Supporting information for

Synthesis of Alkenylgold(I) Compounds via Sequential Hydrozirconation and Zirconium-to-Gold Transmetalation

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I. General Methods

All chemicals were used as received from commercial suppliers unless otherwise noted. 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidine gold(I) chloride was purchased from Strem Chemical Co. All other purchased reagents (alkynes 1a, 1d-1k) were acquired from Sigma-Aldrich. 1-Hexyne (1a) and 1-octene (1i) were purified via distillation prior to use. Diethyl ether and hexane were purified by passage through an alumina column under argon pressure on a push-still solvent system. Dichloromethane-d2 and benzene-d6 were dried over CaH2, degassed using three freeze-pump-thaw cycles, and vacuum transferred prior to use in reactions. All reactions were run in a nitrogen atmosphere glovebox unless otherwise specified. Purification of organogold products was accomplished using oven-dried Acros 50–200 μm basic aluminum oxide (activity I). This oven drying step was found to be critical for successful product isolation. Small volumes of alumina were dried in scintillation vials for a minimum of 12 hours at 140 °C to ensure the entire volume of alumina was completely dried. All proton and carbon NMR spectra were recorded using either a Bruker DRX-500 spectrometer equipped with a cryoprobe, or a Bruker AVANCE600 spectrometer. Chemical shifts are reported in parts per million. NMR spectra are calibrated to residual protiated solvent signals (δ = 5.32 ppm for CD2Cl2, δ = 7.27 ppm for CDCl3, and δ = 7.12 ppm for C6D6 for 1H NMR and δ = 54.00 ppm for CD2Cl2 for 13C NMR). High resolution mass spectrometry data were obtained at The University of California, Irvine. Elemental Analyses were provided by Elemental Analysis, Inc.
II. Synthetic Procedures

1b. Silyl ether 1b was prepared according to a literature procedure.\textsuperscript{1} The product was obtained as a colorless oil (0.52 g, 23\% yield). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz): \(\delta\) 0.07 (s, 6H), 0.90 (s, 9H), 1.74 (m, 2H), 1.93 (s, 1H), 2.28 (m, 2H), 3.70 (t, \(J = 6.0\) Hz, 2H). This spectrum is in agreement with previously reported spectra.\textsuperscript{1}

1c. Ester 1c was prepared according to a literature procedure.\textsuperscript{2} The product was obtained as a colorless oil (10.5 mg, 2\% yield). The low yield resulted from hydrolysis of the product on silica gel, which was not reported in the original procedure. Additional purification was required, which consisted of running the product through a basic alumina plug to separate out material that had hydrolyzed on the initial silica gel column. \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 600 MHz): \(\delta\) 1.43 (s, 9H), 1.54 (m, \(J = 7.3, 9.2\) Hz, 2H), 1.66 (m, \(J = 7.7, 6.3\) Hz, 2H), 1.98 (t, \(J = 2.6\) Hz, 1H), 2.20 (m, 4H). This spectrum is in agreement with previously reported spectra.\textsuperscript{2}

General Reaction Procedure

In a N\textsubscript{2} filled glovebox, Schwartz’s reagent (35.2 mg, 0.136 mmol, 1.36 equiv) was weighed into a dram vial. Alkyne 1 (0.100 mmol, 1.00 equiv) was weighed into another dram vial. To the alkyne was added 0.30 mL of CD\textsubscript{2}Cl\textsubscript{2}, and the resulting solution was added to the vial containing the Schwartz’s reagent. An additional 0.20 mL of CD\textsubscript{2}Cl\textsubscript{2} was used to rinse the
vial previously containing the alkyne and then added to the reaction vial. Starting materials that were liquids were measured using a gastight syringe and added directly to the vial containing Schwartz’s reagent and the final volume of 0.50 mL CD$_2$Cl$_2$. An oven-dried stir bar was added to the vial, which was then capped and allowed to stir for 30 min. The resulting solution was transferred to an oven-dried J. Young tube and examined via $^1$H NMR spectroscopy for completion. Upon completion, the solution was returned to the glovebox. ((2,6-diisopropylphenyl)imidazole-2-ylidene gold(I) chloride) ([(IPr)AuCl]) (62.0 mg, 0.100 mmol, 1.00 equiv) was weighed into a dram vial and dissolved in 0.30 mL of CD$_2$Cl$_2$. The resulting solution was transferred to the original J. Young tube and the vial was rinsed with another 0.20 mL of CD$_2$Cl$_2$, which was also then added to the J. Young tube. The reaction was run for 3 h and monitored further for completion if necessary by $^1$H NMR spectroscopy. Upon completion, the reaction was transferred to a 20 mL scintillation vial in the glovebox and concentrated in vacuo. The resulting residue was extracted using 2 mL of dry 1:1 hexanes:diethyl ether. The solution was filtered through a pipette fitted with an oven-dried glass fiber filter to remove solid zirconocene dichloride. The filtered solution was then passed through a pipette containing basic alumina (c.a. 3 cm height) with additional hexanes:diethyl ether solution (c.a. 5 mL) in order to remove any residual impurities. The filtrate was removed from the glovebox and concentrated in vacuo to yield a white solid. This solid was dried under high vacuum (<50 mTorr) overnight to obtain the final vinylgold product.
2a. 1-Hexyne (1a) (11.4 μL, 0.100 mmol) was employed for the reaction, following the standard procedure. The product was isolated as a white solid (42.8 mg, 72% yield). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 600 MHz): \(\delta\) 0.79 (t, \(J = 6.6\) Hz, 3H), 1.17 (m, 4H), 1.21 (d, \(J = 6.6\) Hz, 12 H), 1.34 (d, \(J = 6.6\) Hz, 12H), 1.87 (q, \(J = 6.6, 12.9\) Hz, 2H), 2.61 (sept, \(J = 6.5, 10.3, 12.1\) Hz, 4H), 5.21 (dt, \(J = 6.6, 18.6\) Hz, 1H), 6.11 (d, \(J = 18.6\) Hz, 1H), 7.13 (s, 2H), 7.32 (d, \(J = 7.8\) Hz, 4H), 7.55 (t, \(J = 7.8\) Hz, 2H). \(^{13}\)C NMR (CD\(_2\)Cl\(_2\), 125 MHz): \(\delta\) 14.4, 23.1, 24.1, 24.7, 29.3, 32.8, 39.0, 123.5, 124.5, 130.6, 135.3, 144.8, 146.4, 154.3, 198.7. HRMS (ESI): [M + Na]\(^+\) calcd. for C\(_{33}\)H\(_{47}\)N\(_2\)AuNa, 691.3303; found, 691.3287. Anal. Calcd. for C\(_{33}\)H\(_{47}\)AuN\(_2\): C, 59.27; H, 7.08; N, 4.19. Found: C, 58.99; H, 7.13; N, 4.13.

2b. Synthesized compound 1b (19.8 mg, 0.100 mmol) was employed in this reaction, following the standard procedure. The product was isolated as a white solid (44.5 mg, 57% yield). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 500 MHz): \(\delta\) 0.84 (s, 3H), 1.21 (d, \(J = 7.0\) Hz, 12H), 1.34 (d, \(J = 7.0\) Hz, 12H), 1.40 (quint, \(J = 7.0, 11.0\) Hz, 2H), 1.90 (q, \(J = 7.5, 14.2\) Hz, 2H), 2.61 (sept, \(J = 7.0, 10.5, 12.3\) Hz, 4H), 3.47 (t, \(J = 6.5\) Hz, 2H), 5.20 (dt \(J = 10.5, 19.5\) Hz, 1H), 6.12 (d, \(J = 18.5\) Hz, 1H), 7.14 (s, 2H), 7.32 (d, \(J = 7.5\) Hz, 4H), 7.53 (t, \(J = 7.0\) Hz, 2H). \(^{13}\)C NMR (CD\(_2\)Cl\(_2\), 125 MHz): \(\delta\) 24.1, 24.7, 26.3, 29.3, 33.7, 35.2, 63.7, 123.4, 124.5, 130.6, 135.3, 144.8, 146.4, 154.3, 198.7. HRMS (ESI): [M + Na]\(^+\) calcd. for C\(_{38}\)H\(_{59}\)OSiN\(_2\)AuNa, 807.3960; found, 807.3976. Anal. Calcd. for C\(_{38}\)H\(_{59}\)AuN\(_2\)OSi: C, 58.15; H, 7.58; N, 3.57. Found: C, 58.52; H, 7.87; N, 3.51.
2c. Synthesized compound 1c (7.8 mg, 0.040 mmol) was added to Schwartz’s reagent (15 mg, 0.054 mmol), following the standard procedure. The complex (IPr)AuCl (26.6 mg, 0.0429 mmol) was added to the reaction. The product was isolated as a white solid (20.6 mg, 62% yield). $^1$H NMR (CD$_2$Cl$_2$, 500 MHz): $\delta$ 1.21 (d, $J = 6.9$ Hz, 12H), 1.34 (d, $J = 6.9$ Hz, 12H), 1.38 (s, 9H), 1.43 (m, 2H), 1.87 (q, $J = 7.5$, 6.9 Hz, 2H), 2.08 (t, $J = 7.5$ Hz, 2H), 2.60 (sept, $J = 6.0$, 11.0, 12.0 Hz, 4H), 5.20 (dt, $J = 6.1$, 18.6 Hz, 1H), 6.12 (d, $J = 18.5$ Hz, 1H), 7.14 (s, 2H), 7.32 (d, $J = 7.8$ Hz, 4H), 7.53 (t, $J = 7.8$ Hz, 2H). $^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz): $\delta$ 24.1, 24.7, 25.6, 28.4, 29.3, 30.0, 36.1, 38.8, 79.9, 123.5, 124.5, 130.6, 135.3, 145.1, 146.5, 154.3, 173.7, 198.7. HRMS (ESI): [M + Na]$^+$ calcd. for C$_{38}$H$_{55}$AuN$_2$O$_2$, 791.3827; found, 791.3824.

2d. Alkyne 1d (11.1 $\mu$L, 0.100 mmol) was employed in the reaction. Standard reaction conditions were followed. Product was isolated as a white solid (46.6 mg, 68% yield). $^1$H NMR (CD$_2$Cl$_2$, 500 MHz): $\delta$ 1.21 (d, $J = 6.9$ Hz, 12H), 1.34 (d, $J = 6.9$ Hz, 12H), 1.67 (m, 2H), 2.00 (q, $J = 7.2$, 13.8 Hz, 2H), 2.61 (sept, $J = 7.0$, 10.0, 12.0 Hz, 4H), 3.42 (t, $J = 7.0$ Hz, 2H), 5.17 (dt, $J = 6.2$, 18.5 Hz, 1H), 6.17 (d, $J = 18.5$ Hz, 1H), 7.14 (s, 2H), 7.32 (d, $J = 7.8$ Hz, 4H), 7.53 (t, $J = 7.8$ Hz, 2H). $^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz): $\delta$ 24.1, 24.7, 29.3, 33.5, 36.1, 45.9, 123.5, 124.5, 130.6, 135.3, 143.1, 146.5, 155.7, 198.4. HRMS (ESI): [M + Na]$^+$ calcd. for C$_{32}$H$_{44}$AuN$_2$Cl, 711.2756; found, 711.2745. Anal. Calcd. for C$_{32}$H$_{44}$AuN$_2$Cl: C, 55.77; H, 6.44; N, 4.07. Found: C, 55.95; H, 6.35; N, 4.06.
2e. Alkyne 1e (4.7 μL, 0.050 mmol) was added to Schwartz’s reagent (17.6 mg, 0.0683 mmol). Standard reaction procedure was followed. The complex (IPr)AuCl was added to the reaction (30.5 mg, 0.0492 mmol). The product was isolated as a white solid (47.5 mg, 66% yield). $^1$H NMR (CD$_2$Cl$_2$, 600 MHz): E isomer: $\delta$ 1.22 (m, 12H), 1.34 (m, 12H), 2.15 (q, $J = 7.8$, 13.8 Hz, 2H), 2.42 (q, $J = 7.8$, 13.8 Hz, 2H), 3.23 (t, $J = 7.8$ Hz, 1H), 2.66-2.55 (m, 4H), 5.17 (dt, $J = 6.6$, 18.6 Hz, 1H), 6.29 (d, $J = 18.6$ Hz, 1H), 7.14 (s, 2H), 7.33 (d, $J = 7.8$ Hz, 4H), 7.53 (t, $J = 7.8$ Hz, 2H). Z isomer: $\delta$ 1.22 (m, 12H), 1.34 (m, 12H), 2.15 (q, $J = 7.8$, 13.8 Hz, 2H), 2.66-2.55 (m, 4H), 3.00 (t, $J = 7.8$ Hz, 1H), 6.08 (quint, $J = 6.6$, 9.3 Hz, 1H), 6.34 (d, $J = 11.4$ Hz, 1H), 7.17 (s, 2H), 7.33 (d, $J = 7.8$ Hz, 4H), 7.53 (t, $J = 7.8$ Hz, 2H). $^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz): $\delta$ 24.0, 24.5, 29.1, 34.3, 35.0, 41.8, 42.7, 123.4, 123.6, 124.3, 124.6, 124.6, 130.5, 130.6, 131.0, 135.0, 139.7, 140.6, 146.1, 146.2, 158.6, 159.0, 197.7, 198.8. HRMS (ESI): [M + Na]$^+$ calcd. for C$_{31}$H$_{42}$N$_2$BrAuNa, 741.2095; found, 741.2069. Anal. Calcd. for C$_{31}$H$_{42}$AuN$_2$Br: C, 51.75; H, 5.88; N, 3.89. Found: C, 52.23; H, 6.05; N, 4.06.

Procedure for Examination of the Isomerization of 2e:

Alkyne 1e (4.70 μL, 0.0500 mmol) was added to 0.5 mL of C$_6$D$_6$ and the resulting solution was added to Schwartz’s reagent (17.6 mg, 0.0683 mmol). The reaction mixture was transferred to a J. Young tube. The reaction was monitored for completion by $^1$H NMR spectroscopy. Upon completion, a solution of (IPr)AuCl (30.5 mg, 0.0492 mmol) in 0.5 mL of C$_6$D$_6$ was added to the reaction. The reaction was monitored for completion by $^1$H NMR spectroscopy. The only product formed was the E isomer. The J Young tube was returned to the glovebox and the solution was separated equally into two scintillation vials. The two vials were
concentrated in vacuo in the glovebox. The residue in the first vial was redissolved in C₆D₆ and added to a clean J Young tube. The residue in the second vial was redissolved in CD₂Cl₂ and added to another clean J Young tube. Each solution was monitored by ¹H NMR spectroscopy immediately after being redissolved and again after 12 h. After 12 h, isomerization of the organogold was evident in the sample in CD₂Cl₂, but no appreciable change was observed for the sample in C₆D₆.

2f. Alkyne 1f (11.0 μL, 0.100 mmol) was employed in the reaction. The product was isolated as a white solid (53.3 mg, 77% yield). ¹H NMR (CD₂Cl₂, 600 MHz): δ 1.23 (d, J = 6.6 Hz, 12H), 1.38 (d, J = 7.2 Hz, 12H), 2.65 (sept, J = 6.0, 8.5, 10.3 Hz, 4H), 6.24 (d, J = 19.2 Hz, 1H), 6.96 (m, 1H), 7.12 (m, 4H), 7.17 (s, 2H), 7.29 (d, J = 19.2 Hz, 1H), 7.34 (d, J = 7.8 Hz, 4H), 7.54 (t, J = 7.8 Hz, 2H). ¹³C NMR (CD₂Cl₂, 125 MHz): δ 24.2, 24.7, 29.3, 123.6, 124.5, 125.4, 125.6, 128.5, 130.7, 135.2, 141.8, 143.1, 146.5, 158.9. HRMS (ESI): [M + Na]⁺ calcd. for C₃₅H₄₃AuN₂Na, 711.2990; found, 711.2971. Anal. Calcd. for C₃₅H₄₃AuN₂: C, 61.04; H, 7.08; N, 4.19. Found: C, 58.99; H, 7.13; N, 4.13.

2g. Alkyne 1g (18.1 mg, 0.100 mmol) was employed in the reaction. The product was isolated as a white solid (47.3 mg, 77% yield). ¹H NMR (CD₂Cl₂, 500 MHz): δ 1.23 (d, J = 7.0 Hz, 12H), 1.37 (d, J = 7.0 Hz, 12H), 2.64 (sept, J = 7.0, 10.5, 12.3 Hz, 4H), 6.19 (d, J = 19.5 Hz, 1H), 7.03
(d, J = 8.5 Hz, 2H), 7.18 (s, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 19.5 Hz, 1H), 7.34 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 8.0 Hz, 2H). $^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz): δ 24.2, 24.8, 29.3, 118.9, 123.6, 124.5, 127.1, 130.8, 131.5, 135.2, 140.8, 141.7, 246.5, 160.6, 197.4. HRMS (ESI): [M + Na]$^+$ calcd. for C$_{35}$H$_{42}$N$_2$BrAuNa, 789.2095; found, 789.2092. Anal. Calcd. for C$_{35}$H$_{42}$AuN$_2$Br: C, 54.77; H, 5.52; N, 3.65. Found: C, 54.83; H, 5.43; N, 3.49.

2h. Alkyne 1h (13.0 μL, 0.100 mmol) was employed in the reaction. Product was isolated as a white solid (41.5 mg, 65% yield). $^1$H NMR (CD$_2$Cl$_2$, 600 MHz): δ 1.23 (d, J = 7.0 Hz, 12H), 1.38 (d, J = 7.0 Hz, 12H), 2.65 (sept, J = 6.5, 10.8, 11.9 Hz, 4H), 3.71 (s, 3H), 6.18 (d, J = 19.2 Hz, 1H), 6.68 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 19.0 Hz, 1H), 7.17 (s, 2H), 7.34 (d, J = 7.8 Hz, 4H), 7.54 (t, J = 7.8 Hz, 2H). $^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz): 24.2, 24.8, 29.3, 55.6, 113.9, 123.6, 124.5, 126.4, 130.7, 135.1, 135.2, 142.4, 146.5, 156.1, 158.1, 197.9. HRMS (ESI): [M + Na]$^+$ calcd. for C$_{36}$H$_{45}$ON$_2$AuNa, 741.3095; found, 741.3088. Anal. Calcd. for C$_{36}$H$_{44}$AuN$_2$Cl: C, 55.77; H, 6.44; N, 4.07. Found: C, 55.95; H, 6.35; N, 4.06.

**Procedure for Transmetalation Reversibility Test:**

In the glovebox, 2a (69.7 mg, 0.104 mmol) was added to a vial with 0.5 mL of CD$_2$Cl$_2$. The resulting solution was transferred to a vial containing zirconocene dichloride (39.7 mg, 0.136 mmol). This solution was then transferred to a J. Young tube. The solution was degassed via three freeze-pump-thaw cycles and placed under 1 atm of CO. The presence of CO was intended to trap any of the reverse transmetalated product formed, as earlier experiments had
shown that the product of CO insertion into the hydrozirconated starting materials would not transmetalate with (IPr)AuCl. The reaction was monitored by \(^1\text{H}\) NMR spectroscopy over 3 d. After 3 d, only the starting organogold \(2a\) and its protodeaurated equivalent, 1-hexene, were observed. The lack of any observable signals corresponding to the hydrozirconated material related to \(2a\) or products of CO insertion suggests there is no significant pathway by which the transmetalation of the hydrozirconated alkynes to the final organogold products is reversible.

**Procedure for Attempted AgSbF\(_4\) Carbenoid Trapping Experiment**

To a solution of 34.7 mg (0.0480 mmol) of \(2e\) in 0.5 mL of CD\(_2\)Cl\(_2\) was added 16.5 mg (1.00 equiv) of AgSbF\(_6\) in a glovebox. The solution was stirred for 30 min. The solution was then filtered through a pipette fitted with a glass fiber filter to remove any precipitate (anticipated to be AgBr). The filtrate was transferred to an NMR tube. Extensive decomposition was observed with no desired carbenoid product identified.

**Procedure for Attempted Methanol Carbenoid Trapping Experiment**

To a solution of 5.0 mg (0.0070 mmol) of \(2e\) in 0.5 mL of CD\(_2\)Cl\(_2\) was added 1.7 μL (0.042 mmol, 6 equiv) of methanol. The solution was transferred to an NMR tube and monitored for signs of reaction at 0.2, 2, 4, 5, and 24 h. Protodeauration to yield the organic bromide was faster than any potential methoxy incorporation, and no methoxy incorporation was identified.

**Procedure for Attempted Styrene Carbenoid Trapping Experiment**

To 5.0 mg (0.0070 mmol) of \(2e\) was added a solution of 2.2 mg (0.021 mmol, 3 equiv) of styrene in 0.5 mL of CD\(_2\)Cl\(_2\). The solution was transferred to an NMR tube and monitored for signs of reaction at 0.2, 2, 4, 5, and 24 h. No cyclopropanation of styrene was observed.
III. NMR Spectra of all Isolated Compounds

\[ \text{NMR Spectra} \]
(IPr)Au

2b

OTBS

$^{13}$C NMR
(IPr)Au−\(\text{C}_2\)Cl

\[^{13}\text{C}\text{ NMR}\]
(IPr)Au

2h

^{13}C NMR
IV. NMR Spectra for Isomerization Experiment of 2e in C₆D₆ and CD₂Cl₂

\[ ^1H \text{ NMR in C₆D₆ before workup} \]
\[(\text{IPr})\text{Au} - \text{Br}  \]

\[2e \]

$^1H$ NMR in C$_6$D$_6$ after 12 h
\( \text{(IPr)Au} - \text{Br} \)

\( 2 \text{e} \)

\( ^1 \text{H NMR in CD}_2\text{Cl}_2 \text{ after 12 h} \)
V. NMR Spectrum for Reversibility Experiment
VI. NMR Spectra for Methanol (1st) and Styrene (2nd) Trapping Experiments
2e in CD$_2$Cl$_2$ with Styrene after 24 h
References
