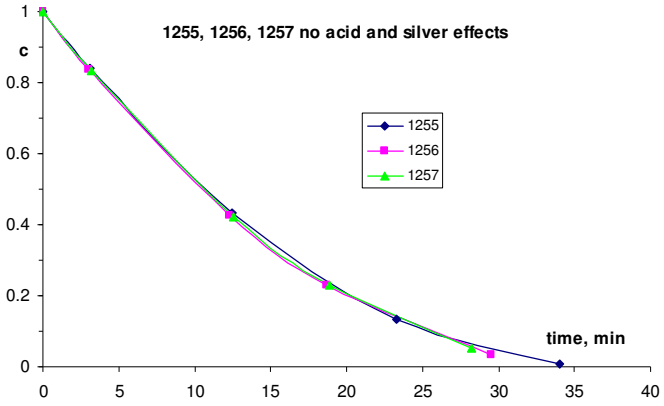
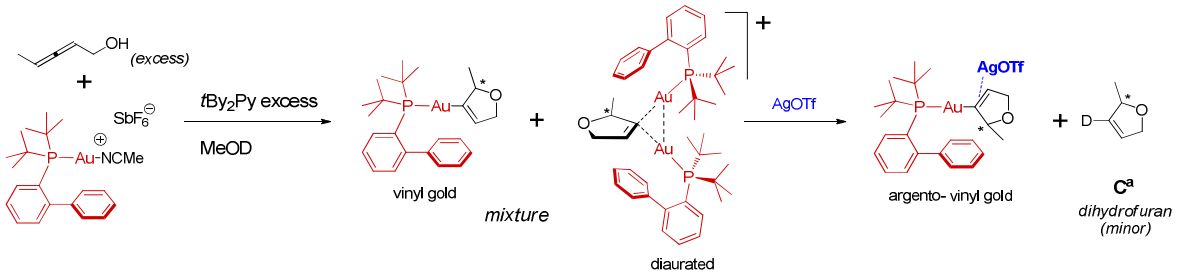


Figure S23. Diagram for experiments 1255–1257.

5.2. Series with impure 3-pentynol-1 and catalyst 2

The sample of pentynol used in this section (from ABCR) was contaminated with 0.2% of 2,3-pentadienol-1 and 0.2% of 2-pentynol-1 impurities (unseparable by distillation).

1368. Characterization of argento vinyl gold originating from the allene impurity



To a solution of 2,3-pentadienol-1 (0.50 mg, 5.9 µmol) and tBu$_2$Py (0.75 mg, 3.9 µmol) in CD_3OD (0.55 mL) was added catalyst **2** (2.05 mg, 2.67 µmol). The reaction mixture was analyzed by NMR to reveal formation of a mixture of vinyl gold species *and* diaurated species, Figure S24. It became clear that this vinyl gold species is quite stable to protodeauration even by tBu$_2$PyH$^+$! Also this experiment demonstrates how unstable the diaurated species is: even here it is not an exclusive product, but still the predominant one.

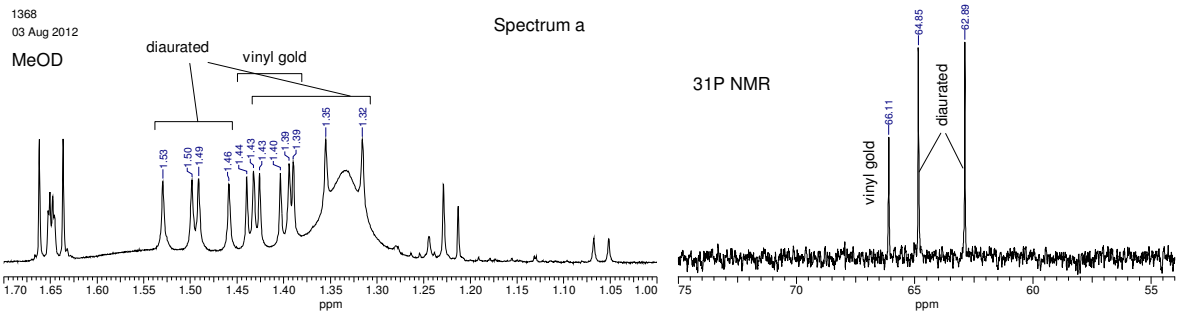


Figure S24. Formation of vinyl gold species *and* diaurated species.

To this solution was then added silver triflate (0.7 mg, 2.7 µmol) and the next NMR spectrum was recorded to reveal complete disappearance of both diaurated species and vinyl gold and formation of a single new organogold product (marked with * in Figure S25). This contains two doublets of *t*-Bu groups at 1.43–1.39 ppm, gives a single phosphorus resonance at 64.66 ppm and has a R:L2 ratio of 1:1, so its structure was assigned as argento vinyl gold species, which is in accordance to Gagne's report.

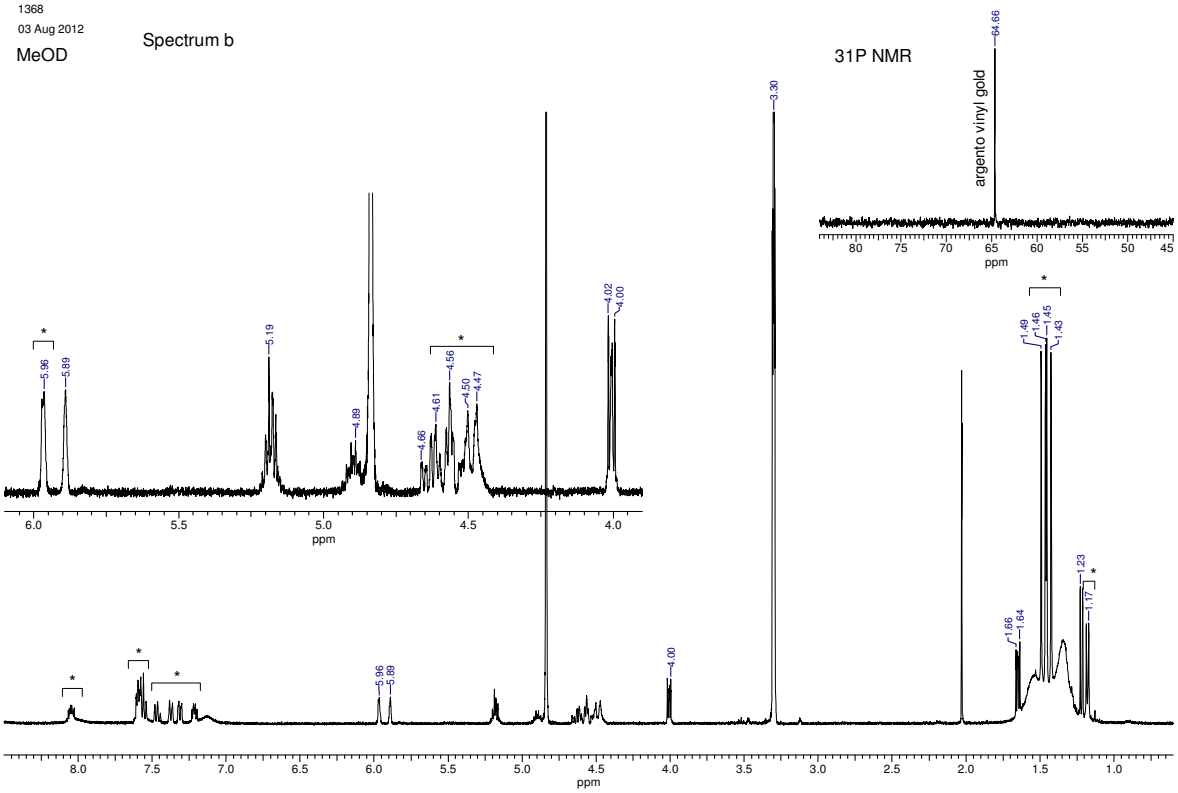
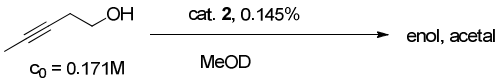
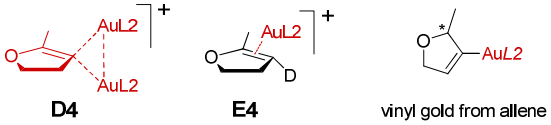


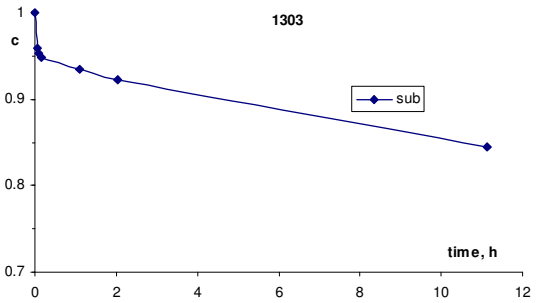
Figure S25. Formation of argento vinyl gold species.

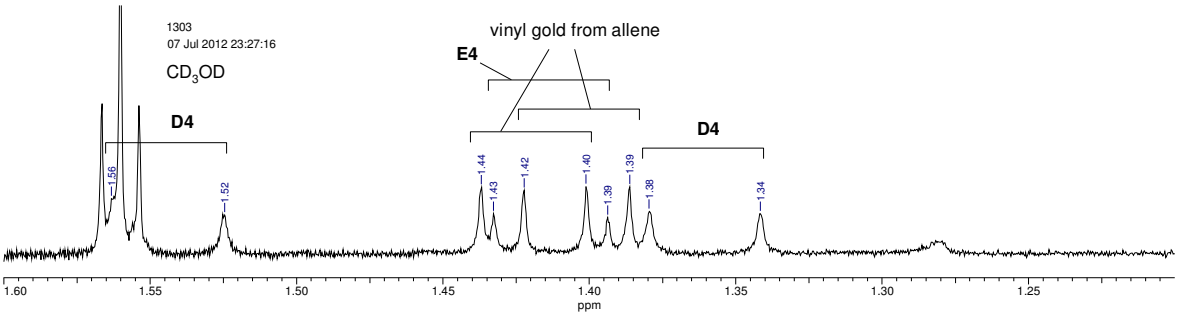
1303 (Pentynol with 0.2% allene impurity!)



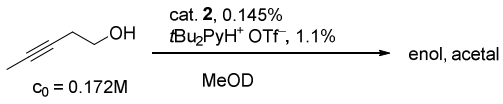
Catalytic species observed, all at the same time:



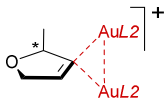




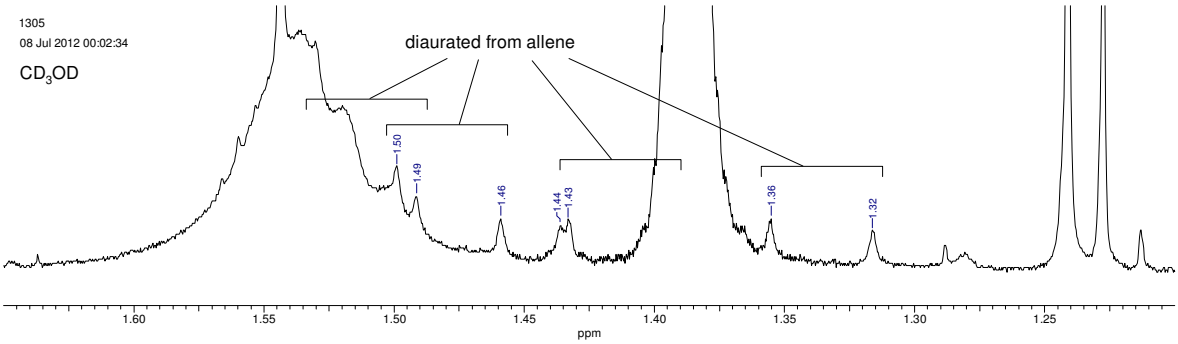
1305 (Pentynol with 0.2% allene impurity!)



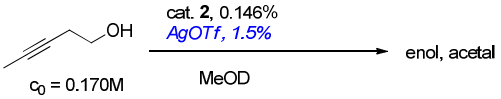
Catalytic species observed:



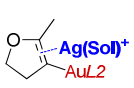
diaurated from allene, major



1306 (Pentynol with 0.2% allene impurity!)

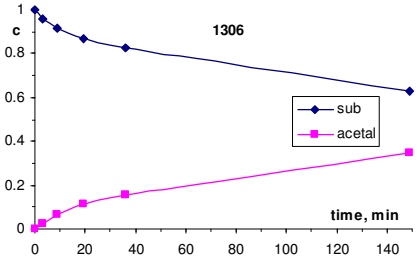


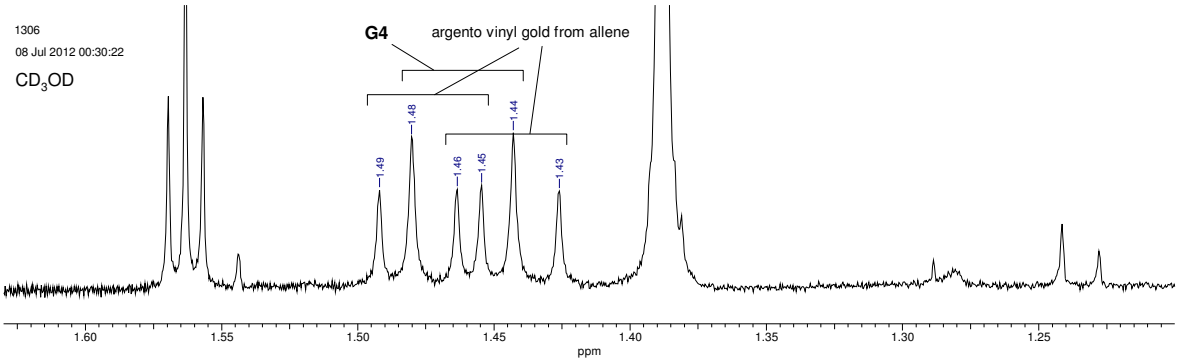
Catalytic species observed:



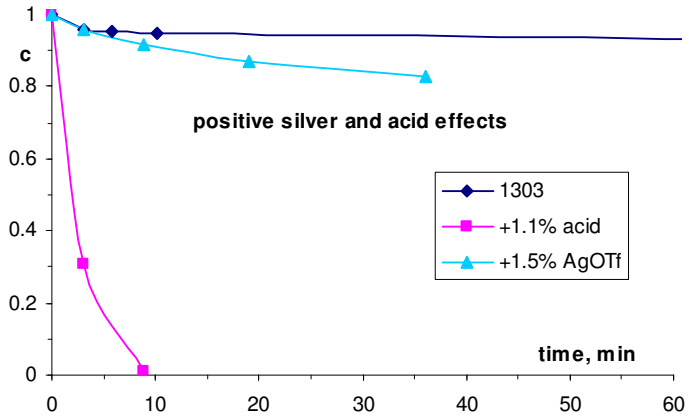
G4

argento- vinyl gold from allene





The combined diagram from experiments 1303, 1305, 1306 below shows the influence of silver (AgOTf) and acid (tBu$_2$PyH$^+$ OTf$^-$) additives on the course of the reaction (positive effects were observed):



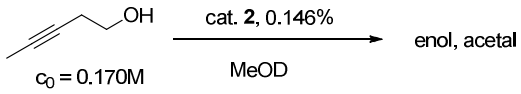
5.3. Series with pure 3-pentynol-1 and catalyst 2

The sample of pentynol used in this section was essentially free of any allene impurity. It was obtained by a single distillation of a commercial sample (from ACROS) in vacuo.

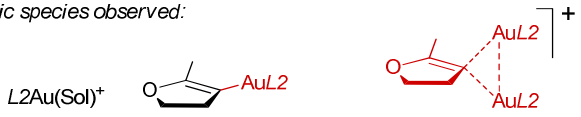
5.3.1. Preliminary experiments

Stock solution A. Catalyst **2** (1.30 mg, 1.68 µmol) and mesitylene (7.41 mg, 61.7 µmol) were dissolved in CD_3OD (till 2.5 mL) in an analytical flask.
Stock solution B. tBu$_2$PyH$^+$ OTf$^-$ (0.81 mg, 2.37 µmol) was dissolved in CD_3OD (1.0 mL) in a vial.
Stock solution C. AgOTf (0.94 mg, 3.66 µmol) was dissolved in CD_3OD (0.50 mL) in a vial.
These solutions were used fresh in experiments 1381–1384, performed in a single day.

1381

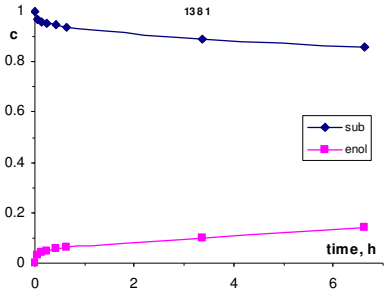


Catalytic species observed:

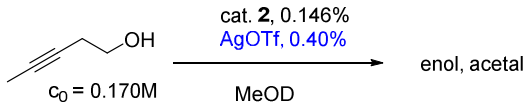


B4 **D4**
(later becomes predominant)

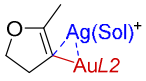
D4 is already predominant at ~8 min reaction time, but becomes the only observable species at ~3 h.



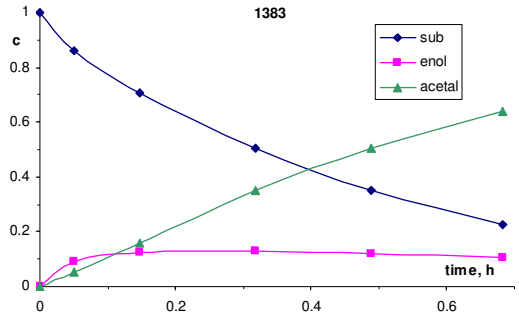
1383



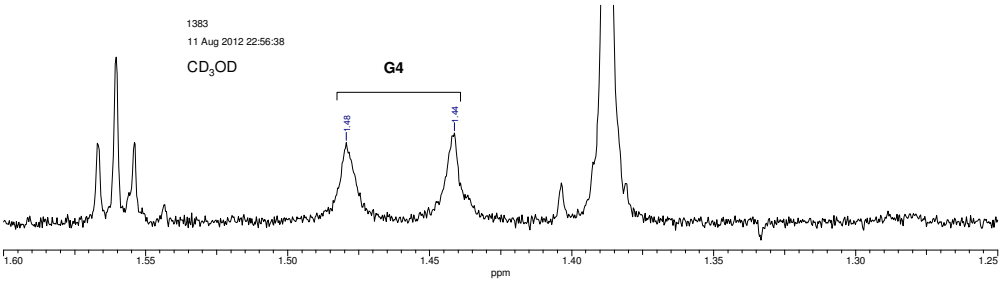
Catalytic species observed:



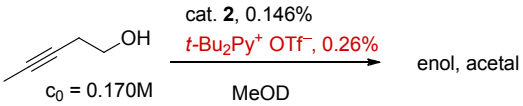
argento vinyl gold **G4**



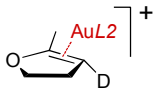
As can be seen from the spectra below, **G4** is a single detectable species already at ~3 min reaction time:



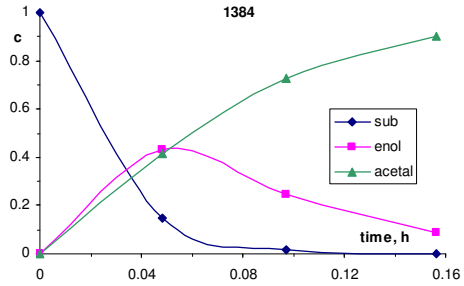
1384



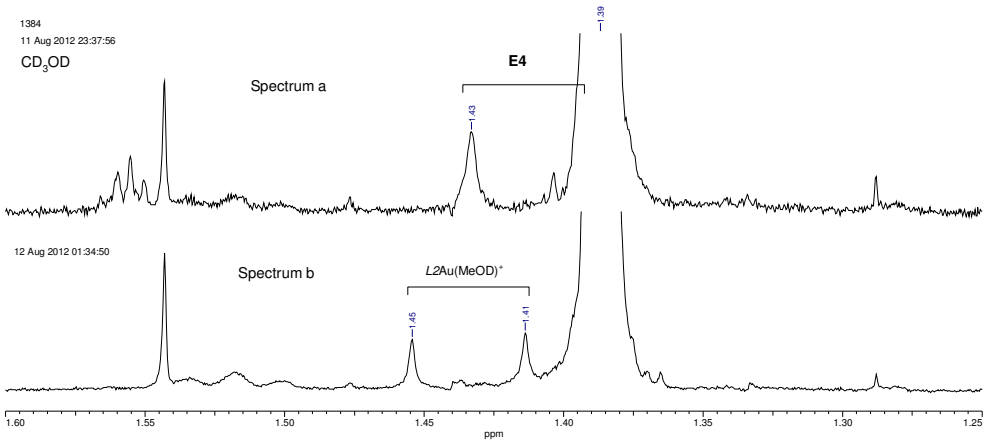
Catalytic species observed:



E4



As can be seen from the spectra below, no diaurated species is formed during the whole reaction course. Instead, **E4** is the only detectable species (Spectrum a), but it disappears when all enol ether converts to the acetal. Then the resonance of *L2*Au(MeOD)$^+$ is fully restored (Spectrum b).



5.3.2. Acid and silver effect in cyclization of 3-pentynol-1

Stock solution A. Catalyst **2** (1.48 mg, 1.92 µmol) and $PhCH_2CH_2Ph$ (3.10 mg, 17.0 µmol) were dissolved in CD_3OD (1.10 mL) in a vial. An NMR spectrum was recorded to establish the molar ratio $PhCH_2CH_2Ph$:Au = 8.47:1. The CH_2 signal of $PhCH_2CH_2Ph$ was then used to determine the total concentration of Au in the reaction mixtures.

Stock solution B. AgOTf (3.02 mg, 11.75 µmol) and trifluoroethanol (TFE, 12.5 mg, 125 µmol) were dissolved in CD_3OD (1.00 mL) in a vial. A ^{19}F NMR spectrum was recorded to establish the molar ratio CF_3CH_2OH:Ag = 100:8.92. The CH_2 signal of CF_3CH_2OH was then used to determine the total concentration of Ag in the reaction mixtures. This was not possible in all experiments because the CF_3CH_2OH signal is overlapped with the acetal signal. In those cases where determination of Ag by integration was not possible, the amount of silver was calculated from the volume of the solution used.

Stock **solution A** (amounts, see Table) was taken in a glass syringe and diluted with CD_3OD, then **solution B** (amounts, see Table), and then with CD_3OD till 0.54 mL directly in the same syringe. This content was poured into a vial with pentyn-3-ol-1 (7.80-7.87 mg, 93.0 µmol) and the time count was started. The reaction mixture was transferred into an NMR tube using a Pasteur pipette and the reaction was further monitored by NMR. Total concentration of Au in every reaction mixture was determined by NMR.

Table S15. Amounts of the substrate, solutions **A**, **D**, **C**, **C2** taken for the experiments.

Exp	Substr **S2**		Sol **A**, mL	Sol **B**, mL
	mg	M		
2368	7.83	0.172	0.08	0
2369	7.80	0.172	0.08	0.01
2370	7.87	0.173	0.08	0.02
2371	7.81	0.172	0.08	0.05
2372	7.84	0.173	0.08	0.10
2373	7.81	0.172	0.08	0.20

The result is given in Table S16 below (the amounts of substr, enol and acetal and sum R are given in equiv relative to the starting substr):

Table S16. Determination of chemical kinetics in exp 2368-2373.

	sol A	Au:CH2	18:33.86
	sol B	Ag:TFE	100:8.92
2368			

substr	0.172 M								
Au	0.15%								
Ag	0.00%								
		eq	eq	eq				eq	
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Me	TFE	sum R
22:38:01	0	1	0	0					1
22:40:18	0.038	0.842	0.158	0	2.85	0.259	14.97		1
22:45:10	0.119	0.824	0.176	0	2.86	0.264	14.96		1
22:52:50	0.247	0.813	0.187	0	2.86	0.266	14.97		1
23:00:34	0.376	0.806	0.194	0	2.86	0.266	14.98		1
24:33:32	1.925	0.77	0.23	0	2.81	0.27	14.91		1
2369									
substr	0.172 M								
Au	0.16%								
Ag	0.13%								
		eq	eq	eq				eq	
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Me	TFE	sum R
23:01:15	0	1	0	0					1
23:03:30	0.038	0.581	0.311	0.11	2.91	0.263	15		1.002
23:08:30	0.121	0.253	0.438	0.309	2.91	0.266	15		1
23:16:10	0.249	0.073	0.463	0.455	2.91	0.266	15		0.991
23:23:50	0.376	0.021	0.462	0.504	2.91	0.264	15		0.987
2370									
substr	0.173 M								
Au	0.16%								
Ag	0.25%								
		eq	eq	eq				eq	
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Me	TFE	sum R
23:24:23	0	1	0	0					1
23:26:32	0.036	0.552	0.183	0.264	2.88	0.262	15	0.019	0.999
23:31:32	0.119	0.101	0.139	0.743	2.85	0.261	15	0.013	0.983
23:39:16	0.248	0	0.108	0.873	2.85	0.263	15	0.007	0.981
2371									
substr	0.172 M								
Au	0.16%								
Ag	0.64%								
		eq	eq	eq				eq	
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Me	TFE	sum R
23:36:22	0	1	0	0					1
23:39:50	0.058	0.634	0.073	0.295	2.87	0.273	15	0.058	1.002
23:45:38	0.154	0.174	0.049	0.761	2.85	0.27	15	0.045	0.984
23:54:22	0.300	0	0.031	0.968	2.85	0.279		0.039	0.999
2372									
substr	0.173 M								
Au	0.16%								
Ag	1.27%								
		eq	eq	eq				eq	
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Me	TFE	sum R
00:28:16	0	1	0	0					1
00:31:16	0.050	0.867	0.038	0.105	2.84	0.273	15	0.126	1.01
00:37:04	0.147	0.622	0.033	0.352	2.83	0.271	15	0.119	1.007
00:53:12	0.416	0.15	0.021	0.812	2.8	0.272	15	0.109	0.983
01:03:28	0.587	0							
2373									
substr	0.172 M								
Au	0.16%								
Ag	2.53%								
		eq	eq	eq				eq	
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Me	TFE	sum R
01:14:52	0	1	0	0					1
01:18:24	0.059	0.913	0.019	0.079	2.81	0.263	15	0.259	1.011
01:24:10	0.155	0.749	0.016	0.241	2.8	0.266	15	0.253	1.006
01:34:26	0.326	0.496	0.014	0.485	2.8	0.265	15	0.246	0.995
01:47:20	0.541	0.244	0.011	0.73	2.78	0.259	15	0.243	0.985
01:57:36	0.712	0.088	0.01	0.885	2.78	0.262	15	0.237	0.983

Observation of resting states.

(Figure S26). In situ NMR indicated that **D4** predominantly formed in experiment 2368 (no additives), while in all other experiments **G4** formed as a single observable organogold species (as a doublet at 1.44–1.48 ppm). The doublet sharpens as more silver additive is present. The sharpening of the signal suggests either the increase of the silver exchange rate or increase of the fraction of **G4** as part of all the organogold species existing in a fast ligand exchange.

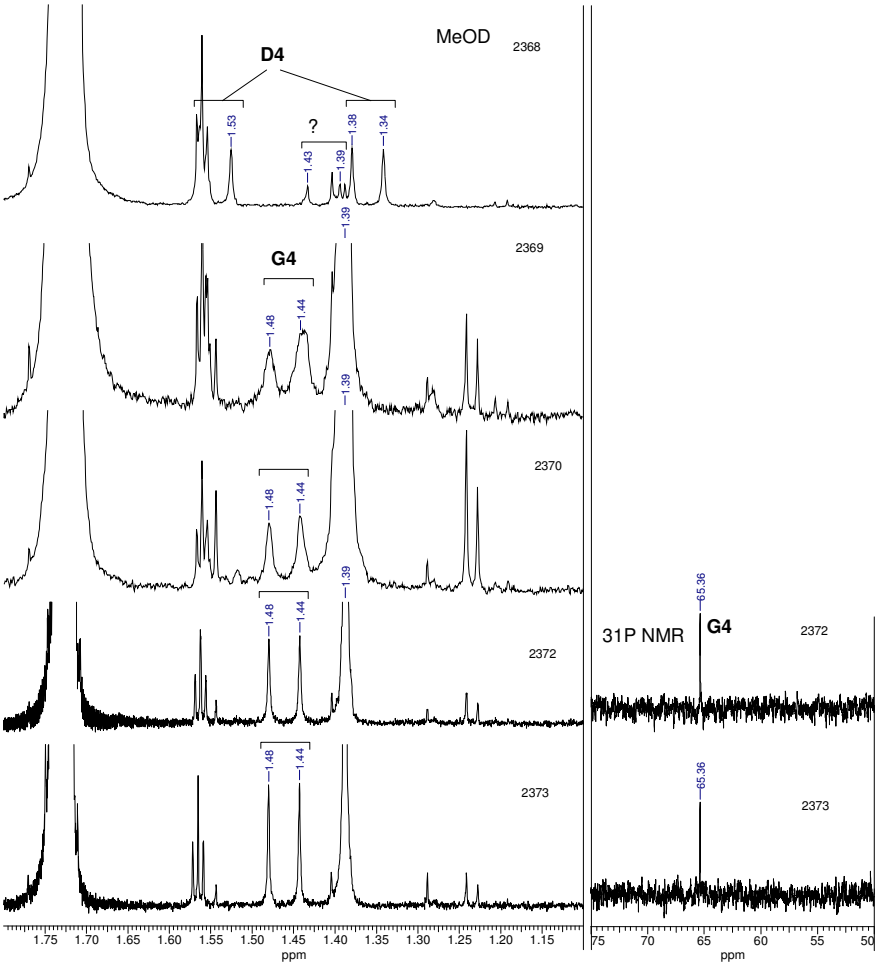


Figure S26. Spectra for experiments 2368–2373.

Analysis of chemical kinetics.

The following diagramm (Figure S27) was built from the data of experiments 2368 (no additive), 2369-2373 (+silver additive) and 1384 (acid additive):

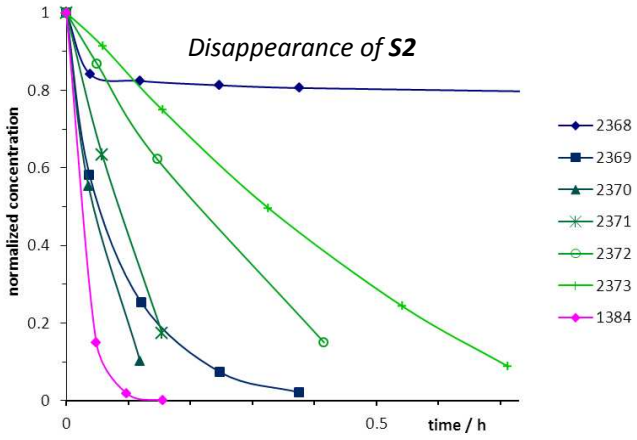


Figure S27. Diagram for experiments 2368–2373 and 1384.

Experiments 2370–2373 were used to estimate the order in silver, Figure S28 (experiments 2368, 2369 are not suitable for that because they contain no or shortage of silver with regard to gold). The curves were approximated as zero-order lines (assuming zero order in substrate):

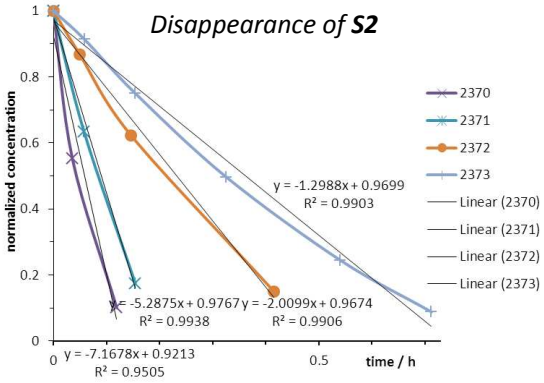


Figure S28. Diagram for experiments 2370–2373 to determine the order in silver.

The order in silver was determined using the slopes of the lines and the calculated amounts of free Ag^+ in the reaction mixture:

Table S17. Determination of the order in silver.

Exp	Au, %	Ag, %	free Ag, %	k	lnAg	lnk
2370	0.155	0.253	0.098	7.17	-2.323	1.970
2371	0.161	0.635	0.474	5.29	-0.747	1.666
2372	0.161	1.27	1.109	2.01	0.103	0.698
2373	0.155	2.53	2.375	1.3	0.865	0.262

The diagram ln*k*=n·ln*Ag* indicated n=–0.88, which corresponds to the minus first order in silver with a moderate accuracy (Figure S29). The overall accuracy of this experiment is not high, mostly because of insufficient accuracy of determination of Ag in reaction mixture (the signal of the TFE standard used to quantify silver is overlapped with the acetal product signal):

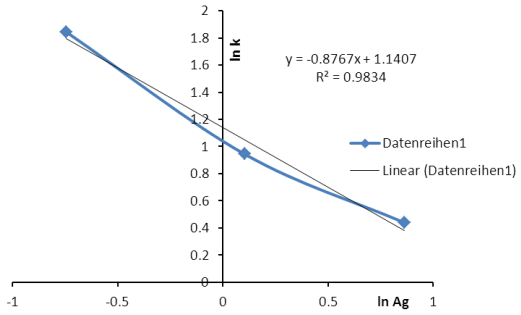


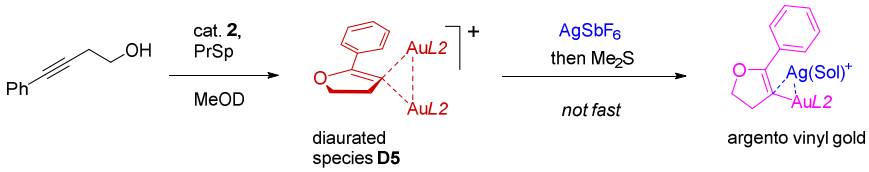
Figure S29. Determination of the order in silver.

Similar result is obtained by the method of initial concentrations (the first kinetic points were taken for calculation).

5.4. Series with 4-phenylbutyn-3-ol-1 and catalyst 2

Preliminary experiments 1279 and 1284 were made to establish spectral characteristics of diaurated species **D5**, argento vinyl gold **G5** and vinyl gold **B5** in CD_3OD.

1279



To a solution of 4-phenylbutyn-3-ol-1 (1.32 mg, 9.0 µmol) and PrSp (0.34 mg, 1.59 µmol) in CD_3OD (0.55 mL) was added catalyst **2** (2.44 mg, 3.16 µmol) and the mixture ultrasonicated for a brief period until complete dissolution of the solid. An NMR examination (Figure S30, Spectrum a) revealed complete formation of diaurated species **D5** and complete disappearance of the base. At this point to the reaction mixture was added $AgSbF_6$ (1.34 mg, 3.9 µmol). The NMR spectrum indicated that a part of the diaurated species converted to a new species, giving a phosphorus resonance at 65.63 ppm. This was assigned to argento vinyl gold species. More $AgSbF_6$ (5.1 mg) was added, but this only improved conversion to the new species and did not cause complete disappearance of the diaurated species (Spectrum b). Next, to the reaction mixture was added Me_2S (excess). This resulted in higher conversion of diaurated species to argento vinyl gold species. Diaurated species decreased, the P resonance of the argento vinyl gold species shifted by 0.05 ppm, the resonance at 2.50 broadened, the liberated gold was present as *L2*$AuSMe_2^+$ (at 63.33 ppm). Upon further addition of Me_2S the initial diaurated species disappeared completely, leaving only argento vinyl gold species and *L2*$AuSMe_2^+$ (Spectrum c). It was concluded that interaction of diaurated species with silver is simply slow, but can be accelerated by Me_2S. Even with Me_2S the reaction is not immediate but goes till completion.

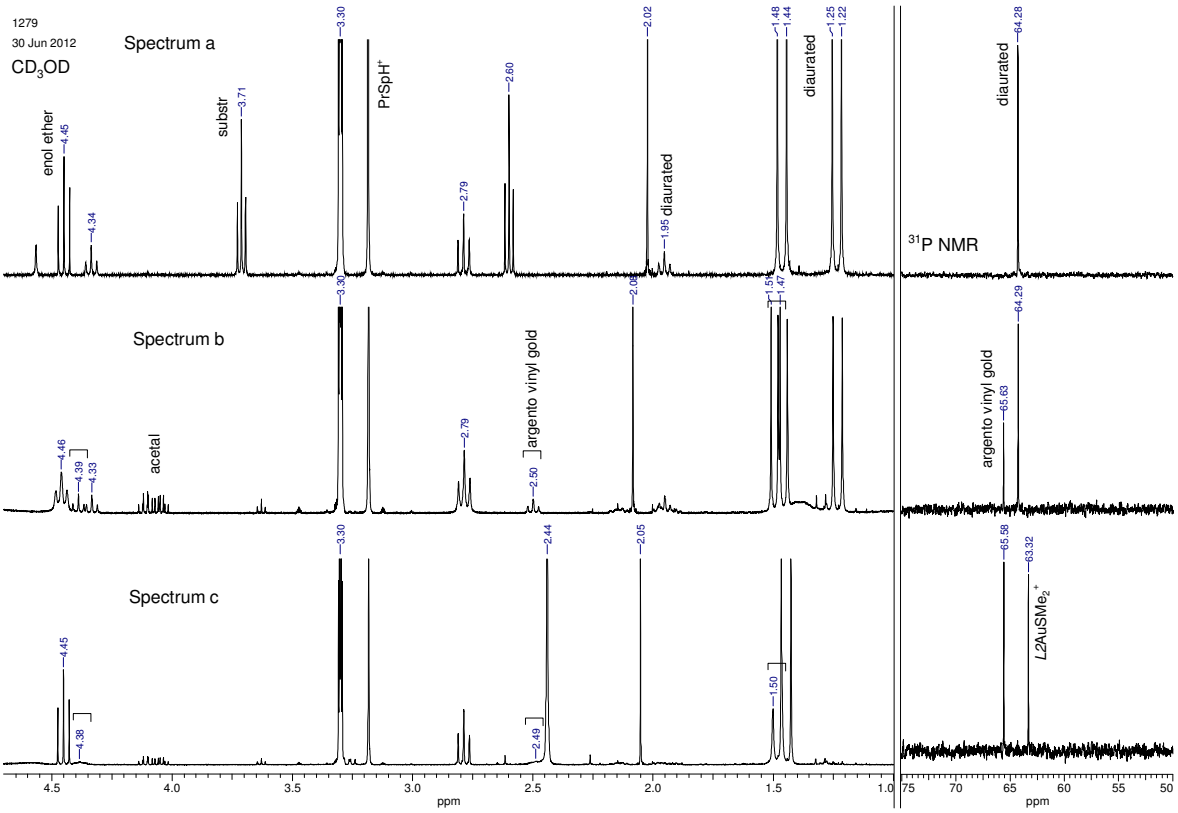
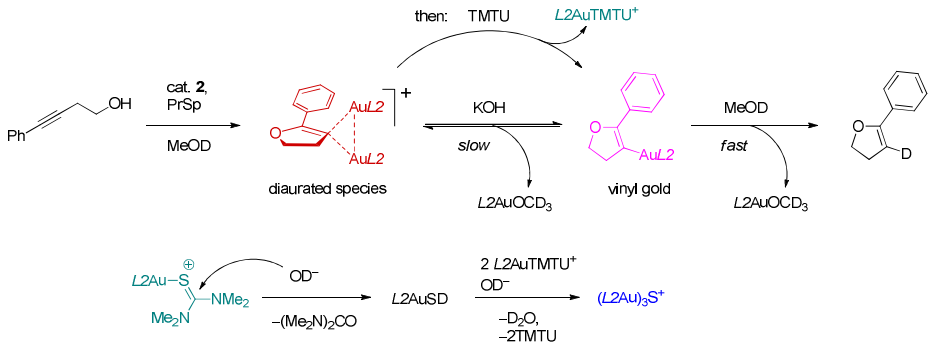


Figure S30. Spectra for experiment 1279.

Diaurated species **D5**. **^{1}H NMR** (400 MHz, CD_3OD), *selected signals:* δ = 4.34 (t, *J*=9.1 Hz, 2H), 1.95 (t, *J*=9.1 Hz, 2H), 1.44-1.48 (d, *J*=15.3 Hz, 18H), 1.22-1.25 (d, *J*=15.3 Hz, 18H). **^{31}P NMR** (CD_3OD): δ = 64.28.

Argento vinyl gold species **G5**. **^{1}H NMR** (400 MHz, CD_3OD), *selected signals:* δ = 4.39 (t, *J*=9.0 Hz, 2H), 2.50 (t, *J*=9.0 Hz, 2H), 1.47-1.51 (d, *J*=15.3 Hz, 18H). **^{31}P NMR** (CD_3OD): δ = 65.63.

1284



To a solution of 4-phenylbutyn-3-ol-1 (0.51 mg, 3.49 µmol) and PrSp (0.34 mg, 1.59 µmol) in CD_3OD (0.55 mL) was added catalyst **2** (1.73 mg, 2.24 µmol) and the mixture ultrasonicated for a brief period until complete dissolution of the solid was observed. NMR examination (Figure S31, Spectrum a) revealed complete formation of diaurated species. To this solution was then added solid KOH (random amount, excess), NMR indicated slow disappearance of diaurated species and formation of *L2*AuOMe (Spectrum b). Obviously the strength of methoxide as a ligand in methanol is not enough to trigger complete dissociation of diaurated species and this process is therefore reversible. Inability to observe

the corresponding vinyl gold in the phosphorus spectrum indicates that vinyl gold, being generated slowly, immediately undergoes protodeauration by methanol to give the corresponding enol ether. Therefore, vinyl gold is not accumulated in stoichiometric amounts, but keeps some small concentration according to the steady state principle. Nevertheless, traces of vinyl gold could be detected in the proton spectra: triplet at 4.10 ppm and doublet at 1.46–1.42 ppm (Spectrum b). To prove the identity of this vinyl gold further manipulations were made. Thus, not waiting till methoxide destroyed all diaurated species, TMTU (stronger ligand) was added. This caused immediate disappearance of all diaurated species, leaving small vinyl gold signals untouched (Spectrum c). Note, that *L2*AuTMTU$^+$ and diaurated species both have the same phosphorus resonance! After some 15 min the spectrum was recorded again, to observe complete disappearance of all vinyl gold signals (Spectrum d), confirming the identity of this compound. By the way, KOH reacted with *L2*AuTMTU$^+$ slowly producing (*L2*Au)$_3$S$^+$.

In result, we have established spectral characteristics of vinyl gold and observed fast protodeauration of this compound simply by methanol. It should be noted that this vinyl gold is less prone to protodeauration than the vinyl gold from 3-pentynol-1, because that vinyl gold is impossible to observe under similar conditions.

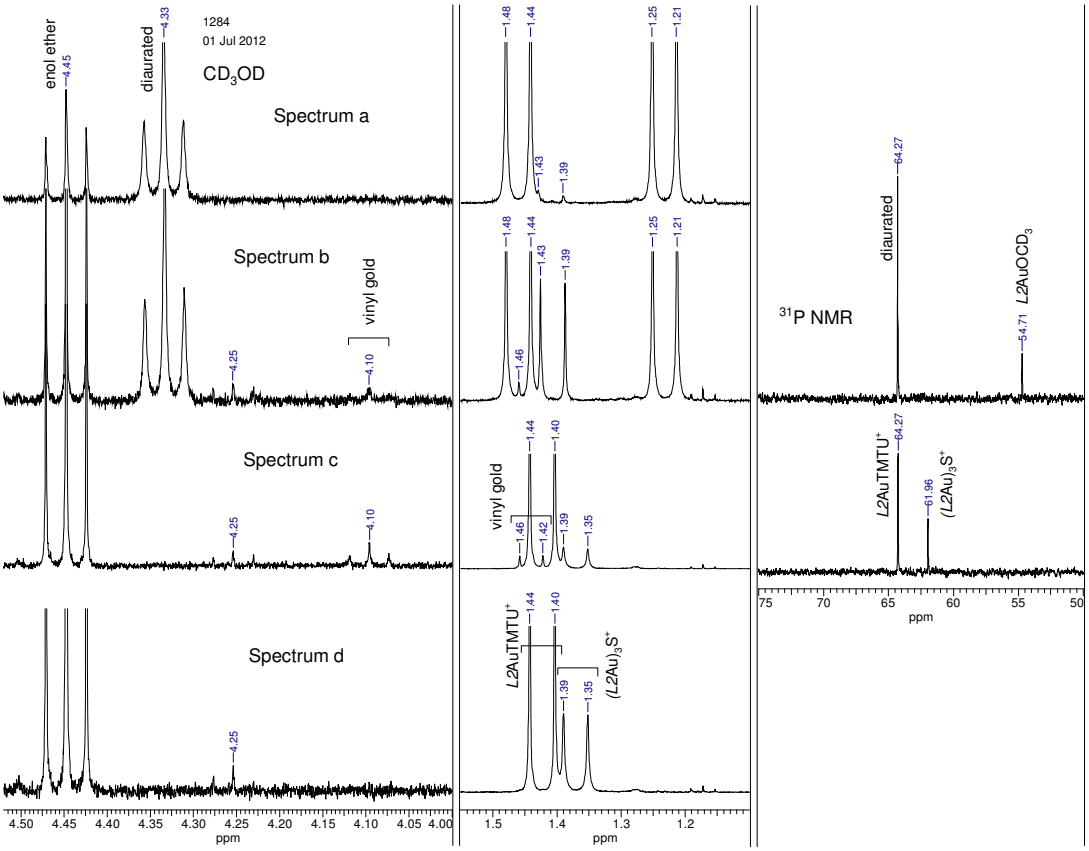


Figure S31. Spectra for experiment 1284.

Vinyl gold **B5**. **^{1}H NMR** (400 MHz, CD_3OD), *selected signals:* δ = 4.10 (t, *J*=9.0 Hz, 2H), 1.42-1.46 (d, *J*=14.5 Hz, 18H).

Determination of silver effect.

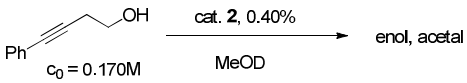
Stock solution A. Catalyst **2** (1.30 mg, 1.68 µmol) and mesitylene (6.72 mg, 55.9 µmol) were dissolved in CD_3OD (till 2.5 mL) in an analytical flask.

Stock solution B. tBu$_2$PyH$^+$ OTf$^-$ (0.81 mg, 2.37 µmol) was dissolved in CD_3OD (1.0 mL) in a vial.

Stock solution C. AgOTf (1.02 mg, 3.97 µmol) was dissolved in CD_3OD (0.50 mL) in a vial.

These solutions were used fresh in experiments 1354–1361 performed in a single day.

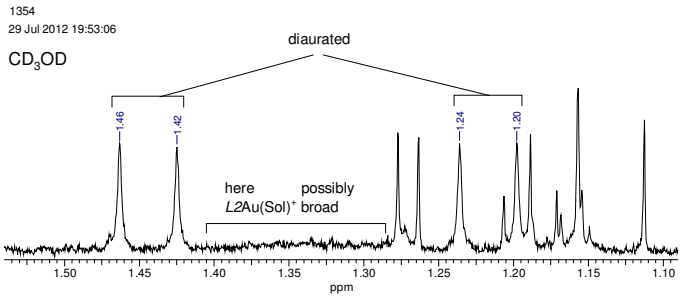
1354

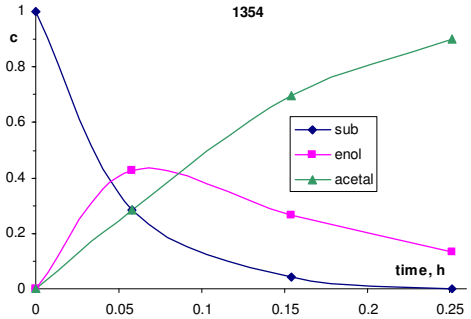


4-Phenylbutyn-3-ol-1 (13.45 mg, 92.0 µmol) was weighted into a vial. Stock **solution A** (0.54 mL, contains 0.363 µmol catalyst, 0.395% mol) was taken in a glass syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table S18 and Diagram below.

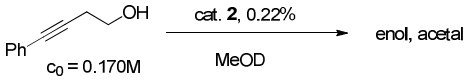
Table S18. Determination of chemical kinetics in exp 1354.

1354									
sub	0.170M								
cat **2**	0.40%								
abs. time	time, h		Mes	sub	enol	acetal	MeOD	mes	sum R
19:49:36	0			*1*	*0*	*0*			1
19:53:06	0.0583	**Spectrum**	3.73	*0.285*	*0.425*	*0.283*	7.17	11.71	0.993
19:58:52	0.154		3.79	*0.043*	*0.265*	*0.696*	7.17	12.11	1.004
20:04:40	0.251		3.83	*0*	*0.132*	*0.899*	7.17	12.58	1.031





1355

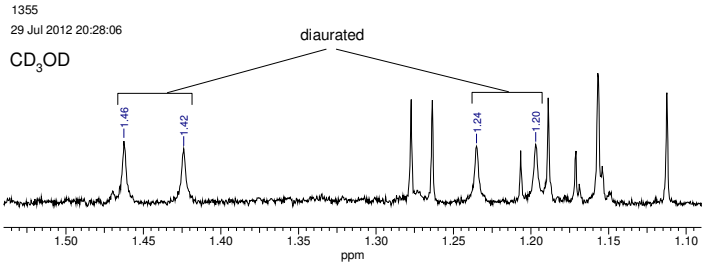


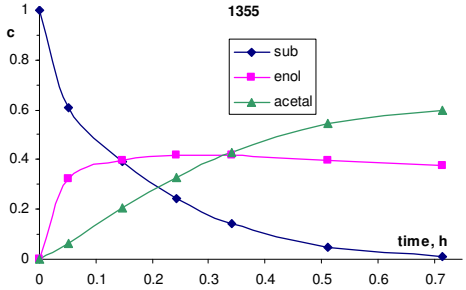
4-Phenylbutyn-3-ol-1 (13.40 mg, 91.7 µmol) was weighted into a vial. Stock **solution A** (0.30 mL, contains 0.202 µmol catalyst, 0.22% mol) was taken in a glass syringe and diluted with CD_3OD till 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and

transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table S19 and Diagram below.

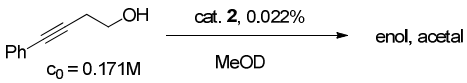
Table S19. Determination of chemical kinetics in exp 1355.

1355									
sub	0.170M								
cat **2**	0.22%								
abs. time	time, h		Mes	sub	enol	acetal	MeOD	mes	sum R
20:25:04	0			*1*	*0*	*0*			1
20:28:06	0.0506	**Spectrum**	2.11	*0.611*	*0.321*	*0.065*	7.12	6.51	0.997
20:33:54	0.147		2.1	*0.39*	*0.398*	*0.207*	7.08	6.56	0.995
20:39:40	0.243		2.08	*0.243*	*0.42*	*0.329*	6.96	6.58	0.992
20:45:28	0.34		2.04	*0.142*	*0.42*	*0.427*	6.76	6.65	0.989
20:55:44	0.511		1.86	*0.046*	*0.396*	*0.543*	5.82	6.57	0.985
21:07:54	0.714		1.74	*0.009*	*0.376*	*0.599*	5.43	6.54	0.984





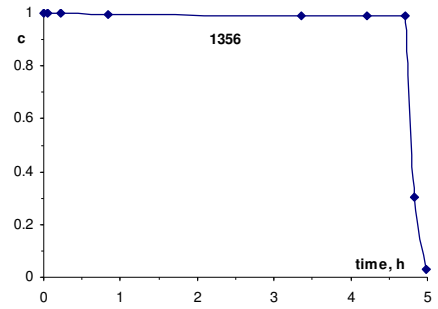
1356



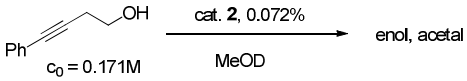
4-Phenylbutyn-3-ol-1 (13.50 mg, 92.3 µmol) was weighted into a vial. Stock **solution A** (0.03 mL, contains 0.0202 µmol catalyst, 0.022% mol) was taken in a small glass syringe and diluted with CD_3OD till 0.54 mL in another syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. During a 4 h period no conversion occurred. Then, at 4.72 h $TsOH \cdot H_2O$ (0.3 mg, 1.58 µmol, 1.7%) was added. Now a fast reaction occurred giving full conversion within 10 min. The result is given in the Table S20 and Diagram below.

Table S20. Determination of chemical kinetics in exp 1356.

1356									
sub	0.171M								
cat **2**	0.022%								
abs. time	time, h		Mes	sub	enol	acetal	MeOD	mes	sum R
21:08:56	0			*1*	*0*	*0*			1
21:11:58	0.051		low	*1*	*0*	*0*	7.13	0.61	1
21:22:14	0.222			*1*	*0*	*0*	7.12	0.61	1
21:59:24	0.841			*0.997*	*0.003*	*0*	7.1	0.6	1
00:30:24	3.36			*0.991*	*0.009*	*0*	7.22	0.62	1
01:22:04	4.22			*0.989*	*0.011*	*0*	7.21	0.61	1
01:51:51	4.72	*added TsOH*							
01:58:16	4.82			*0.302*	*0.008*	*0.661*	7.3	overlap	0.971
02:08:10	4.99			*0.03*	*0*	*0.928*	7.31		0.958



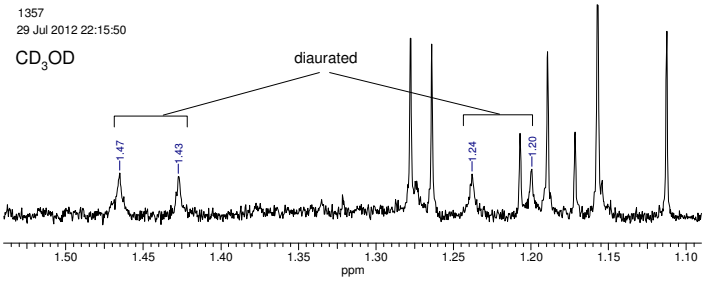
1357

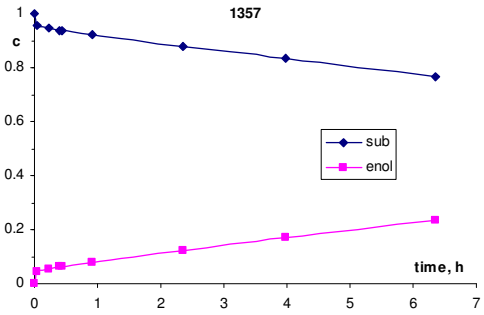


4-Phenylbutyn-3-ol-1 (13.55 mg, 92.7 µmol) was weighted into a vial. Stock **solution A** (0.10 mL, contains 0.0672 µmol catalyst, 0.072% mol) was taken in a glass syringe and diluted with CD_3OD till 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table S21 and Diagram below.

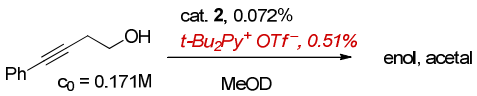
Table S21. Determination of chemical kinetics in exp 1357.

1357									
sub	0.171M								
cat **2**	0.072%								
abs. time	time, h		Mes	sub	enol	acetal	MeOD	mes	sum R
22:12:50	0			*1*	*0*	0			1
22:15:50	0.05	**Spectrum**	0.76	*0.954*	*0.046*	0	7.07	2.28	1
22:26:06	0.221		0.75	*0.944*	*0.056*	0	7.06	2.27	1
22:36:22	0.392		0.74	*0.939*	*0.062*	0	7.05	2.26	1.001
22:39:24	0.443		0.76	*0.937*	*0.064*	0	7.08	2.27	1.001
23:08:26	0.927		0.75	*0.921*	*0.079*	0	7.08	2.28	1
00:33:40	2.347		0.75	*0.879*	*0.122*	0	7.18	2.29	1.001
02:11:42	3.981		0.75	*0.832*	*0.169*	0	7.18	2.29	1.001
04:34:24	6.359		0.75	*0.767*	*0.233*	0	7.18	2.29	1





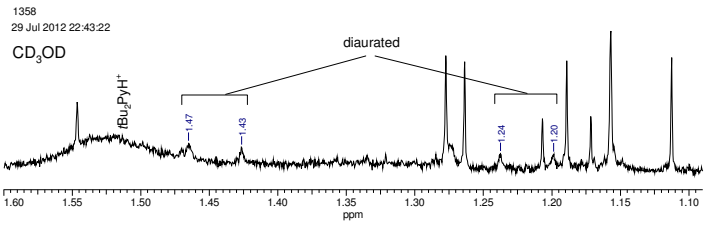
1358

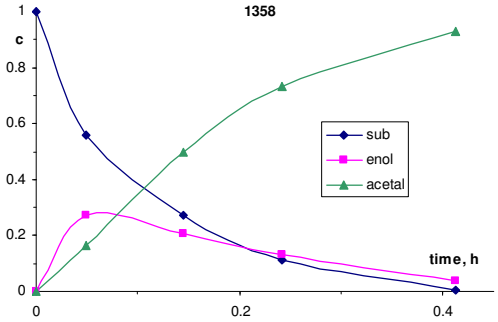


4-Phenylbutyn-3-ol-1 (13.48 mg, 92.2 µmol) was weighted into a vial. Stock **solution A** (0.10 mL, contains 0.0672 µmol catalyst, 0.072% mol) was taken in a glass syringe and diluted with CD_3OD, then with **solution B** (0.20 mL, contains 0.474 µmol, 0.51% acid) and then again with CD_3OD till a total volume of 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table S22 and Diagram below.

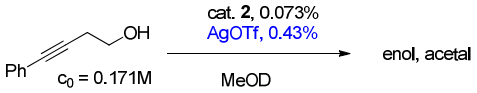
Table S22. Determination of chemical kinetics in exp 1358.

1358									
sub	0.171M								
cat **2**	0.072%								
*t*Bu$_2$PyH$^+$	0.51%								
abs. time	time, h		Mes	sub	enol	acetal	MeOD	mes	sum R
22:40:27	0			*1*	*0*	*0*			1
22:43:22	0.0486	**Spectrum**	0.76	*0.558*	*0.273*	*0.164*	7.07	2.32	0.995
22:49:10	0.145		0.77	*0.271*	*0.208*	*0.496*	7.07	2.34	0.975
22:54:56	0.241		0.76	*0.112*	*0.133*	*0.734*	7.2	2.43	0.979
23:05:12	0.413		0.77	*0.007*	*0.038*	*0.928*	7.22	2.44	0.973





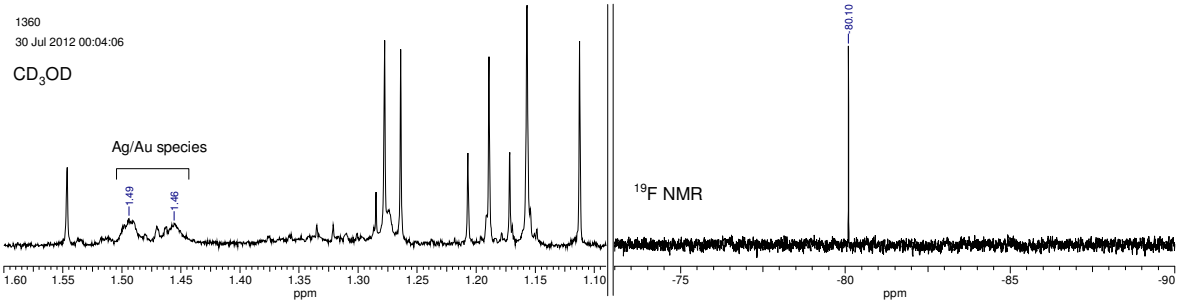
1360

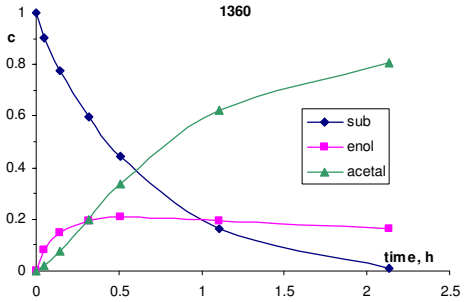


4-Phenylbutyn-3-ol-1 (13.44 mg, 91.9 µmol) was weighted into a vial. Stock **solution A** (0.10 mL, contains 0.0672 µmol catalyst, 0.072% mol) was taken in a glass syringe and diluted with CD_3OD, then with **solution C** (0.05 mL, contains 0.397 µmol, 0.43% silver) and then again with CD_3OD till a total volume of 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table S23 and Diagram below.

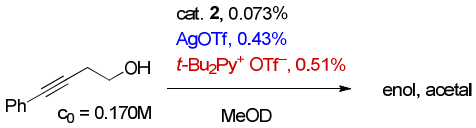
Table S23. Determination of chemical kinetics in exp 1360.

1360								
sub	0.171M							
cat **2**	0.073%							
AgOTf	0.43%							
abs. time	time, h	Mes	sub	enol	acetal	MeOD	mes	sum R
23:56:20	0		*1*	*0*	*0*			1
23:59:14	0.048	0.73	*0.902*	*0.081*	*0.018*	7.09	2.22	1.001
00:05:02	0.145	0.73	*0.775*	*0.149*	*0.076*	7.08	2.24	1
00:15:18	0.316	0.73	*0.598*	*0.195*	*0.201*	7.06	2.25	0.994
00:26:54	0.509	0.74	*0.446*	*0.207*	*0.337*	7.16	2.28	0.99
01:02:36	1.10	0.74	*0.165*	*0.192*	*0.624*	6.96	2.31	0.981
02:04:30	2.14	0.66	*0.011*	*0.161*	*0.804*	5.91	2.33	0.976





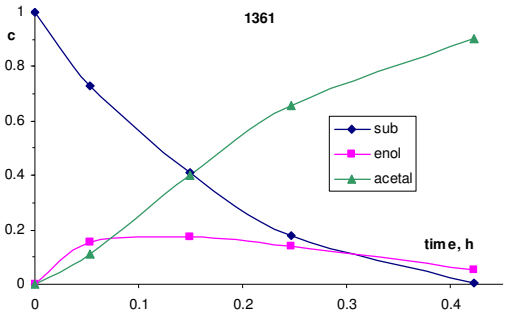
1361



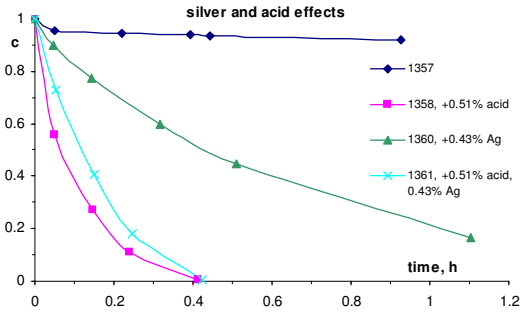
4-Phenylbutyn-3-ol-1 (13.39 mg, 91.6 µmol) was weighted into a vial. Stock **solution A** (0.10 mL, contains 0.0672 µmol catalyst, 0.072% mol) was taken in a glass syringe and diluted with **solution B** (0.20 mL, contains 0.474 µmol, 0.51% acid), with **solution C** (0.05 mL, contains 0.397 µmol, 0.43% silver) and then again with CD_3OD till a total volume of 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table S24 and Diagram below.

Table S24. Determination of chemical kinetics in exp 1361.

1361								
sub	0.170M							
cat **2**	0.073%							
AgOTf	0.43%							
*t*Bu$_2$PyH$^+$	0.51%							
abs. time	time, h	Mes	sub	enol	acetal	MeOD	mes	sum R
00:40:40	0		*1*	*0*	*0*			1
00:43:50	0.053	0.74	*0.73*	*0.155*	*0.11*	7.21	2.27	0.995
00:49:38	0.149	0.75	*0.409*	*0.173*	*0.401*	7.28	2.34	0.983
00:55:26	0.246	0.75	*0.179*	*0.139*	*0.656*	7.33	2.37	0.974
01:06:00	0.422	0.75	*0.006*	*0.054*	*0.904*	7.4	2.41	0.964

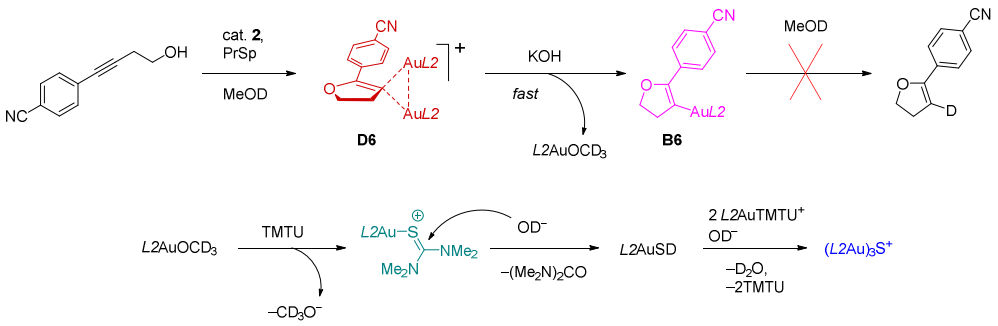


The combined diagram from experiments 1358, 1359, 1360, 1361 below shows the influence of silver and acid additives on the course of the reaction (positive effects observed):



5.5. Series with 4-(4-cyanophenyl)-butyn-3-ol-1 and catalyst 2

1278, 1280 (preliminary experiments to establish the spectral characteristics of the diaurated species **D6**, vinyl gold **B6** and argento vinyl gold **G6** intermediates in CD_3OD)



To a solution of 4-(4-cyanophenyl)-butyn-3-ol-1 (1.1 mg, 6.43 µmol) and PrSp (0.58 mg, 2.71 µmol) in CD_3OD (0.55 mL) was added catalyst **2** (2.48 mg, 3.21 µmol) and the reaction mixture was ultrasonicated for a brief period until complete dissolution of the solid. NMR examination (Figure S32, Spectrum a) revealed predominant formation of diaurated species, however, a small part of the catalyst was present as oxonium compounds (not seen on the phosphorus spectrum), and more interestingly, as vinyl gold (at 66.93 ppm). The ability to observe this vinyl gold indicates its resistance to protodeauration by MeOD and $PrSpH^+$, which is remarkable because other vinyl gold species in this study would not survive these conditions. Next, about 2/3 part of the solution was taken into another NMR tube and treated with solid KOH (0.7 mg), which dissolved readily (the remaining 1/3 part of the solution is used in the next experiment below). NMR examination (Spectrum b) revealed almost complete conversion of the initial diaurated species to vinyl gold and *L2*AuOMe (in its turn, $PrSpH^+$ neutralized back to PrSp). This action proved that the compound at 66.93 ppm is vinyl gold, and not an impurity or side product. Next, to the solution was added TMTU (0.8 mg) to observe complete disappearance of *L2*AuOMe and formation of two new compounds: *L2*AuTMTU$^+$ and $(L2Au)_3S^+$. The latter is originating from *L2*AuTMTU$^+$ by slow saponification of the thioamide moiety by KOH. During this manipulation the vinyl gold stayed intact, which further confirms its identity.

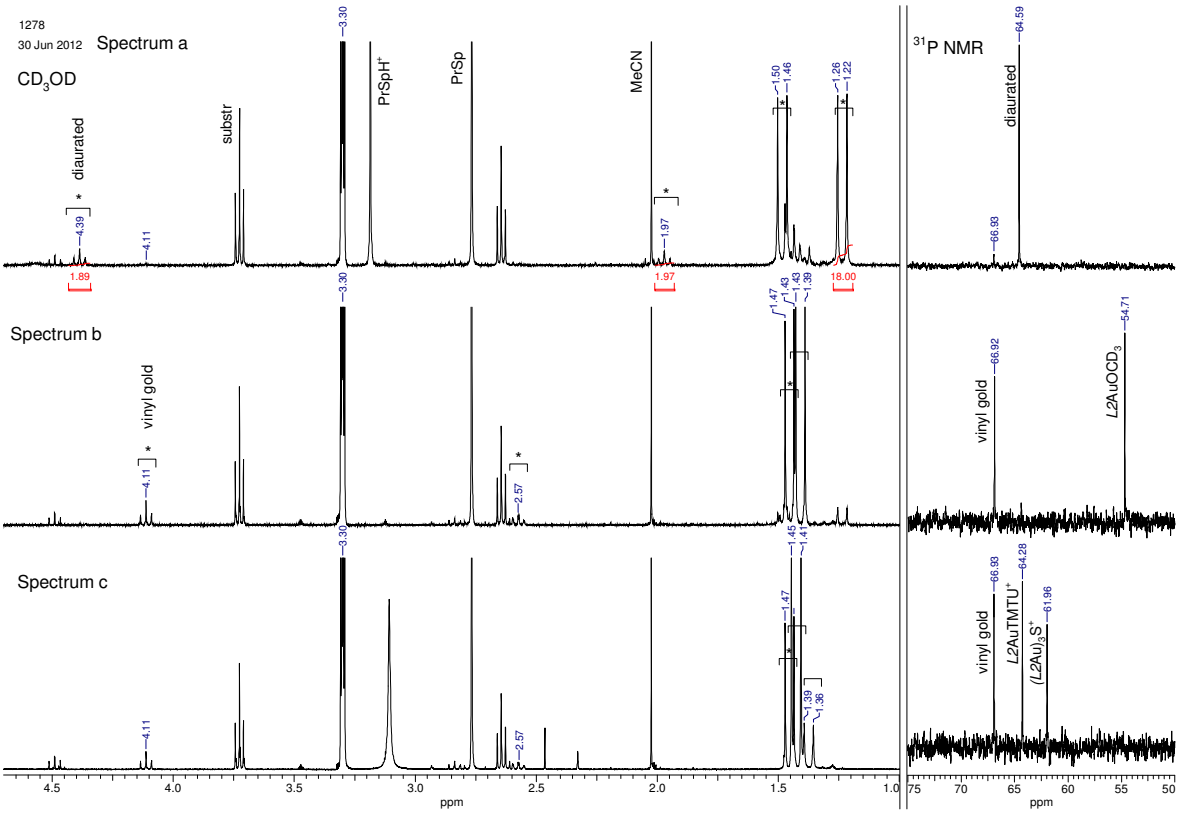


Figure S32. Spectra for experiment 1278.

To the portion containing 1/3 of the solution of diaurated species, obtained as described above, was added catalyst **2** (1.94 mg) to convert the remaining substrate. NMR indicated that this amount of catalyst was in excess (being now as oxonium salt) and the situation was corrected by addition of substrate to reduce the amount of oxonium salt. The resulting situation is shown in Figure S33 in Spectrum d. It is important here that no excess of a base is present. To this solution was then added $AgSbF_6$ (2.80 mg). An NMR spectrum indicated that a part of diaurated species converted to a new species, giving a phosphorus resonance at 65.59 ppm (Spectrum e). This was assigned to argento vinyl gold species. Next, to the solution was added Me_2S (2.7 equiv with respect to gold, according to NMR). This resulted in higher conversion of diaurated species to argento vinyl gold species (Spectrum f). Diaurated species decreased, the P resonance of argento vinyl gold species shifted by 0.04 ppm, the resonance at 2.54 broadened, the liberated gold was present as *L2*$AuSMe_2^+$ (at 63.33 ppm). Upon further addition of Me_2S the initial diaurated species disappeared completely, leaving only argento vinyl gold species and *L2*$AuSMe_2^+$ (spectrum not shown).

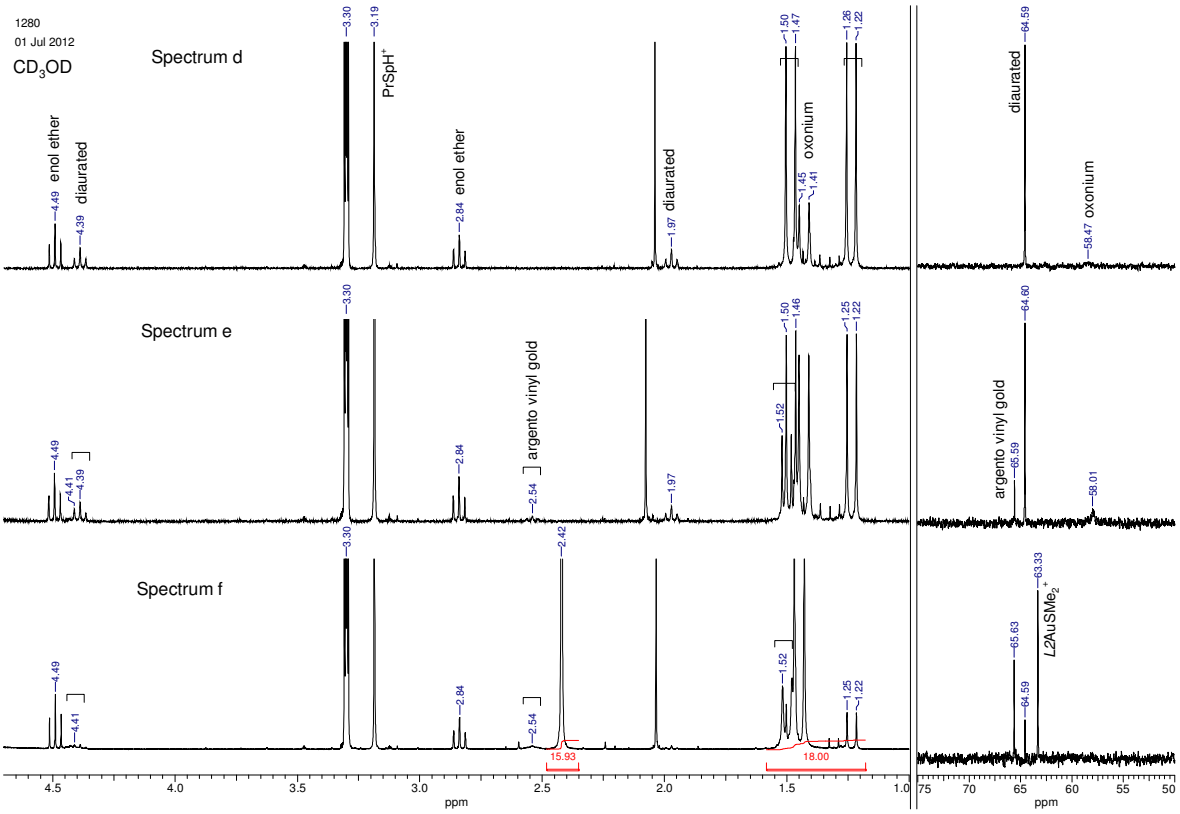


Figure S33. Spectra for experiment 1280.

Compound characterization.

Diaurated species **D6**. **^{1}H NMR** (400 MHz, CD_3OD), *selected signals:* δ = 4.39 (t, *J*=9.4 Hz, 2H), 1.97 (t, *J*=9.4 Hz, 2H), 1.46-1.50 (d, *J*=15.4 Hz, 18H), 1.22-1.25 (d, *J*=15.4 Hz, 18H). **^{31}P NMR** (CD_3OD): δ = 64.59.

Vinyl gold **B6**. **^{1}H NMR** (400 MHz, CD_3OD), *selected signals:* δ = 4.11 (t, *J*=9.0 Hz, 2H), 2.57 (t, *J*=9.0 Hz, 2H), 1.43-1.47 (d, *J*=14.6 Hz, 18H). **^{31}P NMR** (CD_3OD): δ = 66.92.

1274

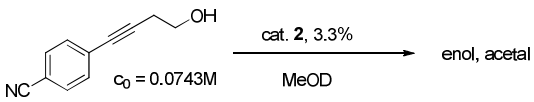


Table S25. Determination of chemical kinetics in exp 1274.

1274		kinetic	almost first order						
c(sub)	0.0743M								
cat **2**	3.30%								
abs time	time. min		Mes	sub	enol	diaur	MeOD	Mes	sum R
15:52:53	0			1	0	0			1
15:56:38	3.75	**Spectrum**	9.47	0.61	0.391	0.0101	16.64	29.61	1.0111
16:10:16	17.4		9.47	0.093	0.879	0.0084	16.66	29.64	0.9804
16:23:52	31.0		9.47	0	0.951	0.0073	16.67	29.79	0.9583

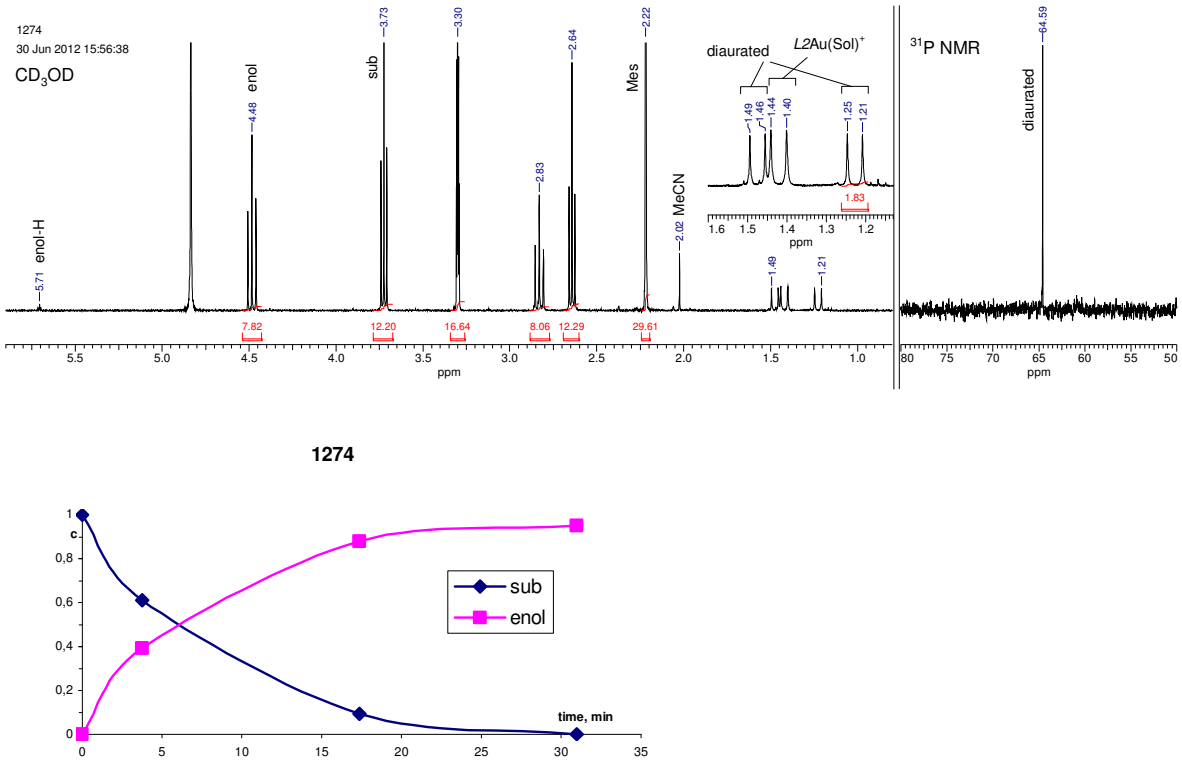


Figure S34. Spectra and Diagram for experiment 1274.

1275

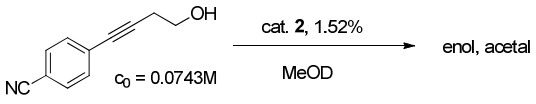
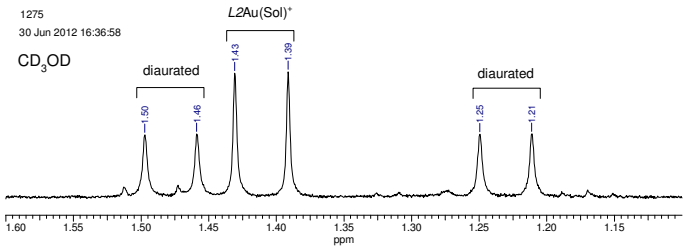


Table S26. Determination of chemical kinetics in exp 1275.

1275			v = ks^(0.83…0.86) almost 1 order							
c(sub)	0.0743M									
cat **2**	1.52%									
abs time	time. min		Mes	sub	enol	diaur	free Au	MeOD	Mes	sum R
16:33:32	0			1	0	0				
16:36:58	0.057	**Spectrum**	4.55	0.973	0.028	0.0047	0.0073	16.59	14.31	1.0057
16:46:26	0.215		4.55	0.913	0.0825	0.0046	0.0074	16.58	14.34	1.0001
17:11:36	0.634		4.55	0.785	0.208	0.0046	0.0074	16.67	14.39	0.9976
17:36:48	1.05		4.55	0.673	0.322	0.0046	0.0077	16.78	14.5	0.9996
17:56:42	1.39		4.55	0.586	0.392	0.0043	0.0073	16.82	14.48	0.9823
18:44:00	2.17		4.55	0.421	0.562	0.00406	0.0073	16.71	14.35	0.98706
19:51:36	3.30		4.55	0.259	0.723	0.0042	0.0077	16.76	14.4	0.9862



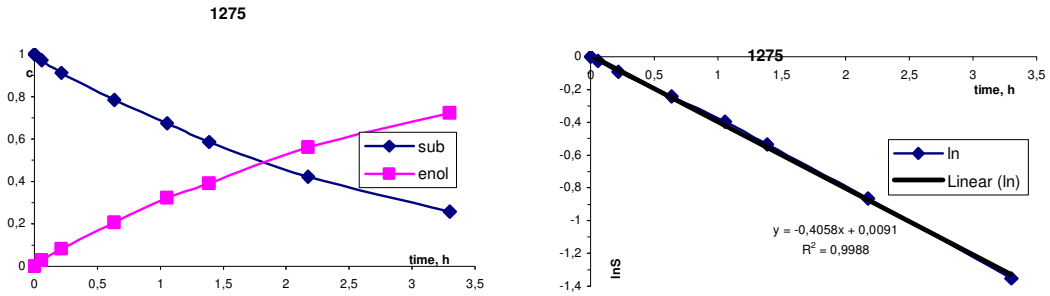


Figure S35. Spectra and Diagram for experiment 1275.

1276

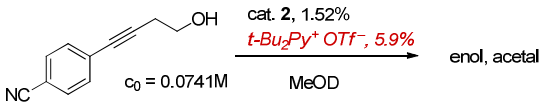
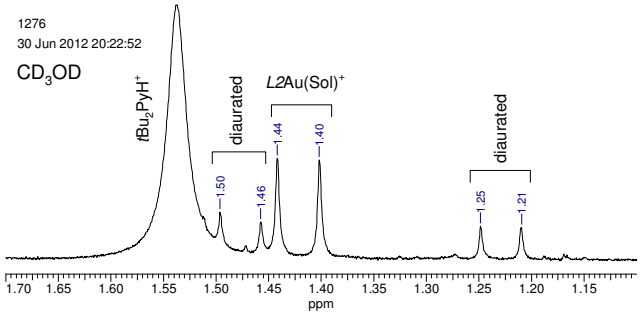


Table S27. Determination of chemical kinetics in exp 1276.

1276			almost first order						
c(sub)	0.0741M								
cat **2**	1.52%								
*t*Bu$_2$PyH$^+$ OTf$^-$	5.90%								
abs time	time. min		Mes	sub	enol	diaur	MeOD	Mes	sum R
20:19:08	0			1	0	0			1
20:22:52	3.73	**Spectrum**	4.43	0.682	0.318	0.0031	16.38	14.03	1.0031
20:32:20	13.2		4.43	0.3	0.674		16.52	14.19	0.974
20:45:58	26.8		4.43	0.064	0.851	0.014	16.4	14.03	0.929



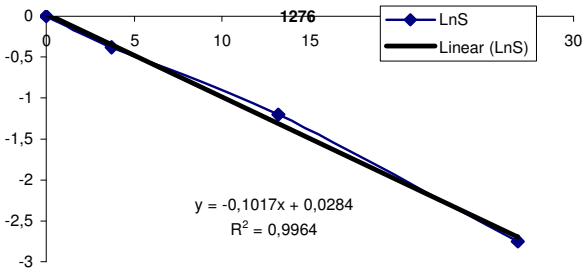


Figure S36. Spectra and Diagram for experiment 1276.

1277

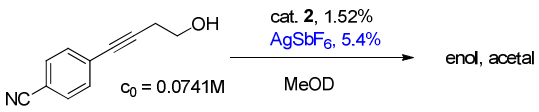
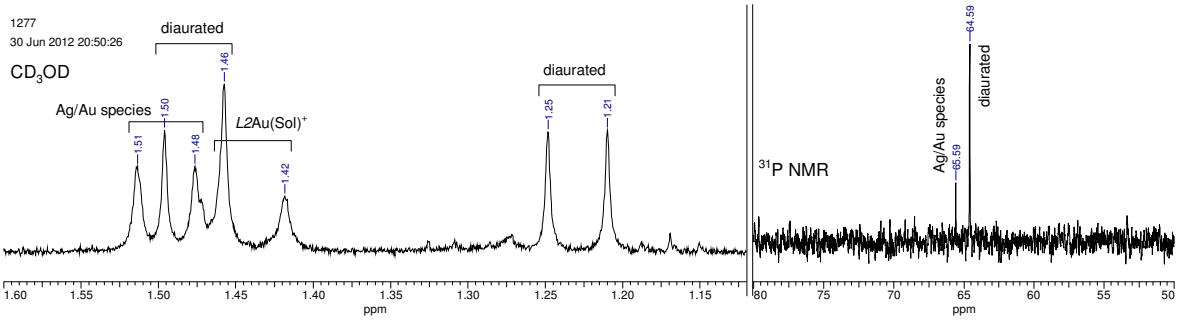


Table S28. Determination of chemical kinetics in exp 1277.

1277			kinetic first order					
c(sub)	0.0741M							
cat **2**	1.52%							
$AgSbF_6$	5.40%							
abs time	time. min		Mes	sub	enol	MeOD	Mes	sum R
20:46:32	0			1	0			1
20:50:26	3.9	**Spectrum**	4.57	0.722	0.278	16.93	14.44	1
20:59:54	13.37		4.57	0.396	0.593	16.93	14.41	0.989
21:13:30	26.97		4.57	0.153	0.821	16.92	14.33	0.974
21:19:14	32.7		4.57	0.0985	0.868	16.93	14.41	0.9665



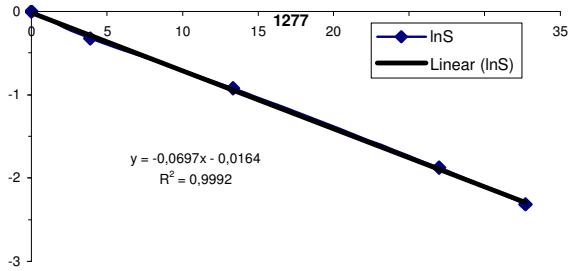


Figure S37. Spectra and Diagram for experiment 1277.

Experiments 1275, 1276 (with tBu$_2$PyH$^+$ OTf$^-$), 1277 (with $AgSbF_6$) at a glance:

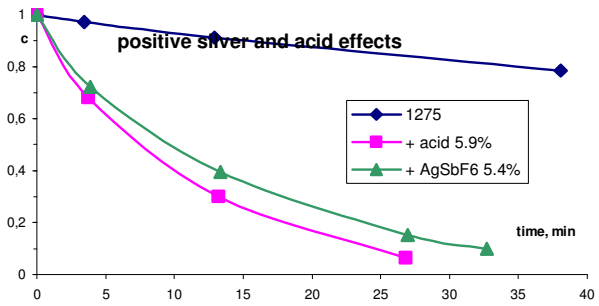


Figure S38. Diagram for experiments 1275, 1276, 1277.

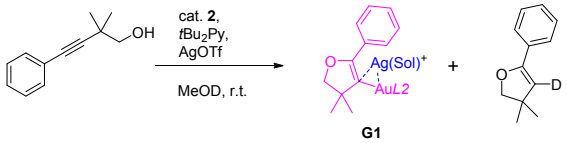
5.6. Series with 2,2-dimethyl-4-phenylbutyn-3-ol-1 and catalyst 2

For a spectrum of 2,2-dimethyl-4-phenylbutyn-3-ol-1 in MeOD see ref. 2.

5.6.1. Preliminary experiments

Stock solution A. Catalyst **2** (0.79 mg, 1.02 µmol) and mesitylene (4.62 mg, 38.4 µmol) were dissolved in CD_3OD (till 2.5 mL) in an analytical flask.

1407. Observation of argento vinyl gold in MeOD



G1

To a mixture of 2,2-dimethyl-4-phenylbutyn-3-ol-1 (1.50 mg, 8.6 µmol) and tBu$_2$Py (0.32 mg, 1.7 µmol) was added **solution A** (0.54 ml, 0.81 µmol Au, additionally containing AgOTf, 2.03 mg, 7.8 µmol) and catalyst **2** (1.68 mg, 2.2 µmol). NMR examination indicated complete formation of argento vinyl gold species **G1** (Figure S39, Spectrum a). (After recording the phosphorus spectrum for 7 min a proton spectrum was recorded again to reveal partial protodeauration). In order to further prove the identity of the compoud, the reaction mixture was neutralized by adding PrSp (0.52 mg, 2.4 µmol) to avoid the progressing slow protodeauration. The solution became slightly turbid because of trace amounts of a tiny dark precipitate (possibly Ag or Ag_2O). Then to this solution was added Me_2S (3 equiv to gold, by NMR). NMR indicated that argento vinyl gold species partially survived, but *L2*AuSMe$_2^+$ was formed as a result of protodemetallation (Spectrum b).

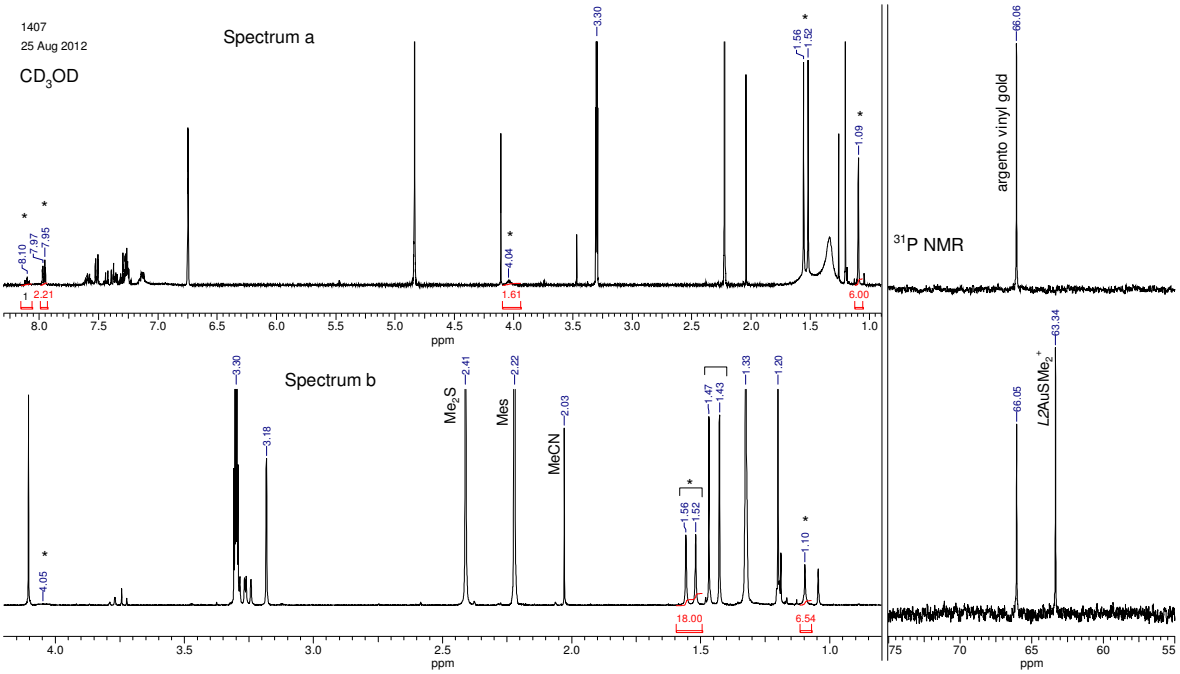


Figure S39. Spectra for experiment 1407.

Argento vinyl gold **G1**. **^{1}H NMR** (400 MHz, CD_3OD), *selected signals:* δ = 4.04 (bs, 2H), 1.52-1.56 (d, *J*=15.0 Hz, 18H), 1.09 (s, 6H). **^{31}P NMR** (CD_3OD): δ = 66.06.

1415

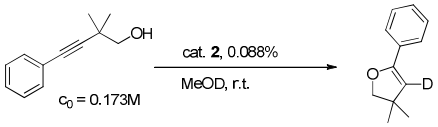


Table S29. Determination of chemical kinetics in exp 1415.

1415						
sub	0.173M					
cat **2**	0.088%					
abs. time	time, h	sub	enol	acetal	MeOD	mes
00:44:42	0	1	0	0		
00:48:42	0.067	0.65	0.35	0	3.49	1.42
00:54:20	0.161	0.428	0.573		3.49	1.44
01:04:28	0.329	0.217	0.779	0.005	3.49	1.44
01:14:34	0.498	0.115	0.878	0.007	3.49	1.45

Vinyl gold is the only observable catalytic species in this experiment.

1417

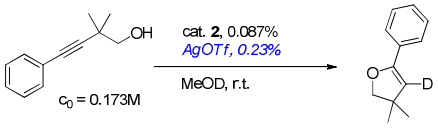
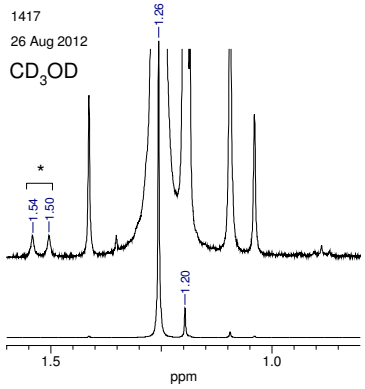


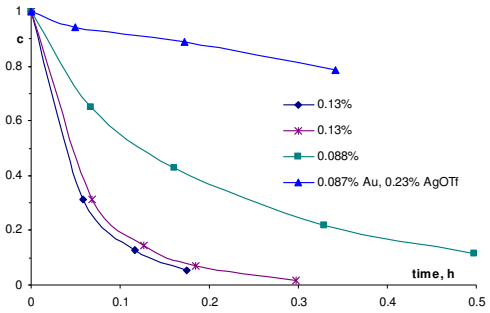
Table S30. Determination of chemical kinetics in exp 1417.

1417						
sub	0.173M					
cat **2**	0.087%					
AgOTf	0.23%					
abs. time	time, h	sub	enol	acetal	MeOD	mes
01:59:01	0	1	0	0		
02:02:00	0.050	0.942	0.058		3.51	1.42
02:09:20	0.172	0.887	0.11	0.016	3.51	1.43
02:19:32	0.342	0.784	0.174	0.044	3.51	1.42

In this experiment argento vinyl gold was the only observable catalytic species (marked with *, a singlet at 1.10 is hidden inside of the satellite peak):



The combined diagram below shows disappearance of the substrate for experiments 1408 (described in a preceding article,[2] 0.131% Au), 1413 (described in the preceding article, 0.131% Au), 1415 (0.088% Au), 1417 (0.087% Au, 0.23% Ag):


1
c
0.8
0.6
0.4
0.2
0
0
0.1
0.2
0.3
0.4
0.5
time, h
0.13%
0.13%
0.088%
0.087% Au, 0.23% AgOTf

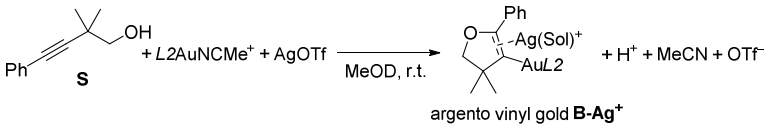
5.6.2. Determination of chemical kinetics

Gold catalyzed cyclization of 2,2-dimethyl-4-phenylbutyn-3-ol-1 in methanol, being not accompanied by formation of diaurated species, was found to be a suitable reaction for the study.

In order to determine the reaction kinetics, a series of experiments was conducted with known starting concentrations of the catalytic inputs:

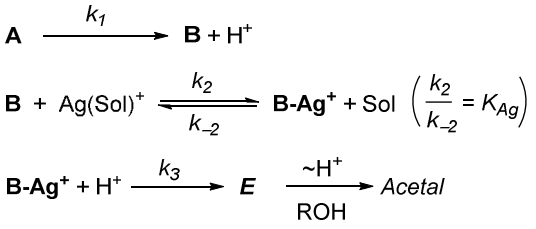
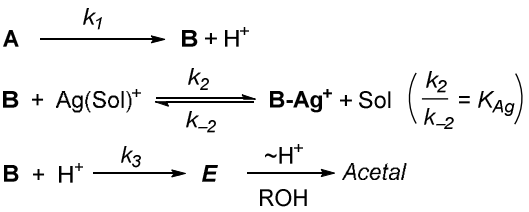
gold c_0(cat. **2**) = c,
silver $c_0(Ag^+) = a$,
acid $c_0(H^+) = h$,

The necessary condition $a>c$ was applied in order to ensure complete formation of argento vinyl gold. Another necessary condition for the experiments is complete and immediate formation of argento vinyl gold in the reaction mixture, which is secured not ideally, but quite well for the given reaction (see below).
According to the reaction stoichiometry, 1 equiv of gold consumes 1 equiv of silver and generates 1 equiv of acid in solution:

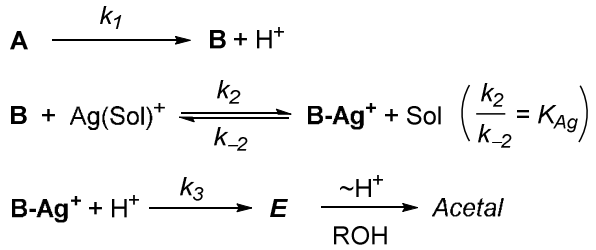


Taking this equation into account, the concentration of argento vinyl gold was determined as *[***B-Ag***] = c*, silver $[Ag^+] = a–c$, acid $[H^+] = c+h$.

With regard to the overall catalytic reaction mechanism two extreme situations were considered:

1. Argento vinyl gold undergoes protodeauration directly by reacting with acid (as a bimolecular reaction):	2. Argento vinyl gold does not undergo protodeauration directly, but first dissociates to vinyl gold **B**, and then **B** reacts with acid (nucleophile assisted dissociative pathway):
	

Case 1. Argento vinyl gold undergoes protodeauration directly by reacting with acid (as a bimolecular reaction).



Steady state approximation is applied for ***B*** (present in negligible amount) and ***B-Ag*$^+$** (present on full amount, = total amount of gold in the system)

$$\begin{cases} \dfrac{d[\mathbf{B}]}{dt} = k_1[\mathbf{A}] - k_2[\mathbf{B}][\mathrm{Ag}^+] + k_{-2}[\mathbf{B\text{-}Ag}] = 0 \\ \dfrac{d[\mathbf{B\text{-}Ag}]}{dt} = k_2[\mathbf{B}][\mathrm{Ag}^+] - k_{-2}[\mathbf{B\text{-}Ag}] - k_3[\mathbf{B\text{-}Ag}][H^+] = 0 \end{cases}$$

From the steady state approximations the following expression for the overall reaction rate is immediately obtained:

$$\text{overall reaction rate: } -\frac{d[\mathbf{S}]}{dt} = k_1[\mathbf{A}] = k_3[\mathbf{B\text{-}Ag}][H^+]$$

According to this equation the reaction should have zero order in substrate, zero order in silver, first order in gold, first order in acid.

Given the known starting concentrations *c(cat.* ***2****) = c*, silver $c(Ag^+) = a$, acid $c(H^+) = h$, and in accordance with the necessary condition that complete formation of argento vinyl gold is achieved, concentration of argento vinyl gold is determined as *[***B-Ag***] = c*, silver $[Ag^+] = a–c$, acid $[H^+] = c+h$. Placing these values into the rate law gives:

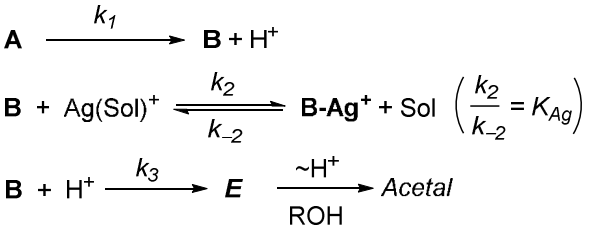
$$-\frac{d[\mathbf{S}]}{dt} = k_3c(c+h)$$

Solution of this equation is

$$\frac{[\mathbf{S}]}{c(c+h)} = -k_{eff}t + const$$

This equation is linear if built in coordinates *{y=[***S***], x=t}*, moreover, the lines must be parallel if built in coordinates *{y=[***S***]/c/(c+h), x=t}*.

Case 2. Argento vinyl gold does not undergo protodeauration directly, but first dissociates to vinyl gold **B**, and then **B** reacts with acid (nucleophile assisted dissociative pathway):



Steady state approximations for **B** and **B-Ag** and the overall reaction rate:

$$\begin{cases} \dfrac{d[\mathbf{B}]}{dt} = k_1[\mathbf{A}] - k_3[\mathbf{B}][H^+] - \underbrace{k_2[\mathbf{B}][Ag^+] + k_{-2}[\mathbf{B\text{-}Ag}]}_{=0} = 0 \\ \dfrac{d[\mathbf{B\text{-}Ag}]}{dt} = k_2[\mathbf{B}][Ag^+] - k_{-2}[\mathbf{B\text{-}Ag}] = 0 \end{cases}$$

$$\text{overall reaction rate: } -\frac{d[\mathbf{S}]}{dt} = k_1[\mathbf{A}] = k_3[\mathbf{B}][H^+]$$

Using the steady state approximation for [**B-Ag**] we come to the following expression for [**B**]:

$$[\mathbf{B}] = \frac{[\mathbf{B\text{-}Ag}]}{K_{Ag}[Ag^+]}$$

Placing this equation into the overall reaction rate expression gives the rate law:

$$\frac{d[\mathbf{S}]}{dt} = -\frac{k_3[\mathbf{B\text{-}Ag}][H^+]}{K_{Ag}[Ag^+]}$$ - the reaction should have zero order in substrate, first order in **B-Ag**, first order in acid, minus first order in Ag^+.

Given the known starting concentrations *c(cat.* ***2****) = c*, silver $c(Ag^+) = a$, acid $c(H^+) = h$, and in accordance with the necessary condition that complete formation of argento vinyl gold is achieved, concentration of argento vinyl gold is determined as *[***B-Ag***] = c*, silver $[Ag^+] = a–c$, acid $[H^+] = c+h$. Placing these values into the rate law gives:

$$\frac{d[\mathbf{S}]}{dt} = -\frac{k_3 c(c+h)}{K_{Ag}(a-c)}$$

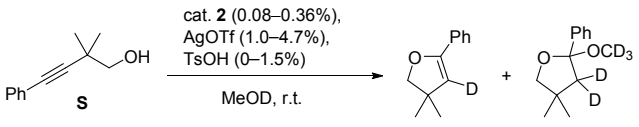
Solution of this equation is

$$\frac{[\mathbf{S}](a-c)}{c(c+h)} = -k_{eff}t + const$$

.

This equation is linear if built in coordinates *{y=[***S***], x=t}*, moreover, the lines must be parallel if built in coordinates *{y=[***S***](a–c)/c/(c+h), x=t}*.

2247-2250. Experimental determination of the reaction kinetics



Stock solution A. Catalyst **2** (1.49 mg, 1.93 μmol) and $PhCH_2CH_2Ph$ (7.54 mg, 41.4 μmol) were dissolved in CD_2Cl_2 (2 drops) and diluted with CD_3OD (1.60 mL) in a vial. An NMR spectrum was recorded to establish the molar ratio $PhCH_2CH_2Ph$:Au = 20.7:1. The CH_2 signal of $PhCH_2CH_2Ph$ was then used to determine the total concentration of Au in the reaction mixtures.

Stock solution D. AgOTf (4.81 mg, 18.7 μmol) and CF_3CH_2OH (18.99 mg, 190 μmol) were dissolved in CD_3OD (1.60 mL) in a vial. A ^{19}F NMR spectrum was recorded to establish the molar ratio CF_3CH_2OH:Ag =

100:9.39. The CH_2 signal of CF_3CH_2OH was then used to determine the total concentration of Ag in the reaction mixtures.

Stock solution C. $TsOH \cdot H_2O$ (1.24 mg, 6.52 μmol) and mesitylene (4.80 mg, 39.9 μmol) were dissolved in CD_3OD (0.54 mL) in a vial. An NMR spectrum was recorded to establish the molar ratio mesitylene:TsOH = 6.33:1. The CH signal of mesitylene was then used to determine total concentration of TsOH in the reaction mixtures.

Solution C2. Solution C (0.10 mL) was diluted with CD_3OD till 0.50 mL.

Stock **solution A** (amounts, see Table) was taken in a glass syringe and diluted with **solution D** (amounts, see Table), then **solution C** (amouns, see Table) and then with CD_3OD till 0.54 mL directly in the same syringe. This content was poured into a vial with 2,2-dimethyl-4-phenylbutyn-3-ol-1 (11.71-11.83 mg, 67.8 μmol) and the time count was started. The reaction mixture was transferred into an NMR tube using a Pasteur pipette and the reaction was further monitored by NMR. Total concentrations of Au, Ag and TsOH in every reaction mixture were determined by NMR (Table S31 and S32).

Table S31. Amounts of the substrate, solutions **A**, **D**, **C**, **C2** taken for the experiments.

Exp	Substr		Sol **A**, mL	Sol **D**, mL	Sol **C**, mL
	mg	M			
2280	11.80	0.125	0.20	0.07	0
2281	11.81	0.126	0.20	0.10	0
2282	11.80	0.125	0.10	0.10	0
2283	11.87	0.126	0.05	0.10	C2, 0.09
2284	11.84	0.126	0.05	0.10	0.05
2285	11.78	0.125	0.05	0.10	0.10
2286	11.86	0.126	0.05	0.20	0.10
2287	11.83	0.126	0.05	0.20	0.05
2288	11.80	0.125	0.05	0.30	0.05

Table S32. Total concentrations of Au, Ag and TsOH and the calculated actual concentrations of argento vinyl gold [AuAg], free silver [Ag^+] and acid [H^+].

Exp	Substr		Cat. **2**		Ag		TsOH		Calculated actual concentrations		
	mg	M	Au (%)	ΣAu (mM)	Ag (%)	ΣAg (mM)	%	mM	[AuAg], mM	[Ag^+], mM	[H^+], mM
2280	11.80	0.125	0.358	0.449	1.04	1.31	0	0	0.449	0.856	0.449
2281	11.81	0.126	0.355	0.446	1.59	1.99	0	0	0.446	1.547	0.446
2282	11.80	0.125	0.175	0.219	1.59	1.99	0	0	0.219	1.772	0.219
2283	11.87	0.126	0.0831	0.105	1.55	1.96	0.272	0.343	0.105	1.850	0.448
2284	11.84	0.126	0.0850	0.107	1.62	2.03	0.760	0.957	0.107	1.926	1.064
2285	11.78	0.125	0.0899	0.113	1.58	1.98	1.527	1.912	0.113	1.863	2.025
2286	11.86	0.126	0.0821	0.104	3.11	3.92	1.527	1.925	0.104	3.815	2.029
2287	11.83	0.126	0.0831	0.104	3.12	3.92	0.775	0.975	0.104	3.816	1.079
2288	11.80	0.125	0.0812	0.102	4.65	5.83	0.749	0.939	0.102	5.729	1.041

Calculation of concentrations:

[AuAg] = ΣAu;
[Ag^+] = ΣAg – ΣAu;
[H^+] = ΣAu + TsOH

The results are given in the Tables S33 and Diagrams below

Table S33. Determination of chemical kinetics for experiments 2280-2288.

2280

substr	0.125 M											
Au	0.358%											
Ag	1.04%											
TsOH	0.00%	eq	eq	eq					eq			
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Mes	Ar	TFE	sum R	S*Ag/Au/H	S/Au/H, μM^{-1}
23:42:45	0	1	0	0						1	532	0.621
23:44:50	0.035	0.631	0.208	0.161	4.95	1.483		28.63	0.172	1	336	0.392
23:48:30	0.096	0.126	0.237	0.643	4.95	1.51		28.89	0.176	1.006	67	0.078

2281

substr	0.126 M

Au	0.355%											
Ag	1.59%											
TsOH	0.00%	eq	eq	eq					eq			
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Mes	Ar	TFE	sum R	S*Ag/Au/H	S/Au/H, μM^{-1}
00:01:46	0	1	0	0						1	977	0.632
00:04:52	0.052	0.687	0.144	0.17	4.97	1.47		28.57	0.169	1.001	671	0.434
00:08:34	0.113	0.369	0.155	0.479	4.97	1.49		28.73	0.173	1.003	361	0.233
00:12:16	0.175	0.101	0.142	0.763	4.97			28.84	0.176	1.006	99	0.064

2282

substr	0.125 M											
Au	0.175%											
Ag	1.59%											
TsOH	0.00%	eq	eq	eq					eq			
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Mes	Ar	TFE	sum R	S*Ag/Au/H	
00:18:00	0	1	0	0						1	4631	
00:20:24	0.040	0.957	0.033	0.011	4.95	0.723		26.58	0.169	1.001	4432	
00:25:22	0.123	0.885	0.059	0.054	4.95			26.57		0.998	4098	
00:33:04	0.251	0.784	0.071	0.142	4.95			26.6		0.997	3630	
00:46:02	0.467	0.62	0.072	0.304	4.95			26.67		0.996	2871	
00:59:04	0.684	0.47	0.07	0.456	4.95			26.72		0.996	2176	
01:14:30	0.942	0.309	0.067	0.618	4.95	0.751		26.62	0.173	0.994	1431	

2283

substr	0.126 M											
Au	0.0831%											
Ag	1.55%											
TsOH	0.272%	eq	eq	eq					eq			
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Mes	Ar	TFE	sum R	S*Ag/Au/H	S*Ag/Au, M
01:14:54	0	1	0	0						1	4973	2.227
01:17:00	0.035	0.961	0.024	0.016	4.92	0.344	0.258	25.67	0.165	1.001	4779	2.140
01:22:02	0.119	0.888	0.034	0.076	4.92			25.69		0.998	4416	1.977
01:29:44	0.247	0.777	0.035	0.182	4.92			25.61		0.994	3864	1.730
01:37:22	0.374	0.675	0.034	0.286	4.92		0.263	25.65	0.167	0.995	3357	1.503

2284

substr	0.126 M												
Au	0.0850%												
Ag	1.62%												
TsOH	0.760%	eq	eq	eq					eq				
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Mes	Ar	TFE	sum R	S*Ag/Au/H	S/Au/H, μM^{-1}	S*Ag/Au, M
01:40:55	0	1	0	0						1	2129	1.105	2.265
01:42:54	0.033	0.876	0.032	0.092	4.96	0.352	0.722	25.81	0.172	1	1865	0.968	1.984
01:48:00	0.118	0.602	0.031	0.369	4.96			25.97		1.002	1281	0.665	1.364
01:55:46	0.248	0.234	0.029	0.737	4.96			25.96		1	498	0.259	0.530
02:00:44	0.330	0.028	0.025	0.942	4.96		0.733	26.01	0.181	0.995	60	0.031	0.063

2285

substr	0.125 M											
Au	0.0899%											
Ag	1.58%											
TsOH	1.53%	eq	eq	eq					eq			
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Mes	Ar	TFE	sum R	S*Ag/Au/H	
02:01:09	0	1	0	0						1	1024	
02:03:16	0.035	0.759	0.034	0.207	4.96	0.372	1.45	26	0.168	1	777	
02:08:18	0.119	0.277	0.03	0.682	4.9	0.374	1.45	25.82	0.172	0.989	284	
02:11:58	0.180	0.008	0.019	0.953	4.86	0.39	1.45	25.77	0.174	0.98	8	

2286

substr	0.126 M												
Au	0.0821%												
Ag	3.11%												
TsOH	1.53%	eq	eq	eq					eq				
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Mes	Ar	TFE	sum R	S*Ag/Au/H	S*Ag/Au, M	
02:15:29	0	1	0	0						1	2290	4.645	
02:17:26	0.033	0.883	0.016	0.101	4.9	0.34	1.45	25.87	0.331	1	2022	4.102	
02:22:26	0.116	0.627	0.016	0.357	4.91	0.347	1.45	25.97	0.335	1	1436	2.913	
02:30:04	0.243	0.276	0.016	0.695	4.87	0.354	1.45	25.73	0.342	0.987	632	1.282	
02:35:04	0.326	0.076	0.015	0.898	4.86	0.352	1.45	25.79	0.342	0.989	174	0.353	

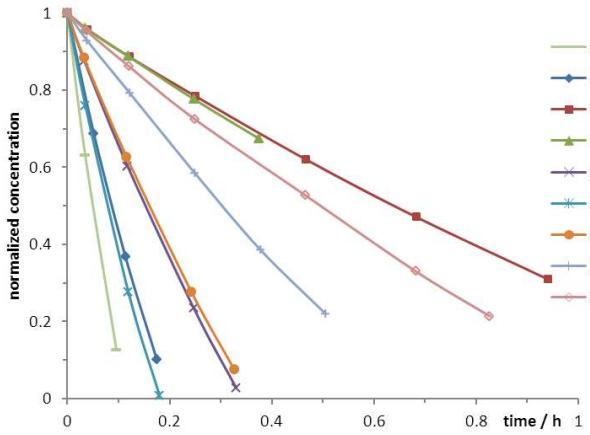
2287

substr	0.126 M												
Au	0.0831%												
Ag	3.12%												
TsOH	0.775%	eq	eq	eq					eq				
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Mes	Ar	TFE	sum R	S*Ag/Au/H	S/Au/H, μM^{-1}	S*Ag/Au, M
02:35:20	0	1	0	0						1	4255	1.115	4.593
02:37:40	0.039	0.928	0.016	0.055	4.93	0.344	0.736	25.8	0.332	0.999	3949	1.035	4.262

02:42:38	0.122	0.793	0.016	0.199	4.96	0.348	0.736	26.02	0.336	1.008	3374	0.884	3.642
02:50:20	0.250	0.584	0.016	0.398	4.92	0.356	0.736	25.84	0.337	0.998	2485	0.651	2.682
02:58:00	0.378	0.386	0.015	0.573	4.81	0.348	0.736	25.26	0.332	0.974	1642	0.430	1.773
03:05:40	0.506	0.22	0.015	0.76	4.9		0.736	25.82	0.341	0.995	936	0.245	1.010

2288												
substr	0.125 M											
Au	0.0812%											
Ag	4.65%											
TsOH	0.749%	eq	eq	eq					eq			
abs. time	time, h	substr	enol	acetal	MeOD	CH2	Mes	Ar	TFE	sum R	S*Ag/Au/H	S/Au/H, μM^{-1}
03:06:00	0	1	0	0						1	6780	1.183
03:08:16	0.038	0.953	0.01	0.036	4.92	0.336	0.711	25.69	0.495	0.999	6461	1.128
03:13:16	0.121	0.861	0.011	0.123	4.9	0.334	0.711	25.56	0.494	0.995	5837	1.019
03:20:56	0.249	0.725	0.011	0.249	4.86	0.339	0.711	25.4	0.492	0.985	4915	0.858
03:33:58	0.466	0.527	0.011	0.459	4.91	0.338	0.711	25.75	0.504	0.997	3573	0.624
03:46:56	0.682	0.33	0.011	0.633	4.8	0.342	0.711	25.11	0.492	0.974	2237	0.391
03:55:36	0.827	0.214	0.011	0.754	4.82	0.34	0.711	25.31	0.494	0.979	1451	0.253

Disappearance of the substrate:



	Substr, M	Au (%)	Ag (%)	TsOH (%)
2280	0.125	0.358	1.04	0
2281	0.126	0.355	1.59	0
2282	0.125	0.175	1.59	0
2283	0.126	0.0831	1.55	0.272
2284	0.126	0.0850	1.62	0.760
2285	0.125	0.0899	1.58	1.527
2286	0.126	0.0821	3.11	1.527
2287	0.126	0.0831	3.12	0.775
2288	0.125	0.0812	4.65	0.749

Figure S40. Kinetic curves for experiments 2280-2288.

Analysis of results

Observation of the resting state of the catalyst by NMR.

In all experiments argento vinyl gold **G1** was formed as a single resting state, which is seen by NMR in all experiments at all conversions at all times (with a single exception at t=0.18 h, c=0.008 in exp 2285, which is at >99% conversion), for example:

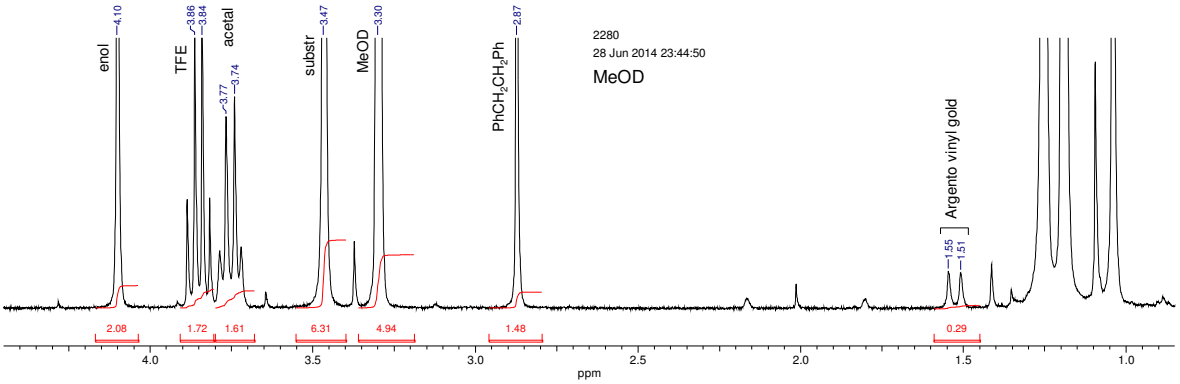


Figure S41. ^{1}H NMR spectrum at 0.035 h of experiment 2280.

At conversions of the substrate >99% argento vinyl gold will start to fade away and *L2*Au(Sol)$^+$ will start to form, for example at t=0.18 h, c=0.008 in exp 2285:

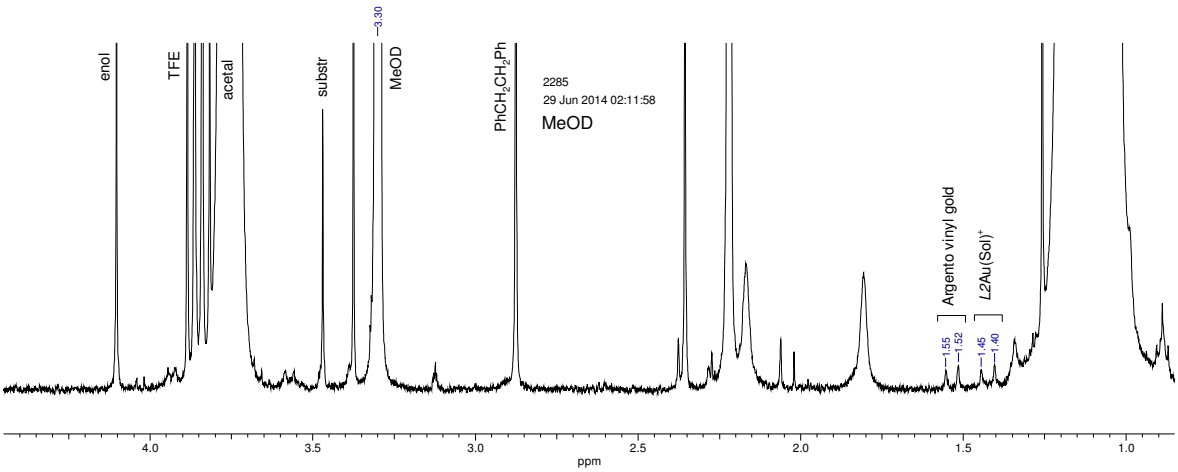


Figure S42. ^{1}H NMR spectrum at 0.18 h of experiment 2285.

Analysis of chemical kinetics

The experimental general order in substrate is determined by finding *n* to best fit the experimental data into the linear equation $y = [\mathbf{S}]^{1-n} = -(1-n)k_{eff}t + const$, that is a solution of a general equation for the reaction rate:

$$-\frac{d[\mathbf{S}]}{dt} = k_{eff}[\mathbf{S}]^n \xrightarrow{\text{solution}} [\mathbf{S}]^{1-n} = -(1-n)k_{eff}t + const$$

Best linearity is observed at n = 0.1-0.3 order in substrate. The slight deviation from the theoretically predicted zero order law is not explained. Pleasingly, the nonlinearity is slight, therefore each curve satisfactory fits into a linear equation, as shown on Figure S43:

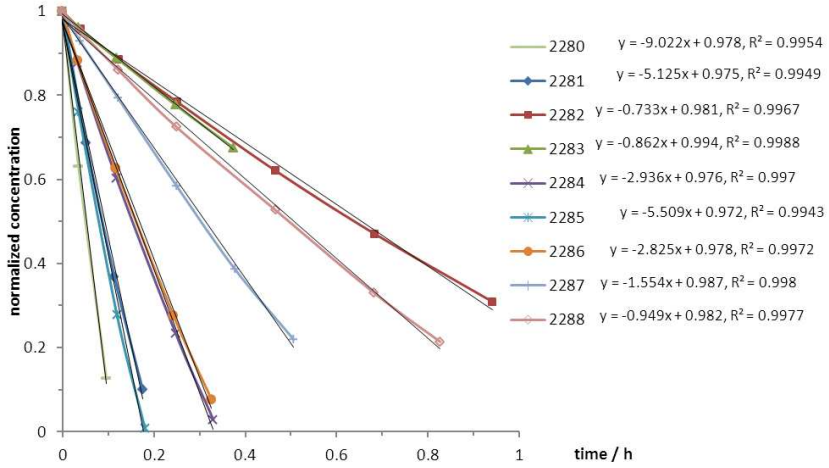
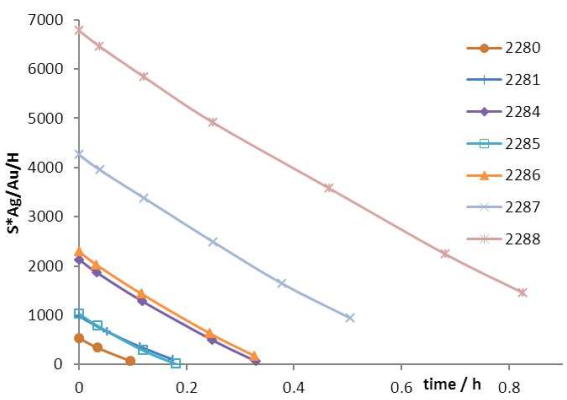


Figure S43. "Satisfactory" linear fit of experimental data into a linear equation [S] = –kt + const.

Further analysis indicates, that the reaction has first order in gold, first order in acid and **minus first order in silver**. The minus first order in silver confirms the nucleophile assisted dissociative pathway for protonolysis of argento vinyl gold.



Exp	k, h^{-1}
2280	4798
2281	5008
2284	6249
2285	5640
2286	6468
2287	6611
2288	6435

$k = (6.4\pm0.2)\cdot10^3\ h^{-1}$

Figure S44. Linear graphs $y = [S][Ag^+]/[RAuAg^+]/[H^+] = -kt + const$.

Table S34. Determination of the order in silver and acid.

For Ag^+	AuAg, mM	Ag, mM	H, mM	slope	lnAg	ln(-Slope)
2280	0.449	0.856	0.449	-5.6052	-0.155	1.724
2281	0.446	1.547	0.446	-3.238	0.436	1.175
2284	0.107	1.926	1.064	-3.2446	0.655	1.177
2287	0.104	3.816	1.079	-1.7325	1.339	0.550
2288	0.102	5.729	1.041	-1.1233	1.745	0.116

For H^+	AuAg, mM	Ag, mM	H, mM	slope	lnH	ln(-Slope)
2283	0.105	1.850	0.448	-1.9193	-0.804	0.652
2284	0.107	1.926	1.064	-6.6491	0.062	1.894
2286	0.104	3.815	2.029	-13.124	0.708	2.574
2287	0.104	3.816	1.079	-7.1357	0.076	1.965

Determination of order in Ag^+:

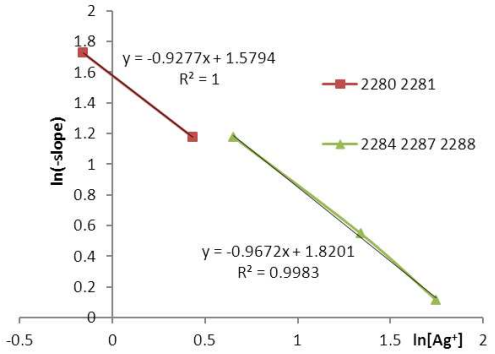


Figure S45. Linear graphs $y = ln(-slope) = n\cdot ln[Ag^+, mM] + const$, n = –1 is found.

Determination of order in H^+:

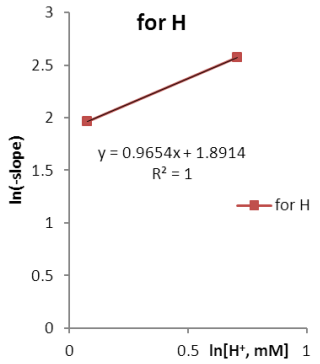
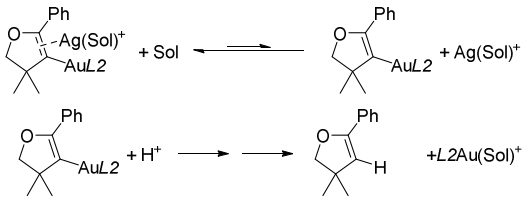


Figure S46. Linear graph *y = ln(-slope) = n·ln[H$^+$, mM] + const*, n = 1 is found.

Note. In the presence of excess of Ag^+ and H^+, gold can be applied at very low amounts without having to worry about accidental poisons in the reaction mixture. However, if the excess of Ag^+ and H^+ is sufficiently low, the poisons can influence the actual concentrations of free Ag^+ and, most likely, H^+. (The most likely poisons are OH^- or HCO_3^- after washing the NMR tubes). This can make problems for accurate determination of chemical kinetics at very low catalyst loadings. For example, an underestimated value of $4\cdot10^3$–$5\cdot10^3$ h^{-1} is obtained for the rate constant in experiments 2280, 2281 and some other experiments not shown here. The value of $(6.4\pm0.2)\cdot10^3$ h^{-1} obtained at higher amounts of Ag^+ and H^+ (experiments 2284, 2286, 2287, 2288) seems more reliable.

Conclusion

Argento vinyl gold undergoes protonolysis through a nucleophile assisted dissociative pathway:

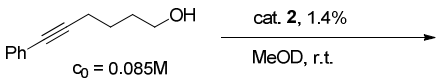


5.7. Series with 6-phenylhexyn-5-ol-1 and catalyst 2

Stock solution A. Catalyst **2** (2.80 mg, 3.63 µmol) and mesitylene (8.33 mg, 69.3 µmol) were dissolved in CD_3OD (till 2.5 mL) in an analytical flask.

Stock solution B. Catalyst **2** (2.92 mg, 3.78 µmol) and mesitylene (5.41 mg, 45.0 µmol) were dissolved in CD_3OD (till 2.5 mL) in an analytical flask.

1286



6-Phenylhexyn-5-ol-1 (8.00 mg, 46.0 µmol) was weighted into a vial. Stock **solution A** (0.45 mL, contains 0.653 µmol catalyst, 1.4% mol) was taken in a glass syringe and diluted with CD_3OD till 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table and Diagram below.

Table S35. Determination of the chemical kinetics for exp 1286.

1286		kinetic first order						
c(sub)	0.085M							
cat **2**	1.40%							
abs time	time, h	Mes	sub	6-exo	MeOD	Mes	sum R	LnS
19:08:44	0		1	0			1	0
19:12:10	0.057	8.24	0.797	0.142	14.58	25.97	0.939	-0.2269
19:21:50	0.218	8.24	0.453	0.397	14.52	25.93	0.85	-0.7919
19:47:00	0.638	8.24	0.106	0.614	14.54	26.01	0.72	-2.2443
20:00:36	0.864	8.24	0.05	0.649	14.56	26.07	0.699	-2.9957

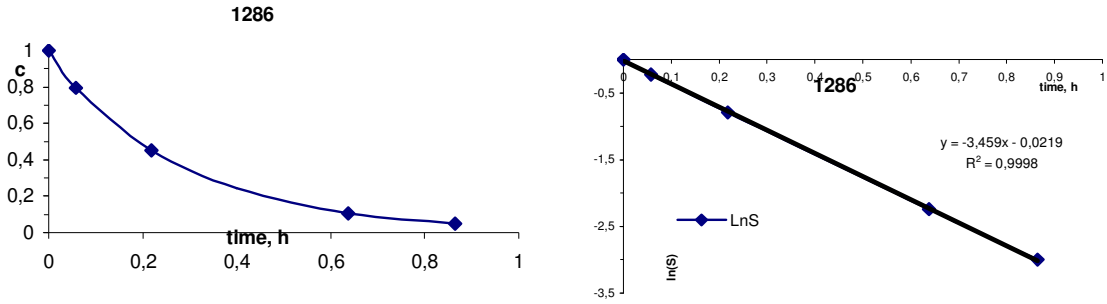


Figure S47. Diagram for experiment 1286.

In this experiment the gold catalyst predominantly was present as a free form *L2*Au(Sol)$^+$ and partially as diaurated species (Figure S48). By the chemical shift of the *t*Bu doublet, predominance of *L2*Au(enol)$^+$ could be suggested, all forms of *L2*Au(Sol)$^+$ are in fast ligand exchange and therefore invisible in the phosphorus spectrum (broad). The phosphorus spectrum indicates only diaurated species. From the proton spectrum it could therefore be concluded that diaurated species are only minor among the others.

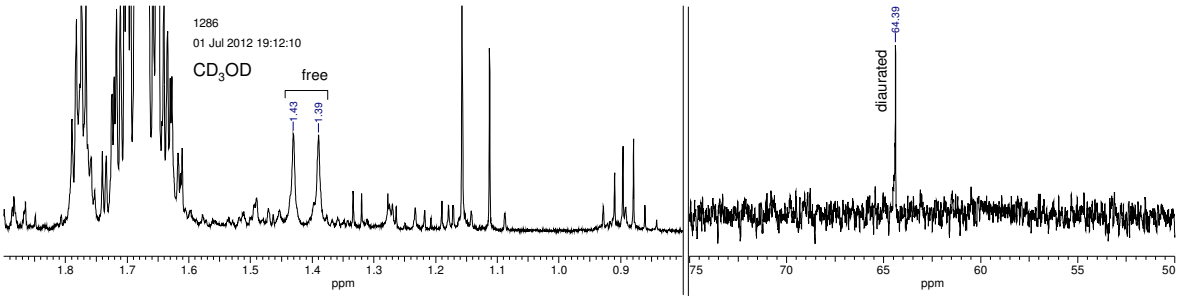
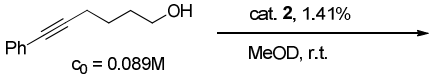


Figure S48. Spectra for experiment 1286.

1401

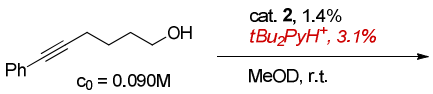


6-Phenylhexyn-5-ol-1 (8.41 mg, 48.3 µmol) was weighted into a vial. Stock **solution B** (0.45 mL, contains 0.680 µmol catalyst, 1.41% mol) was taken in a glass syringe and diluted with CD_3OD till 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table.

Table S36. Determination of the chemical kinetics for exp 1401.

1401					
c(sub)	0.089M				
cat **2**	1.41%				
abs. time	time, h	sub	MeOD	mes	lnSub
14:22:14	0	1			0
14:25:48	0.059	0.827	10.57	11.55	-0.190
14:31:34	0.156	0.589	10.57	11.64	-0.529
14:40:20	0.302	0.372	10.57	11.76	-0.989
14:50:34	0.472	0.212	10.57	11.81	-1.551
14:55:40	0.557	0.174	10.57	12.25	-1.749

1402

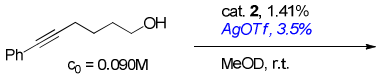


6-Phenylhexyn-5-ol-1 (8.44 mg, 48.5 µmol) and tBu$_2$PyH$^+$ OTf$^-$ (0.51 mg, 1.5 µmol, 3.1%) were weighted into a vial. Stock **solution B** (0.45 mL, contains 0.680 µmol catalyst, 1.40% mol) was taken in a glass syringe and diluted with CD_3OD till 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table.

Table S37. Determination of the chemical kinetics for exp 1402.

1402					
c(sub)	0.090M				
cat **2**	1.40%				
tBu$_2$PyH$^+$	3.1%				
abs. time	time, h	sub	MeOD	mes	lnSub
14:56:01	0	1			0
14:59:14	0.054	0.82	10.8	11.82	-0.198
15:04:56	0.149	0.553	10.8	11.89	-0.592
15:13:40	0.294	0.312	10.8	12.04	-1.165
15:21:40	0.428	0.185	10.8	11.94	-1.687

1403

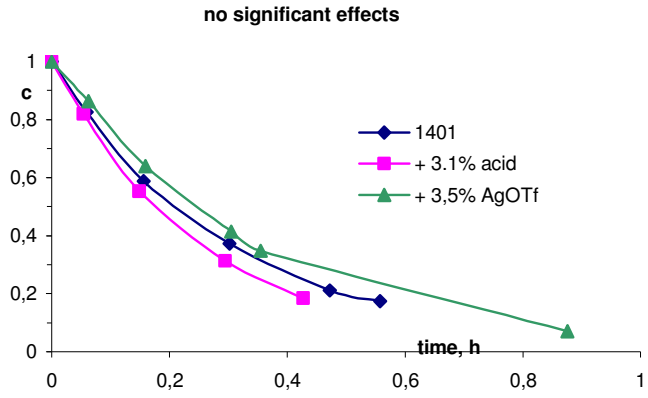


6-Phenylhexyn-5-ol-1 (8.40 mg, 48.3 µmol) was weighted into a vial. Stock **solution B** (0.45 mL, contains 0.680 µmol catalyst, 1.41% mol) was taken in a glass syringe and diluted with a solution of AgOTf (0.44 mg, 1.71 µmol, 3.5%) in CD_3OD (0.09 mL) till 0.54 mL directly in the syringe. The content of the syringe was quickly transferred into the vial with the substrate and the time count started. The reaction mixture was briefly shaken for a moment and transferred into an NMR tube using a Pasteur pipette. The reaction mixture was further monitored by NMR. The result is given in the Table.

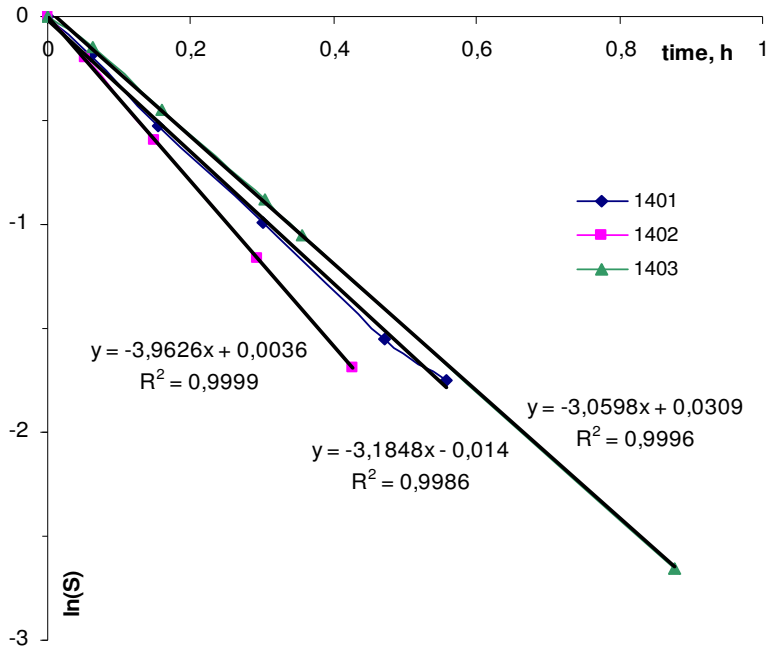
Table S38. Determination of the chemical kinetics for exp 1403.

1403					
c(sub)	0.090M				
cat **2**	1.41%				
AgOTf	3.5%				
abs. time	time, h	sub	MeOD	mes	lnSub
15:21:52	0	1			0
15:25:36	0.062	0.863	10.53	11.49	-0.147
15:31:24	0.159	0.639	10.53	11.67	-0.448
15:40:08	0.304	0.415	10.53	11.66	-0.879
15:43:10	0.355	0.348	10.53	11.59	-1.056
16:14:26	0.876	0.07	10.53	11.77	-2.659

A combined Diagram for experiments 1401–1403, showing the influence of acid and silver on the reaction, is given below:



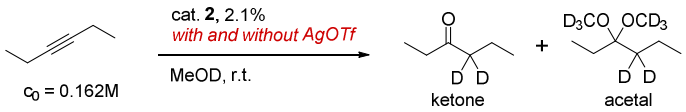
A combined logarithmic Diagram for experiments 1401–1403 demonstrates the first order in substrate in each case:


0
-1
-2
-3
0
0,2
0,4
0,6
0,8
1
time, h
ln(S)
1401
1402
1403
y = -3,9626x + 0,0036
R2 = 0,9999
y = -3,1848x - 0,014
R2 = 0,9986
y = -3,0598x + 0,0309
R2 = 0,9996

5.8. Series with hexyne-3 and catalyst 2

Stock solution A. $PhCH_2CH_2Ph$ (11.46 mg, 62.9 µmol) and hex-3-yne (38.88 mg, 473 µmol) were dissolved in CD_3OD (1.00 mL) in a vial.

Stock solution B. Catalyst **2** (4.01 mg, 5.19 µmol) was dissolved in CD_2Cl_2 (5 drops) and diluted with CD_3OD (0.5 mL) in a vial.



2243

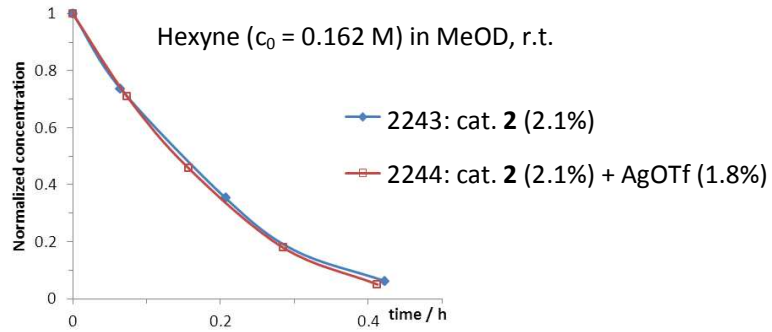
Stock **solution A** (0.20 mL, contains approximately 89 µmol hex-3-yne) was taken in a glass syringe and diluted with **solution B** (0.20 mL, contains 2.1 % catalyst **2**, exact amount will be determined by NMR) and then with CD_3OD till 0.55 mL directly in the same syringe. The time count was started. The whole content of the syringe was transferred into an NMR tube and the reaction was monitored by NMR.

2244

Stock **solution A** (0.20 mL, contains approximately 89 µmol hex-3-yne) was taken in a glass syringe and diluted with a solution of AgOTf (0.39 mg, 1.52 µmol) in CD_3OD (0.1 mL), then **solution B** (0.20 mL, contains 2.1 % catalyst **2**, exact amount will be determined by NMR) and then again with CD_3OD till 0.55 mL directly in the same syringe. The time count was started. The whole content of the syringe was transferred into an NMR tube. Small random amount of CF_3CH_2OH (<1 mg) was added. The reaction was further monitored by NMR. The amount of silver was determined using ^1H and ^{19}F NMR (by using the ^{19}F signals of CF_3CH_2OH and OTf, and the ^1H signal of CF_3CH_2OH). The results of both experiments are given in the Table and Diagram below.

Table S39. Determination of the chemical kinetics for exp 2243-2244.

2243							
Substr	0.162 M						
Au	2.07%						
abs. time	time, h	Substr	ketone	acetal	MeOD	CH2	sum R
16:30:28	0	1		0		5.99	
16:34:22	0.065	0.736		0.093	7.41	5.99	
16:42:52	0.207	0.353		0.36	7.37	5.99	
16:55:50	0.423	0.062		0.682	7.35	5.99	
2244							
Substr	0.162 M						
Au	2.07%						
Ag	1.80%						
abs. time	time, h	Substr	ketone	acetal	MeOD	CH2	sum R
16:59:14	0	1	0	0			1
17:03:38	0.073	0.71	0.205	0.096	7.39	5.99	1.011
17:08:40	0.157	0.457	0.298	0.27	7.38	5.99	1.025
17:16:20	0.285	0.179	0.325	0.528	7.38	5.99	1.032
17:24:00	0.413	0.05	0.323	0.66	7.34	5.99	1.033
17:31:44	0.542	0.02	0.317	0.703	7.38	5.99	1.04



6. Coordination chemistry of Ag^+

2303-2305. NMR titration of Ag^+ in $CDCl_3$ using various nucleophiles

A small portion of AgOTf (0.3–2.1 mg) was dissolved in a minimum of THF-*d8* (4-10 mg). Then $CDCl_3$ (0.6 mL) was poured into this solution. This caused predominant precipitation of AgOTf back (as a tiny precipitate). However, it was possible to register the ^{19}F NMR of the residual AgOTf in solution several times (not always reproducible). A small random amount of CF_3CO_2Me was added as an internal standard allowing quantitative control of AgOTf in solution from a combination of ^{1}H and ^{19}F NMR spectra. Then a nucleophile (see Table) was introduced several times. This caused immediate dissolution of AgOTf, forming a soluble complex already after the first addition (it always contained > 1 equiv of a nucleophile). ^{1}H, ^{31}P (if applicable) and ^{19}F NMR spectra were recorded after each addition. Various nucleophiles were used. For any nucleophile at any Ag^+/Nu ratio all NMR spectra showed a single pattern for bound and free nucleophile indicating always fast ligand exchange in $Ag(Nu)_n^+$/Nu system. Always a single OTf^- resonance at slightly variable chemical shift was observed in all ^{19}F NMR spectra. Relative amounts of the components were determined from NMR spectra. The results are shown in the Table below.

Table S40. Results of NMR titrations. Amounts of the nucleophiles are given in equiv relative to AgOTf (=1 equiv). Selected chemical shifts are given (δ).

2303

Lut	PPh3	δLut	δLut	δLut	δF	δP	comment
0	0						
3.1	0	7.61	7.12	2.72	-78.49		
3.1	2.35	7.46	6.95	2.51	-77.86	10.6	
3.1	3.2	7.44	6.93	2.5	-77.98	8.9	
3.1	5.3	7.44	6.93	2.5	-78.06	-0.5	

2304

TMTU	PPh3	δTMTU	δF	δP	
0	0		-77.04		residual AgOTf
2.5 eq	0	3.17	-78.06		
4.2 eq	0	3.14	-78.11		
6.5 eq	0	3.11	-78.14		
10.4 eq	0	3.09	-78.16		
10.4 eq	5.1	3.04	-78.1	1.77	

2305

	δMe2S	δLut	δTMTU	δF	δP
0					
add Me2S 4.4 eq	3.17			-77.45	
add Lut 3.8 eq	2.17	2.62		-78.18	
add TMTU 2.2 eq	2.1	2.52	3.18	-78.11	
ΣTMTU 5.2 eq	2.1	2.5	3.12	-78.13	
add PPh3 5.2 eq	2.1	2.5	3.04	-78.09	2.56

2306

Me2S	Lut	δMe2S	δLut	δF	δP
0					
10 eq		2.2		-77.45	
10 eq	28	2.11	2.53	-78.39	

2307

MeCN	δMeCN	δLut	δTMTU	δF	δP	
0				-77.04		residual AgOTf
4.8	2.05			-77.38		AgOTf not completely dissolved
add PPh3 1.8 eq	1.99			-77.61	broad	
ΣPPh3 3.4 eq	1.99			-78.01	7.77	

Synthesis of $Ag(Lut)_2OTf$

$$AgOTf + 2Lut \xrightarrow[MeOH]{} Ag(Lut)_2OTf$$

AgOTf (9.57 mg, 37.3 µmol) was dissolved in MeOH (60 mg) and 2,6-lutidine (15.2 mg, 142 µmol, 3.8 equiv) was added. Since the stoichiometry of the reaction was a priori not known, excess of lutidine was used to ensure formation of a product with the highest coordination number. The solution was evaporated in vacuo and the residue was dissolved in a minimum $CDCl_3$ (few drops). Layering of this solution with pentane caused smooth precipitation of the complex as a white crystalline precipitate (excess of lutidine remained in solution). The filtrate was decanted out using a Pasteur pipette with a piece of cotton at the tip. Same way the solid was washed with pentane three times and then dried in vacuo to yield the final product as a white crystalline solid in quantitative yield (17.2 mg, 98%). Using CF_3CO_2Me as an internal standard, the molecular composition of the complex was established by ^1H and ^{19}F NMR.

$Ag(Lut)_2OTf$, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.71 (t, *J*=7.7 Hz, 2H), 7.23 (d, *J*=7.7 Hz, 4H), 2.83 (s, 12H). **^{19}F NMR** ($CDCl_3$): δ = –78.43.

Competitive binding of a nucleophile to LAu^+ and Ag^+

2268. Distribution of PPh_3 among LAu^+ and Ag^+ in MeOD.

$$L2Au(MeOD)^+ + Ph_3PAg^+ \xrightarrow[MeOD]{} L2AuPPh_3^+ + (MeOD)Ag^+$$

A solution of AgOTf (0.81 mg, 1.31 equiv), complex **2** (1 equiv) and PPh_3 (1.15 equiv) was prepared in CD_3OD (0.5 mL). CF_3CH_2OH was used as internal standard. NMR spectra indicated complete formation of $L2AuPPh_3^+$ (δP = 68.36 (d, *J*=296.1 Hz), 43.48 (d, *J*=296.1 Hz) ppm).

2323. Distribution of PPh_3 among LAu^+ and Ag^+ in the presence of Lut as a background nucleophile in $CDCl_3$

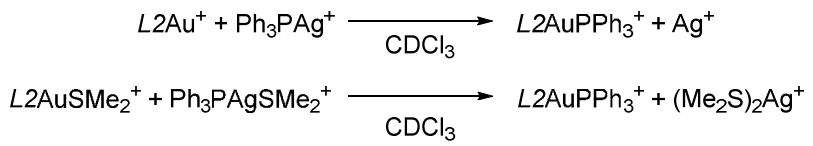
$$L2AuLut^+ + Ph_3PAgLut^+ \underset{CDCl_3}{\rightleftharpoons} L2AuPPh_3^+ + Lut_2Ag^+$$

$Ag(Lut)_2OTf$ (0.75 mg, 1.59 µmol) and PPh_3 (0.46 mg, 1.76 µmol) were dissolved in $CDCl_3$ (0.55 mL). ^1H, ^{31}P and ^{19}F NMR spectra were recorded. Then complex **2** (1.24 mg, 1.61 µmol) was added and NMR spectra were recorded. In this system PPh_3 was predominantly bound to silver.

2323

Ag	Lut	PPh3	L2Au	δP	δF	δLut	L2AuLut	L2AuPPh3	ΣAu
1	2	1.14	0	broad		2.62	0	0	
1	2	1.14			-78.14	2.73	0.71	0.26	0.97

2324. Distribution of PPh_3 among LAu^+ and Ag^+ in the absence and presence of Me_2S as a background nucleophile in $CDCl_3$



AgOTf (0.38 mg, 1.48 µmol) was dissolved in a minimum of THF-*d8* (4-6 mg). Then $CDCl_3$ (0.6 mL) was poured into this solution. PPh_3 (0.35 mg, 1.34 µmol) was added. CF_3CO_2Me was added as an internal standard. ^1H, ^{31}P and ^{19}F NMR spectra were recorded. Then complex **2** (1.08 mg, 1.40 µmol) was added and NMR spectra were recorded. Relative amounts of the components were determined from NMR spectra. They showed PPh_3 to quantitatively move to gold while free AgOTf predominantly precipitated out from the solution. Then Me_2S was added. This immediately returned silver into solution, but did not change the distribution of PPh_3 among silver and gold: *L2*$AuPPh_3^+$ remained the single PPh_3-containing species.

2324

Ag	Me2S	PPh3	L2Au	δP	δF	δMe2S	L2AuSMe2	L2AuPPh3
1	0	0.85	0	17.34	-77.02		0	0
0.25	0	0.85	1		-77.2			0.85
1.2	5.2	0.85	1		-77.5	2.32	0.15	0.85

7. References

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