Mechanistic Analysis of Gold(I)-Catalyzed Intramolecular Allene Hydroalkoxylation Reveals an Off-Cycle Bis(gold) Vinyl Species and Reversible C–O Bond Formation

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Supporting Information

Experimental procedures, analytical and spectroscopic data for new phosphine gold(I) vinyl complexes, X-ray crystallographic data, and kinetic data (16 pages).

Experimental

General Methods. Reactions were performed under a nitrogen atmosphere employing standard Schlenk and glovebox techniques unless specified otherwise. NMR spectra were obtained on a Varian spectrometer operating at 500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR, and 202 MHz for ^{31}P NMR in CD_2Cl_2 at 25 °C unless noted otherwise. IR spectra were obtained on a Nicolet Avatar 360-FT IR spectrometer. Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ). Mass spectra were obtained on an Applied Biosystems Voyager-DE Pro MALDI mass spectrometer operating at a mass range of 500-4000u with a dihydroxyacetophenone matrix (10 mg/1 mL CD_2Cl_2) and was calibrated with PEG1000. Methylene chloride was purified by passage through columns of activated alumina under nitrogen. $CDCl_3$ and CD_2Cl_2 were dried over CaH_2 and distilled under nitrogen prior to use. 2,2-Diphenyl-4,5-hexadien-1-ol (**1**) was synthesized using a published procedure.[S1] (L)AuCl [L = P(*t*-Bu)$_2$*o*-biphenyl], *p*-toluenesulfonic acid monohydrate, AgOTs, and hexanes were purchased from major chemical suppliers and were used as received. Anhydrous *p*-toluenesulfonic acid was obtained by heating *p*-toluenesulfonic acid monohydrate under vacuum at 110 °C for 4 h followed by recrystallization from anhydrous ethyl acetate.[S2] Error limits for rate constants were determined by linear least squares analysis of the raw data plots. NMR probe temperatures were calibrated using a neat methanol thermometer.

Syntheses

p*-Toluenesulfonic acid-O-*d. A solution of anhydrous *p*-toluenesulfonic acid (0.90 g, 5.2 mmol) was refluxed in D_2O (5 mL) and concentrated under vacuum. The sequence was repeated three additional times and the resulting solid (presumably DOTs•D_2O) was heated under vacuum at 110 °C for 4 h and recrystallized from anhydrous ethyl acetate to give DOTs (≥90% *d*). Deuterium incorporation was determined by integration of the proton resonance at δ 9.28 in anhydrous DMSO-d_6/CD_2Cl_2 (*v/v* = 5:95) and by comparison to the integration of an authentic sample of HOTs in

anhydrous DMSO-d_6/CD_2Cl_2 (*v/v* = 5:95).

2,2-Diphenyl-4,5-hexadien-1-ol-O-*d* (1-O-*d*). 2,2-Diphenyl-4,5-hexadien-1-ol (**1**: 0.13 g, 0.52 mmol) was refluxed in D_2O (3 mL) and concentrated under vacuum. The sequence was repeated two additional times and on the third iteration, the resulting mixture was extracted with anhydrous ether and dried under vacuum to give pure **1**-O-*d* (≥90% *d*). Deuterium incorporation was determined by ^{1}H NMR integration of the hydroxyl resonance at δ 1.52 in CD_2Cl_2 and by comparison to the integration of the hydroxyl resonance of pure **1** in CD_2Cl_2.

1,1-Dideuterio-2,2-diphenyl-4,5-hexadien-1-ol (1-d_2). A solution of methyl 2,2-diphenylhexa-4,5-dienoate (0.38 g, 1.37 mmol) in ether (5 mL) was added dropwise to a suspension of $LiAlD_4$ (107 mg, 2.74 mmol) in ether (25 mL) at 0°C and the resulting suspension stirred for 1 h. The reaction mixture was treated sequentially with water (0.14 mL), aqueous NaOH (15 wt. %, 0.14 mL), and water (0.14 mL) at 0 °C. The suspension was filtered through Celite, dried ($MgSO_4$), and concentrated under vacuum to give **1**-d_2 (330 mg, 95%) with ≥95% deuterium incorporation as determined by the absence of a detectable ^{1}H NMR resonance at δ 4.2 corresponding to the C1 protons.

(L)AuOTs. A suspension of (L)AuCl (100 mg, 0.19 mmol) and AgOTs (53 mg, 0.19 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for 1 h. The resulting suspension was filtered through a plug of Celite and the filtrate was concentrated to ~1 mL, diluted with hexanes (10 mL) and cooled at 4 °C overnight to give (L)AuOTs (104 mg, 83 %) as a colorless powder. ^{1}H NMR: δ 7.78 (t, *J* = 7.5 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 7.50 - 7.40 (m, 2 H), 7.31 - 7.19 (m, 4 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.05 (d, *J* = 7.5 Hz, 2 H), 2.30 (s, 3 H), 1.26 (d, *J* = 16.0 Hz, 18 H). ^{13}C{^{1}H} NMR: δ 150.1 (d, *J* = 12.0 Hz), 142.3 (d, *J* = 6.7 Hz), 142.0, 141.3, 133.4 (d, *J* = 3.9 Hz), 133.3 (d, *J* = 7.2 Hz), 129.6, 129.1, 128.8, 128.5, 127.3 (d, *J* = 7.1 Hz), 126.7, 124.7 (d, *J* = 49.6 Hz), 38.2 (d, *J* = 28.2 Hz), 30.9 (d, *J* = 6.2 Hz), 21.5. ^{31}P{^{1}H} NMR: δ 56.1. Anal. Calcd (found) for $C_{27}H_{34}AuO_3PS$: H, 5.14 (5.09); C, 48.65 (48.57).

(L)Au[η^1-C(=CH$_2$)CHOCH$_2$CPh$_2$CH$_2$] (3). A toluene solution of 2,2-diphenyl-4,5-hexadien-1-ol (**1**) (30 mg, 0.12 mmol) and triethylamine (24 mg, 0.24 mmol) was added dropwise via syringe to a

stirred suspension of (L)AuCl (64 mg, 0.12 mmol) and AgOTs (34 mg, 0.12 mmol) in toluene (2 mL), and the reaction mixture was stirred at room temperature for 1.5 h. The resulting suspension was dissolved in ether and treated with aqueous NH_4Cl (15 mL). The layers were separated, the aqueous layer was extracted with ether (2 × 10 mL), and the combined organic extracts were dried ($MgSO_4$) and concentrated under vacuum. The resulting solid was dissolved in boiling hexanes (10 mL) and cooled at 4 °C for 48 h to form **3** (78 mg, 87 %) as colorless crystals. ^{1}H NMR (25 °C, $CDCl_3$): δ 7.81 (t, *J* = 6.5 Hz, 1 H), 7.37 (t, *J* = 7.5 Hz, 2 H), 7.29 (d, *J* = 7.5 Hz, 3 H), 7.26 - 7.03 (m, 13 H), 5.48 (dd, *J* = 4, 14 Hz, 1 H), 4.57 (d, *J* = 8.5 Hz, 1 H), 4.45 (t, *J* = 5.5 Hz, 1 H), 4.37 (td, *J* = 5.5, 10.5 Hz, 1 H), 3.98 (d, *J* = 8.5 Hz, 1 H), 2.48 - 2.35 (m, 2 H), 1.32 (d, *J* = 14.5 Hz, 9 H), 1.27 (d, *J* = 14.5 Hz, 9 H). ^{13}C{^{1}H} NMR (25 °C, $CDCl_3$): δ 182.7 (d, *J* = 103.8 Hz), 150.3 (d, *J* = 16.4 Hz), 147.6, 146.6, 142.5 (d, *J* = 5.7 Hz), 135.1, 133.0, 129.8, 129.2 (d, *J* = 42.8 Hz), 128.5, 128.0, 127.6, 127.4, 126.2, 125.9 (d, *J* = 28.9 Hz), 117.1, 88.23, 88.20, 56.0, 47.5, 37.3 (d, *J* = 18.3 Hz), 37.2 (d, *J* = 19.1), 31.0 (d, *J* = 6.7 Hz), 30.7 (d, *J* = 6.8 Hz). ^{31}P{^{1}H} NMR (25 °C, $CDCl_3$): δ 65.6. Anal. calcd (found) for $C_{38}H_{44}AuOP$: H, 5.96 (6.06); C, 61.29 (61.14).

$[(L)Au]_2[C(=CH_2)\overline{CHOCH_2CPh_2CH_2}]$ (4). Mono(gold) vinyl complex **3** (15 mg, 0.02 mmol), (L)AuOTs (13.4 mg, 0.02 mmol), and 1,3-dimethoxybenzene (0.5 μL; 3.8 μmol; internal standard) were combined in an NMR tube under nitrogen and dissolved in CD_2Cl_2 (0.5 mL) at 25 °C to form **4** in 98 ± 5% yield as determined by ^{1}H NMR analysis and as the exclusive phosphorous-containing species as determined by ^{31}P NMR spectroscopy. ^{1}H NMR (0 °C, CD_2Cl_2): δ 7.82 (t, *J* = 6 Hz, 2 H), 7.64 (d, *J* = 7.5 Hz, 2 H), 7.52 (br s, 4 H), 7.42 - 7.06 (m, 24 H), 4.83 (d, *J* = 4 Hz, 1 H), 4.66 (d, *J* = 8.5 Hz, 1 H), 4.27 (br s, 1 H), 3.87 (d, *J* = 8.5 Hz, 1 H), 3.50 (d, *J* = 4.5 Hz, 1 H), 2.38 (dd, *J* = 5.0, 11.5 Hz, 1 H), 2.31 (s, 3 H), 2.21 (t, *J* = 11.5 Hz, 1 H), 1.38 (d, *J* = 15.0 Hz, 9 H), 1.36 (d, *J* = 15.0 Hz, 9 H), 1.30 (d, *J* = 15.0 Hz, 9 H), 1.27 (d, *J* = 15.0 Hz, 9 H). ^{13}C{^{1}H} NMR (–60 °C, CD_2Cl_2): δ 148.4 (d, *J* = 14.7 Hz), 148.3 (d, *J* = 14.4 Hz), 145.7, 144,5, 143.1 (d, *J* = 6.2 Hz), 143.0 (d, *J* = 5.3 Hz), 138.5, 134.2 (d, *J* =

20.7 Hz), 132.9, 130.6, 129.2 (d, *J* = 9.1 Hz), 129.1, 128.5 (d, *J* = 24.4 Hz), 128.3, 128.1, 128.0, 127.2, 126.7 (d, *J* = 12.5 Hz), 126.4 (d, *J* = 33.5 Hz), 125.7, 125.4, 125.1, 107.4, 85.8, 76.4, 55.5, 45.9, 37.4 - 36.7 (m, 4 C), 30.8 - 29.7 (m, 12 C). $^{31}P\{^{1}H\}$ NMR (0 °C, CD_2Cl_2): δ 61.8, 60.9 (1:1). MALDI-MS calcd (found) for $C_{58}H_{71}Au_2OP_2$ (M^+): 1239.4 (1240.2).

Protonolysis experiments

Room temperature reaction of 3 with HOTs. *p*-Toluenesulfonic acid monohydrate (7.6 mg, 0.04 mmol) was added to an NMR tube containing a solution of **3** (10 mg, 0.013 mmol) and 1,3-dimethyoxybenzene (0.5 μL, 3.8 μmol) in CD_2Cl_2 (0.5 mL) at room temperature. The contents of the tube were mixed thoroughly and the tube was placed in the probe of an NMR spectrometer maintained at 25 °C. ^{1}H NMR Analysis of the resulting solution within 10 min revealed formation of **2** in 99 ± 5% yield and ^{31}P NMR analysis revealed formation of (L)AuOTs (δ 56.0) as the exclusive phosphorous containing species.

Low temperature reaction of 3 with HOTs. *p*-Toluenesulfonic acid monohydrate (5.0 mg, 0.026 mmol) was added to an NMR tube containing a solution of **3** (15 mg, 0.02 mmol) and 1,3-dimethyoxybenzene (1 μL, 7.6 μmol) in CD_2Cl_2 (0.5 mL) at –78 °C. The contents of the tube were mixed thoroughly and the tube was placed in the probe of an NMR spectrometer pre-cooled at –80 °C. ^{1}H and ^{31}P NMR analysis of the resulting solution within 5 min revealed resonances corresponding to **1** (~46%) [^{1}H NMR: δ 4.59 (br s, 2 H), 4.51 (quint, *J* = 7.0 Hz, 1 H)], **4** (~46%) [^{1}H NMR: δ 4.78, 4.60 (d, *J* = 8.5 Hz), 4.14, 3.73 (d, *J* = 8.5 Hz), and 3.26; ^{31}P NMR: δ 60.0, 58.9 (1:1)], and **2** (8%) [^{1}H NMR: δ 5.82 (ddd, *J* = 5.2, 10.6, 17.4 Hz, 1 H), 5.15 (d, *J* = 17.6 Hz, 1 H), 5.06 (d, *J* = 10.8 Hz, 1 H)]. Warming this solution at 0 °C for ~10 min led to complete consumption of **4** and formation of a 1:1 mixture of **2** and (L)AuOTs [^{31}P NMR: δ 54.1] in 97 ± 5% yield by ^{1}H NMR analysis.

Stoichiometric reactions of 4 with HOTs/DOTs. A solution of anhydrous *p*-toluenesulfonic acid (3.8 mg, 0.022 mmol) in DMSO-d_6/CD_2Cl_2 (*v/v* = 5:95; 40 μL) was added via syringe to an NMR

tube containing a solution of **4** (0.02 mmol) [generated *in situ* from reaction of **3** (15 mg, 0.02 mmol) and (L)AuOTs (13.4 mg, 0.02 mmol) at –78 °C] and 1,3-dimethoxybenzene (0.5 μL; 3.8 μmol; internal standard) in CD_2Cl_2 (0.50 mL) at –78 °C. The contents of the tube were mixed thoroughly at –78 °C and the tube was placed in the probe of an NMR spectrometer precooled at 5 °C and monitored periodically by ^{1}H NMR spectroscopy. The concentration of **4** was determined by integration of the doublet at δ 3.92 corresponding to a tetrahydrofuranyl ring proton of **4** relative to the methoxy resonance of 1,3-dimethoxybenzene (δ 3.78). The initial rate of reaction was determined from a plot of ln[**4**] versus time over ~20% conversion where k_{init} = 3.55 ± 0.06 × 10^{-4} s^{-1} (Figure S1). Initial rates for the reaction of **4** with HOTs were determined as a function of [HOTs] from 38 to 152 mM, which established the zeroth-order dependence of the rate on [HOTs] (Table S1). Similarly, reaction of **4** (38 mM) with anhydrous DOTs (40 mM) at 5 °C to form **2**-d_1 (79% *d*) gave an initial rate constant of k_{int} = 3.9 ± 0.1 × 10^{-4} s^{-1} (Figure S1, eq S1), which corresponds to a deuterium KIE of k_H/k_D = 0.92 ± 0.03. The extent of deuterium incorporation into the internal vinylic position of **2**-d_1 was determined by ^{1}H NMR integration of the internal olefinic resonance integration at δ 5.92 (eq S1).

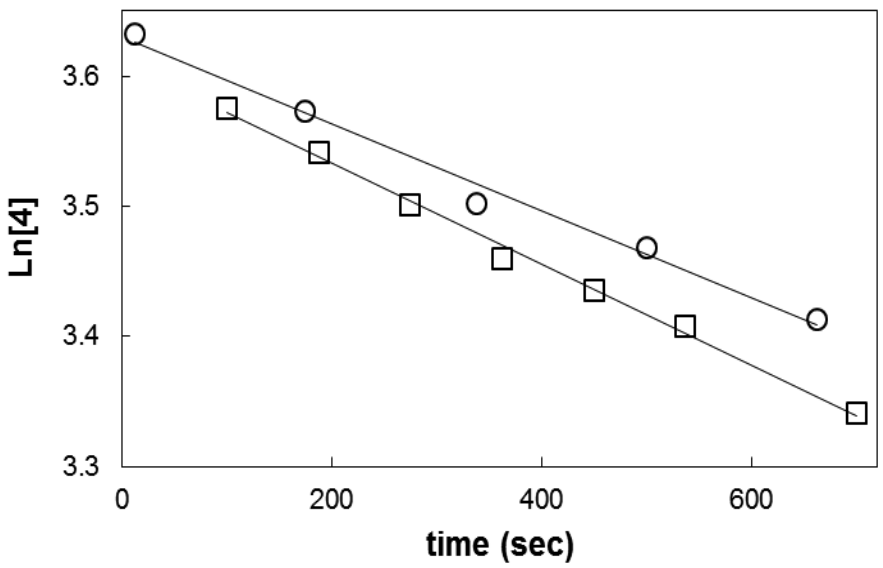
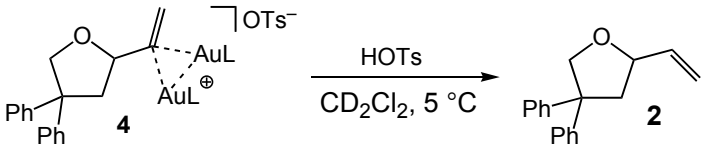


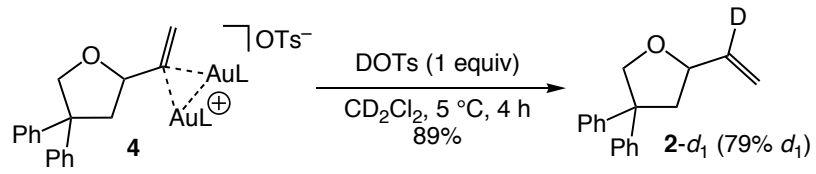
Figure S1. First-order plots for the reaction of **4** with HOTs (o) and DOTs (□) in CD_2Cl_2 at 5 °C ($[\mathbf{4}]_o$ = [HOTs] = [DOTs] = 38 mM).

Table S1. First-order rate constants for reaction of **4** ($[\mathbf{4}]_0$ = 38 mM) with anhydrous HOTs in CD_2Cl_2 at 5 °C as a function of [HOTs] over the concentration range 38-152 mM and for the reaction of **4** ($[\mathbf{4}]_o$ = 38 mM) with DOTs ($[HOTs]_o$= 38 mM) in CD_2Cl_2 at 5 °C.



Entry	[HOTs] (mM)[a]	(10^4) k_{obs} (s^{-1})[b]
1	38	3.5 ± 0.2
2[c]	38	3.9 ± 0.2
3	76	3.4 ± 0.1
4	152	3.2 ± 0.4

[a]0.5 M stock solution in DMSO-d_6/CD_2Cl_2 (*v/v* = 5:95). [b]Observed rate constants measured using ^{1}H NMR. [c]Reaction conducted using anhydrous DOTs.



eq S1

Stoichiometric and catalytic reactions of 1 with (L)AuOTs

Stoichiometric reaction of 1 with (L)AuOTs. A solution of **1** (7.5 mg, 0.030 mmol) in CD_2Cl_2 (0.2 mL) was added to a solution of (L)AuOTs (20 mg, 0.030 mmol) and 1,3-dimethoxybenzene (1 μL, 7.6 μmol; internal standard) in CD_2Cl_2 (0.3 mL) in an NMR tube at –78 °C. The contents of the tube were mixed thoroughly and the tube was placed in the probe of an NMR spectrometer precooled at –80 °C and analyzed periodically by ^{1}H and ^{31}P NMR spectroscopy. Spectra recorded within 5 min revealed resonances corresponding to **1** (~48%) [^{1}H NMR: δ 4.59 (br s, 2 H), 4.51 (quint, *J* = 7.0 Hz, 1 H)], **4** (~46%) [^{1}H NMR: δ 4.78, 4.60 (d, *J* = 8.5 Hz), 4.14, 3.73 (d, *J* = 8.5 Hz), and 3.26; ^{31}P NMR: δ 60.0, 58.9 (1:1)], and **2** (≤ 5%) [^{1}H NMR: δ 5.82 (ddd, *J* = 5.2, 10.6, 17.4 Hz, 1 H), 5.15 (d, *J* = 17.6 Hz, 1 H), 5.06 (d, *J* = 10.8 Hz, 1 H). The solution was warmed at –30 °C and monitored over the full reaction course (3 h) to form **2** in 94% yield with concomitant formation of (L)AuOTs as the exclusive phosphorous containing species as determined by ^{31}P NMR spectroscopy.

Spectroscopic analysis of 1 with catalytic (L)AuOTs. A solution of **1** (15 mg, 0.06 mmol, 116 mM), (L)AuOTs (2.0 mg, 3.0 μmol, 5.8 mM), and 1,3-dimethoxybenzene (0.8 μL; 6.1 μmol; internal standard) in CD_2Cl_2 (0.4 mL) was generated in an NMR tube at –78 °C. The contents of the tube were mixed thoroughly, placed in the probe of an NMR spectrometer precooled at –30 °C, and the solution was monitored periodically by ^{1}H and ^{31}P NMR spectroscopy. Analysis within 5 min (~5% conversion) revealed formation of **4** (~3.0 mM) as the exclusive phosphorous-containing species. Continued analysis of the solution revealed a constant concentration of **4** (~3.0 mM) throughout ~95% consumption of **1**, after which time the resonances corresponding to **4** disappeared with appearance of a single resonance at δ 56.1 corresponding to (L)AuOTs and with formation of **2** in 97 ± 5% yield as determined by ^{1}H NMR integration.

KIE of catalytic hydroalkoxylation/deuterioalkoxylation of 1/1-*O-d*. A solution of **1** (15 mg, 0.06 mmol), (L)AuOTs (2.0 mg, 3.0 μmol, 5.8 mM), and 1,3-dimethoxybenzene (0.8 μL; 6.1 μmol; internal standard) in CD_2Cl_2 (0.40 mL) was generated in an NMR tube at –78 °C. The contents of the tube were mixed thoroughly and the tube was placed in the probe of an NMR spectrometer precooled at –30 °C and the solution was monitored periodically by ^{1}H NMR spectroscopy. The concentration of **1** was determined by integration of the α-allenyl methylene resonance of **1** (δ 2.92) relative to the methoxy resonance of 1,3-dimethoxybenzene (δ 3.80). A plot of ln [**1**] versus time was linear over ~3 half-lives with a pseudo first order rate constant of k_{obs} = 2.71 ± 0.05 × 10^{-4} s^{-1} (Figure S2). An analogous experiment involving the reaction of **1**-*O*-*d* (113 mM) and (L)AuOTs (5.7 mM) at –30 °C to form **2**-d_1 (85% *d*) gave a pseudo first-order rate constant of k_{obs} = 5.1 ± 0.1 × 10^{-5} s^{-1} (Figure S2), which corresponds to a deuterium KIE of k_H/k_D = 5.31 ± 0.03. The extent of deuterium incorporation into the internal vinylic position of **2**-d_1 was determined by ^{1}H NMR integration of the internal olefinic resonance integration at δ 5.92 (eq S2).

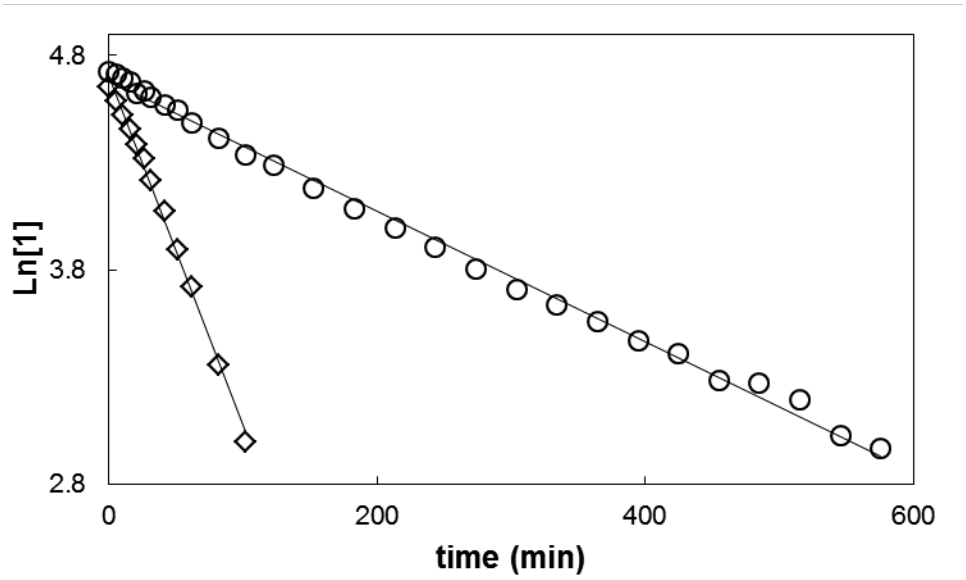
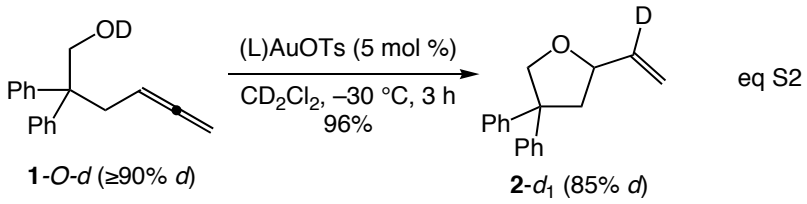


Figure S2. Pseudo first-order plots for the conversion of **1** to **2** (◊) and **1**-*O*-*d* to **2**-d_1 (o) catalyzed by (L)AuOTs in CD_2Cl_2 at –30 °C ([**1**]$_o$ = [**1**-O-*d*]$_o$ = 116 mM, [(L)AuOTs] = 5.8 mM).



1-*O*-*d* (≥90% *d*) **2**-d_1 (85% *d*) eq S2

***in situ* Analysis of 4 under catalytic conditions.** A solution of **1** (0.25 mg, 1.0 μmol, 2.0 mM), (L)AuOTs (1.3 mg, 2.0 μmol, 4.0 mM), and mesitylene (0.12 mg, 1.0 μmol) in CD_2Cl_2 (0.15 mL) was generated in an NMR tube at –78 °C. The contents of the tube were mixed thoroughly, placed in the probe of an NMR spectrometer precooled at –60 °C, and the solution was analyzed by ^{1}H NMR spectroscopy. Analysis within 3 min revealed formation of **4** (84%) and **2** (16%) (Figure S3) as determined by integration of the ^{1}H NMR resonances at δ 3.81 (**4**) and δ 4.03 (**2**) relative to the mesitylene peak at δ 6.70. The tube was removed from the spectrometer, cooled at –78 °C, and a solution of **1**-d_2 (5 mg, 20.0 μmol, 28.6 mM) in CD_2Cl_2 (0.20 mL) was added to the tube via syringe. The resulting solution was mixed thoroughly at –78 °C and the tube was placed in the probe of an NMR spectrometer precooled at –60 °C, warmed at –45 °C, and analyzed at five-minute intervals for 195 min (7% conversion) by ^{1}H NMR spectroscopy. The concentrations of **4** and **2** were determined as described above and the concentrations of (**4** + **4**-d_2) and (**2** + **2**-d_2) were determined by integration of ^{1}H NMR resonances at δ 3.38 and δ 5.09, respectively, relative to the mesitylene peak at δ 6.70 (Figure S4). Plots of [**4**], [**4** + **4**-d_2], [**2**], and [**2** + **2**-d_2] versus time produced initial rate values for the consumption of **4** (k_4 = –3.84 × 10^{-3} mM/min), the consumption of **4** + **4**-d_2 (k_{4tot} = –0.61 × 10^{-3} mM/min), the formation of **2** (k_2 = 0.74 × 10^{-3} mM/min) and the appearance of **2** + **2**-d_2 (k_{2tot} = 9.11 × 10^{-3} mM/min) (Figure S5).

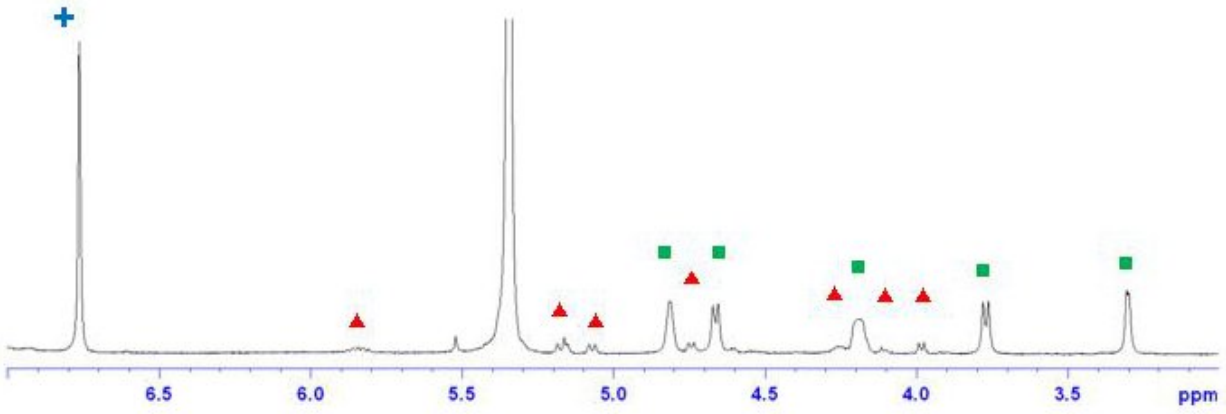


Figure S3. Partial ^{1}H NMR spectrum for the reaction of **1** (2.0 mM) with (L)AuOTs (4.0 mM) in CD_2Cl_2 (0.5 mL) at –78 °C to form a mixture of **4** (84%; resonances indicated with ■) and **2** (16%; resonances indicated with ▲) (signal marked with ✚ corresponds to mesitylene).

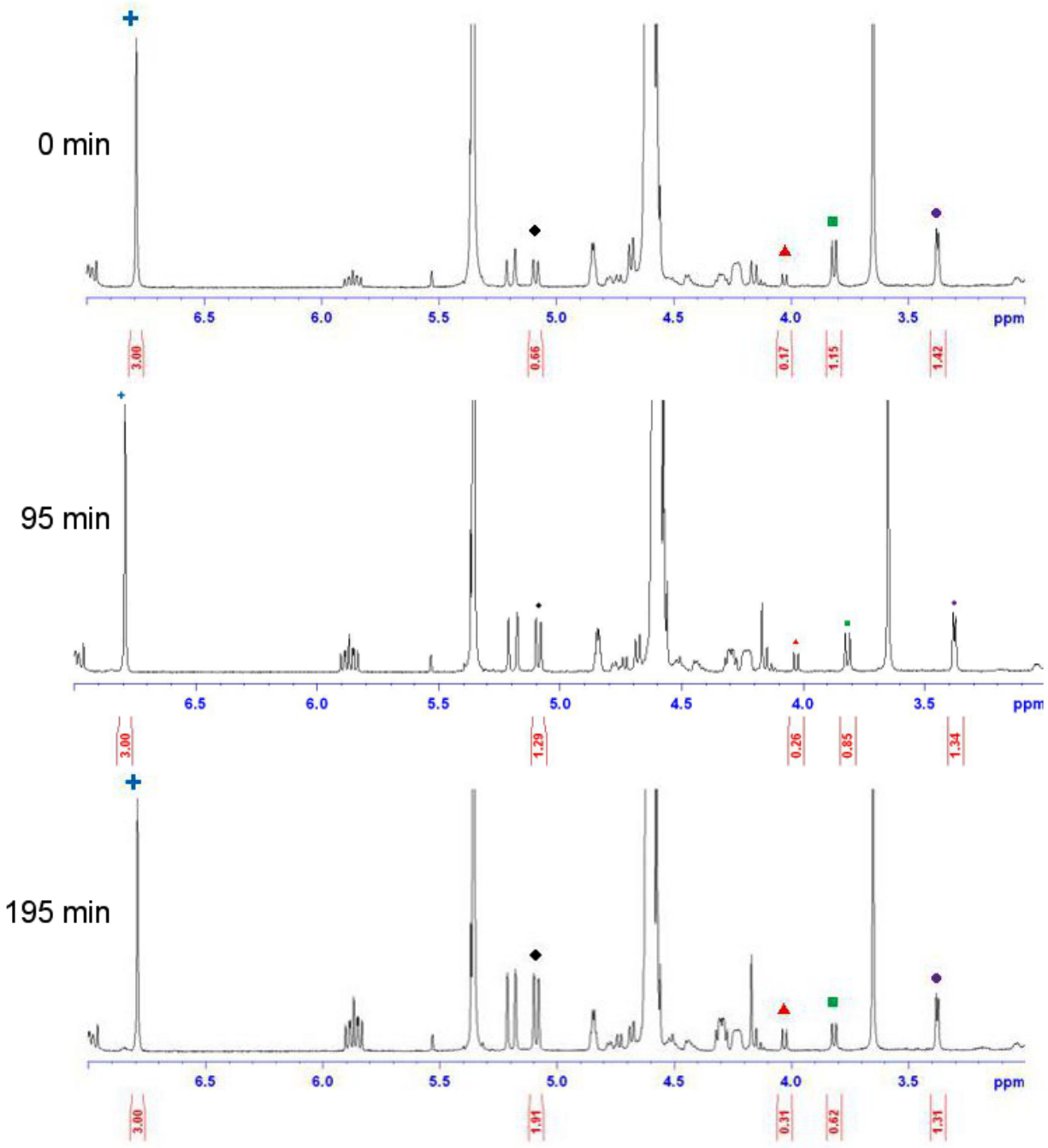


Figure S4. Partial ^{1}H NMR spectra of the reaction of **1**-d_2 (29 mM) with *in situ* generated **4** (1.4 mM) in CD_2Cl_2 (0.7 mL) at –45 °C for 0, 95, and 195 min (top to bottom; ~2 – 7% conversion) showing resonances used to determine the concentrations of **4** (■), [**4** + **4**-d_2] (●), **2** (▲), and [**2** + **2**-d_2] (◆) relative to the methyl resonance of mesitylene (✚).

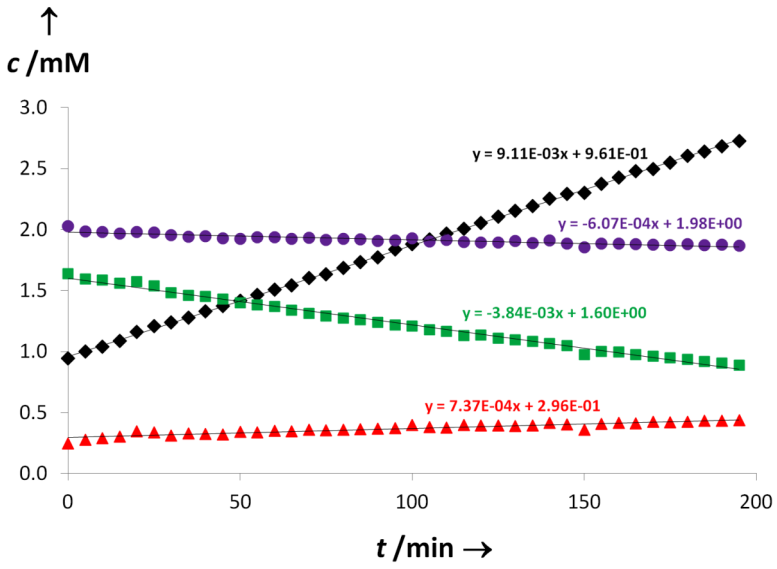


Figure S5. Concentration versus time plots for the cyclization of **1**-d_2 (29 mM) catalyzed by *in situ* generated **4** (1.4 mM) in CD_2Cl_2 at –45 °C from ~2% to ~7% conversion: [**2** + **2**-d_2] (♦); [**2**] (▲); [**4** + **4**-d_2] (●); [**4**] (■).

Initial rate values extracted from Figure S4 as described in the previous paragraph were used to determine that ~80% of monogold vinyl complex **3**, generated via disproportionation of **4**, that undergoes cycloreversion and **2**/**2**-d_2 ligand exchange (r_{-1}) rather than protodemetallation (r_2) by dividing the calculated rate of **4** consumption by the rate of **2** formation:

$$\frac{r_{-1}}{r_2} = \frac{|k_4| - |k_{4tot}|}{k_2} = \frac{3.84 - 0.61}{0.74} = \frac{4.36}{1}$$

This ratio can be converted to percentages the following:

$$r_{-1}(\%) = \frac{4.36}{4.36+1} \times 100\% = 81.3\% \quad \text{and} \quad r_2(\%) = \frac{1}{4.36+1} \times 100\% = 18.7\%$$

Likewise, these initial rate values were used to determine that ~70% of deuterated mono(gold) vinyl complex **3**-d_2 undergoes protodeauration to form **2**-d_2 (r_3) without formation of bis(gold) vinyl complex **4**-d_2 (r_4) by dividing the calculated rate of **2**-d_2 formation by the calculated rate of **4**-d_2 formation:

$$\frac{r_3}{r_4} = \left|\frac{k_{2tot} - k_2}{|k_{4tot}| - |k_4|}\right| = \left|\frac{9.11 - 0.74}{0.61 - 3.84}\right| = \frac{2.59}{1}$$

This ratio can be converted to percentages the following:

$$r_3(\%) = \frac{2.59}{2.59+1} \times 100\% = 72.1\% \quad \text{and} \quad r_4(\%) = \frac{1}{2.59+1} \times 100\% = 27.9\%$$

X-ray Crystal Structure of 3

Crystals of **3** suitable for X-ray diffraction were obtained by cooling a concentrated hexanes solution of **3** at 4 °C. The crystal was mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker-Nonius Kappa Axis X8 Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were determined from a symmetry constrained fit of 4663 reflections with 4.46° < 2θ < 63.6°. The data collection strategy was a number of ω and φ scans which collected data up to 75.86° (2θ). The frame integration was performed using SAINT.[S3] The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using TWINABS.[S4] During the initial indexing, it was determined that the crystal was non-merohedrally twinned by a 180º rotation about the b* axis. The orientation matricies for both components were determined. The structure was solved by direct

methods using the XS program.[S5] All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The refinement included reflection data from both fractions. The twin fraction of the first domain refined to a value of 0.4528(9). The refinement proceeded smoothly. However, the esd's for molecular geometry were larger than expected due to the difference in the numbers of reflections between the single component data and the twinned data. The structural model was fit to the data using full matrix least-squares based on F^2. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the XL program from SHELXTL;[S6] graphic plots were produced using the NRCVAX crystallographic program suite.

Table S1. Crystal and Structure Refinement Data for **3**.

empirical formula	$C_{38}H_{44}AuOP$	
fw	744.67	
T (K)	110(1)	
λ (Å)	0.71073	
crystal system	triclinic	
space group	P-1	
unit cell dimensions	a = 10.4836(10) Å	α = 78.881(4)°
	b = 12.0170(12) Å	β = 78.768(4)°
	c = 13.9089(13) Å	γ = 67.199(5)°
V (Å^3)	1571.0(3)	
Z	2	
D_{calc} (Mg/m^3)	1.574	
abs coeff (mm^{-1})	4.762	
total no. of reflns	29017	
no. of unique reflns	29017	
no. params refined/ restrained	377/0	
R_{int}	0.0471	
F(000)	748	
crystal size (mm^3)	0.40 × 0.16 × 0.06	
color and habit	colorless plate	
Goodness-of-fit on F^2	1.119	
Final R indices [I>2σ(I)]	$R1$ = 0.0415, $wR2$ = 0.1061	
R indices (all data)	$R1$ = 0.0516, $wR2$ = 0.1167	
max, min Δρ (e$^-$/Å^3)	5.034, -2.020	

References

S1. Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Qian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2006**, *128*, 9066.

S2. Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*; Elsevier: Burlington, MA, 2003; pp. 370.

S3. Bruker-Nonius, SAINT version 2009.9, **2009**, Bruker-Nonius, Madison, WI 53711, USA.

S4. Bruker-Nonius, TWINABS version 2009.9, **2009**, Bruker-Nonius, Madison, WI 53711, USA.

S5. Bruker-AXS, XS version 2009.9, **2009**, Bruker-AXS, Madison, WI 53711, USA.

S6. Bruker-AXS, XL version 2009.9, **2009**, Bruker-AXS, Madison, WI 53711, USA.