Supporting Information

Synthesis and characterization of catalytically active thiazolium gold(I)-carbenes

Clément C. Dince, Roy A. Meoded and Donald Hilvert*

Laboratory of Organic Chemistry, ETH Zurich, 8093 Zurich, Switzerland
*e-mail: hilvert@org.chem.ethz.ch; Fax: +41 44 632 3176; Tel: +41 44 632 1486

1. GENERAL PROCEDURES

Reagents and biologics (ABCR, Acros, Aldrich, Bachem Fluka, and TCI) were purchased as reagent grade and used without further purification. Solvents for flash column chromatography (FC), plug filtrations, and extraction were of technical grade. Dry solvents for reactions were purified by a solvent drying system (LC Technology Solutions Inc. SP-105) under nitrogen atmosphere (H2O content <10 ppm as determined by Karl-Fischer titration). All other solvents were purchased in p.a. quality. For all aqueous solutions, deionized water was used. Enzymes were produced by recombinant methods using standard procedures[1].

Reactions were performed under an Ar or N_2 atmosphere in oven-dried or flame-dried glassware. Flash column chromatography (FC) was carried out using silica gel (particle size: 40–63 µm, 230–400 mesh ASTM; Fluka). Analytical thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 F254 (Merck); visualization with a UV lamp (254 nm) or staining with potassium permanganate solution. Evaporation in vacuo was performed at 40–60 °C and 900–10 mbar. Reported yields refer to spectroscopically and chromatographically pure compounds that were dried under high vacuum (10^{-2} mbar) before analytical characterization. Nomenclature follows the suggestions proposed by the computer program ChemBioDraw by CambridgeSoft. The atoms were labeled arbitrarily, if necessary. Liquid chromatography-mass spectrometry (LCMS) analyses were performed on a Dionex UltiMate 3000 RSLC connected to a Surveyor MSQ Plus mass spectrometer; a reversed–phase RESTEK Pinnacle II C18 (4.6 x 50 mm) column was used, running a gradient of 5 to 100% CH3CN in H2O over 6.5 min and 100% CH3CN for 2.5 min. ^{1}H- and ^{13}C-Nuclear magnetic resonance (NMR) spectra were recorded on Varian Gemini 300, Varian Mercury 300, Bruker ARX 300, Bruker DRX 400, and Bruker AV 400 spectrometers at 300 MHz or 400 MHz (^{1}H) and 75 MHz or 100 MHz (^{13}C), respectively. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane using the residual deuterated solvent signals as an internal reference. Data for ^{1}H-NMR are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens). Coupling constants *J* are given in Hz and the resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broad). All spectra were recorded at 25 °C. Matrix Assisted Laser Desorption Ionisation (MALDI) analyses were performed on a Bruker Daltonics Microflex. The matrix was 2,5-dihydroxybenzoic acid (DHB) or α-cyano-4-hydroxycinnamic acid (CHCA). Elemental analysis experiments were performed by the Microanalysis laboratory of the Laboratory of Organic Chemistry at the ETH Zurich. Determination of the elements C, H, N, S and O was carried out with instruments provided by the company LECO. Halogens (F, Cl, Br, I) were obtained according to the Schöniger method[2],and collected in an absorbing liquid medium. Determination was done by titrimetric analysis (Cl, Br, I).

2. MOLECULAR CLONING

General procedures. *E. coli* strain XL-1 blue (Stratagene) (genotype: *recA1 endA1 gyrA96 thi-1 hsdR17 supE44 relA1 lac* [F' *proAB lacI*^{q}Z **Δ***M15* Tn*10* (Tetr)]) was used for cytoplasmic overexpression of plasmids, and *E. coli* BL21 Gold(DE3) strain (genotype: *E. coli* B F- *ompT hsdS*(rB-mB-) *dcm*+ Tetr *gal* **λ**(DE3) *endA* Hte) was used for protein production. Nucleic acid manipulations were performed following standard procedures[1]. After transformation of XL-1 blue, cells were grown on Lysogeny broth plates containing 150 µg/mL ampicillin (LB_{Amp}) overnight at 37 °C. Single colonies were used to inoculate 5 mL overnight cultures and plasmids were isolated and purified with JETquick kits on a miniprep scale. DNA concentrations were measured with a NanoDrop spectrophotometer. All primers were synthesized and purified by Mycrosynth (Balgach, Switzerland). DNA sequencing was performed by Mycrosynth. After sequence verification, plasmids containing genes of interest were subcloned into *E. coli* BL21 Gold(DE3) for protein production.

Plasmids. *pMG211-thi80.* The gene encoding thiamin pyrophosphokinase (TPPK) (thi80) was extracted from yeast genomic DNA using cloning primers TPPK *fwd* (TGA TAA CAT ATG AGC GAG GAG TGT ATT GAA AATC) and *rev (*TTA TCA CTC GAG CAA AAA ATC TAT TAA TTT ATC AAC G) designed to exploit NdeI and XhoI restriction sites present in the pMG211 vector[3]. The gene was introduced into this vector to equip the protein with a C-terminal His_6-tag via a Leu-Glu linker. pMG211 is derived from pKSS[4] and features a pKSS origin of replication, ampicillin resistance encoded by the *bla* gene, and a dual promoter system consisting of a sal and a T7 promoter in tandem. While *lacI* codes for the T7 repressor and therefore leads to IPTG inducibilty, *nahR* encodes an activator of sal and renders the promoter responsive to salicylate. Sequencing primers were the following: *fwd* TAAT ACG ACT CAC TAT AGG and *rev* TGC TAG TTA TTG CTC AGC GG.

3. PRODUCTION OF THIAMIN PYROPHOSPHOKINASE

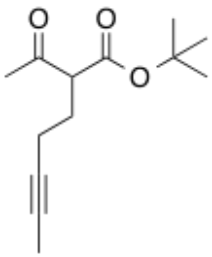
Cell culture. 500mL LB-medium supplemented with ampicillin (150 µg/mL) was inoculated with 0.5mL overnight culture of BL21-Gold(DE3) cells harboring a pMG211-thi80 plasmid encoding TPPK. The cell culture was grown at 30 °C and 250 rpm to an OD600 of 0.6. The production of TPPK was induced with 2mL 250mM IPTG (1mM final concentration) and the cell culture was incubated at 30 °C and 250 rpm for 6 h.

Cell harvesting and lysis. Cells were harvested by centrifugation at 5,000 g and 4 °C for 20 min. The cell pellet was stored at -20 °C overnight and resuspended in 3 volumes of sonication buffer (25 mM Tris-HCl pH 8, 300 mM NaCl, 20 mM $MgCl_2$, 1 mM DTT or TCEP) in the presence of lysozyme (1 mg/mL), DNAse (0.1 mg/mL), half a tablet of protease inhibitor cocktail (Roche Diagnostics) and subsequently lysed by sonication (0.5 cycles, amplitude 60,

5x1 min with a 1 min break between cycles). Cell debris was removed by centrifugation (14,000 g, 4 °C, 20 min).

Protein purification. Proteins in clear lysate were purified by Ni-NTA chromatography (Qiagen). The resin column was pre-equilibrated in sonication buffer containing 20 mM imidazole. The column was washed with the same solution before elution with 250 mM imidazole in sonication buffer. Buffer was exchanged by dialysis in SnakeSkin dialysis tubing 3,500MWCO (Thermo Scientific) against 2 x 3L of dialysis buffer (25 mM Tris-HCl pH 8, 20 mM $MgCl_2$, 1 mM DTT or TCEP) at 4 °C. When needed, proteins were purified further by size exclusion FPLC on a Superdex 75 HR 10/30 (GE Healthcare) with the respective dialysis buffer. The protein solutions were stored at 4 °C. Protein concentration was determined with a NanoDrop spectrophotometer using a calculated extinction coefficient at 280 nm of 37,860 M^{-1} cm^{-1} (http://web.expasy.org/protparam/). Protein purity was assessed by SDS-PAGE and protein identity was confirmed by electrospray ionization mass spectrometry after buffer was exchanged to water - 0.1% formic acid.

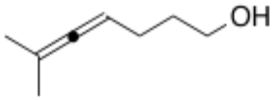
4. CHEMICAL AND ENZYMATIC SYNTHESES



tert-Butyl 2-acetylhept-5-ynoate (8). Following a procedure described by Toste[5], triethylamine (7.9 mL; 57.1 mmol; 1.2 equivalents) was added to a solution of 3-pentyn-1-ol (4 g; 47.6 mmol; 1 equivalent) in dry dichloromethane in a 100 mL round bottom flask equipped with a magnetic stir bar under nitrogen and at 0 °C. After 15 min, mesyl chloride (4.06 mL; 52.3 mmol; 1.1 equivalents) was added dropwise and the reaction was allowed to warm to room temperature for 30 min. The reaction was poured into 50 mL of water and extracted with 3 x 30 mL of dichloromethane. The combined organics were washed with brine (25 mL), dried, filtered and concentrated under vacuum. The crude methanesulfonic acid pent-3-ynyl ester product was used without further purification.

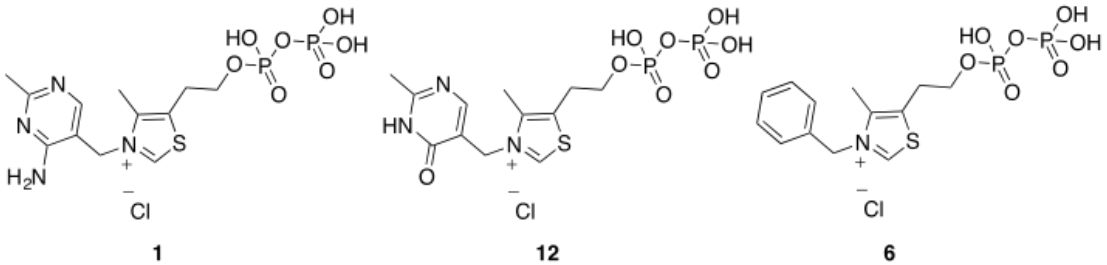
To a suspension of sodium hydride (0.264 g; 6.6 mmol; 1.06 equivalents) in 8 mL of a 1:1 mixture of THF and DMF was added potassium iodide (0.61 g; 3.7 mmol; 0.6 equivalents). The solution was cooled to 0 °C and treated dropwise with *tert*-butyl acetanoate. The resulting solution was allowed to warm to room temperature for 30 min and the methanesulfonic acid pent-3-ynyl ester obtained previously was added. The reaction mixture was heated to 95 °C for 8 h, quenched with 5 mL of 1N HCl and extracted with ether (3x10 mL). The combined organics were washed with brine (2x10 mL), dried, filtered,

concentrated under vacuum and purified by flash chromatography (hexane/EtOac, 7:1). Compound **8** was obtained as a colorless oil in 21% yield over two steps (342 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.57 (t, *J* = 7.2 Hz, 1H), 2.25 (s, 3H), 2.17 (tdd, *J* = 6.8, 3.4, 1.8 Hz, 2H), 2.01 - 1.92 (m, 2H), 1.77 (t, *J* = 2.6 Hz, 3H), 1.46 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.41, 168.75, 82.14, 77.60, 77.05, 59.45, 29.39, 28.06, 27.24, 16.78, 3.62; **MS** (ESI): *m/z* 225.2 (100, $[M+H]^+$), calcd $[C_{13}H_{21}O_3]^+$: 225.31



6-Methylhepta-4,5-dien-1-ol (10). Following a procedure by Malacria,[6] n-BuLi (1.6 M in hexanes; 6.85 mL; 10.96 mmol; 1.1 equivalents) was added to a solution of dimethylallene (0.678 g; 9.96 mmol; 1 equivalent) in dry THF (10 mL) at -78 °C. After stirring for 2 h at -78 °C, a solution of 3-bromo-1-(2-tetrahydro-pyranyloxy)propane (2 g; 8.96 mmol; 0.9 equivalents) in dry THF (10 mL) was added and the mixture was allowed to warm to room temperature for 3h, then diluted with diethyl ether (50 mL) and washed with a saturated aqueous solution of ammonium chloride (50 mL). The organic layer was separated and washed with brine (2x40 mL), dried, concentrated under vacuum, and purified by flash chromatography (pentane/diethyl ether, 9:1) to afford the desired product 2-((6-methylhepta-4,5-dien-1-yl)oxy)-tetrahydro-2H-pyran in 91% yield (1.904 g).

To a solution in methanol (16 mL) of the product obtained previously was added *para*-toluenesulfonic acid monohydrate (125 mg; 0.66 mmol; 0.073 equivalents). The reaction mixture was stirred at 25 °C for 2 h and then partitioned between diethyl ether (3x50 mL) and a saturated aqueous solution of sodium bicarbonate (50 mL). The organics were washed with brine (20 mL), dried, filtered, concentrated under vacuum, and the residue was purified by flash chromatography with pentane/diethyl ether. The product 6-methylhepta-4,5-dien-1-ol **(10)** was obtained as colorless oil in 30% yield (347 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.97 (tp, *J* = 6.0, 2.9 Hz, 1H), 3.68 (p, *J* = 6.6 Hz, 2H), 2.04 (q, *J* = 7.1 Hz, 2H), 1.71 - 1.63 (m, 8H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.87, 95.62, 88.27, 62.65, 32.11, 25.62, 20.86.



General procedure for the enzymatic pyrophosphorylation of TPP analogs. The commercially available thiazolium chloride salts of vitamin B1 (**2**), oxythiamin (**3**) and benzylthiazolium (**4**) (5 mM) were individually incubated with TPPK (5 µM) and adenosine 5'-triphosphate (ATP) (10 mM), $MgCl_2$ (20 mM) in 100 µL of 25 mM Tris-HCl buffer at pH 8.0

at 37 °C for 2 h. The reaction was followed by reversed phase TLC (water/acetonitrile, 7:3) and purified by preparative HPLC (column: VP250/21 NUCLEODUR 100-7 C_{18} (Macherey-Nagel), gradient: acetonitrile 0.08% TFA/H2O 0.1% TFA from 5:95 to 60:40 in 95 min). Product masses were determined by LCMS.

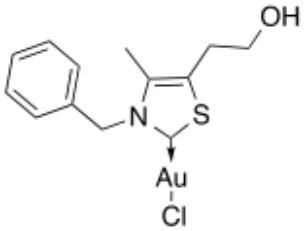
(1) MS (ESI): *m/z* 424.93 (100, $[M\text{-}Cl]^+$), calcd $[C_{12}H_{19}N_4O_7P_2S]^+$: 425.04.

(12) MS (ESI): *m/z* 425.93 (100, $[M\text{-}Cl]^+$), calcd $[C_{12}H_{18}N_3O_8P_2S]^+$: 426.03.

(6) ^{1}H NMR (300 MHz, D_2O) δ 9.59 (s, 1H), 7.54 - 7.42 (m, 3H), 7.36 - 7.27 (m, 2H), 5.63 (s, 2H), 4.23 - 4.09 (m, 2H), 3.25 (t, *J* = 5.5 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, D_2O) δ 180.91, 155.28, 134.90, 131.74, 129.46, 128.31, 64.73, 56.74, 27.48, 11.18; **^{31}P NMR** (243 MHz, D_2O) δ -11.01 (s), -11.64 (s); **MS** (ESI): *m/z* 393.93 (100, $[M\text{-}Cl]^+$), calcd $[C_{13}H_{18}NO_7P_2S]^+$: 394.29.

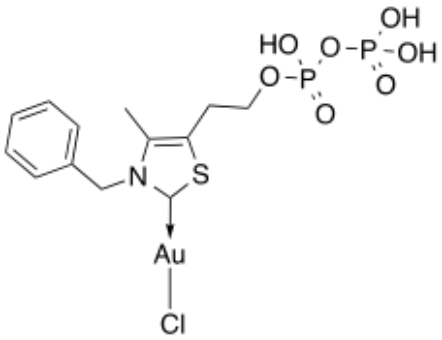
Sol-gel preparation. TPPK (2.5 mL; 1.7 mg/mL) was mixed with 120 µL of ATP solution (220 mM, pH 8) and incubated for 15 min. The gel solution was prepared separately by mixing 1 mL of tetramethyl orthosilicate (TMOS) with 1.3 mL HCl (2.5 mM), and incubated for 30 min at 40 °C and 30 min at 4 °C. Finally, both solutions were combined and stored at 4 °C to promote gel formation overnight. The supernatant was removed and the gel was washed with an equivalent volume of TPPK sonication buffer at room temperature under stirring (250 rpm) for 1 day.

General procedure for the enzymatic pyrophosphorylation of TPP derivatives in sol-gel. A reaction buffer of equivalent volume to the sol-gel, containing benzylthiazolium (**4**) (10 mM), adenosine 5'-triphosphate (ATP) (15 mM), $MgCl_2$ (40 mM) in of 25 mM Tris-HCl buffer at pH 8.0 was added on top of the sol-gel. The reaction was performed at 37 °C for 18 h. The reaction was followed by reversed phase TLC (water/acetonitrile, 7:3) and the supernatant was purified by preparative HPLC (column: VP250/21 NUCLEODUR 100-7 C_{18} (Macherey-Nagel), gradient: acetonitrile 0.08% TFA/H2O 0.1% TFA from 5:95 to 60:40 in 95 min).



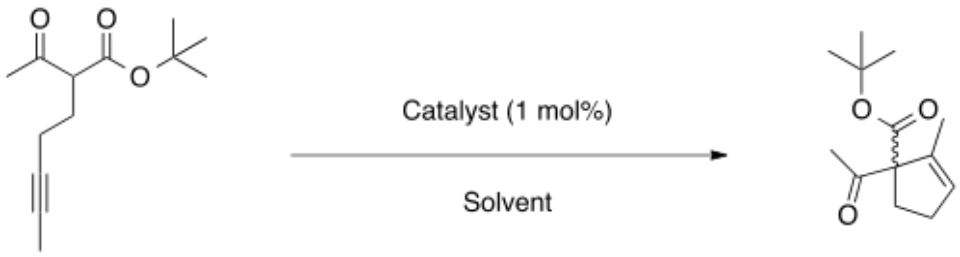
3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazol-3-ium gold(I) chloride (5). In a 25 mL round bottom flask equipped with a magnetic stir bar, benthylthiazolium (**4**) (40 mg; 0.15 mmol; 1 equivalent) and dimethylsulfide gold(I) chloride (48 mg; 0.163 mmol; 1.1 equivalents) were dissolved in 50 mM Tris-HCl buffer pH 9 (8 mL; 19 mM). After quick sonication, the reaction mixture was stirred at 45 °C for 2 h. Based on our preliminary observations that purple colloidal gold formed faster when reactions involving gold were

performed in the light, this reaction was carried out in the dark as a precaution. The reaction was extracted with EtOAc (4x15 mL). The combined organics were dried, filtered and concentrated under vacuum. The residue was recrystallized by slow diffusion of pentane in a solution of EtOAc. The solvent was removed and the solid was dried under high vacuum to afford a white solid in 90% yield (62.04 mg). Crystals were obtained by slow diffusion of pentane in EtOAc. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 - 7.15 (m, 3H), 7.10 - 7.03 (m, 2H), 5.63 (s, 2H), 3.63 (t, J = 6.0 Hz, 2H), 2.76 (t, J = 6.0 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.17, 140.60, 133.91, 133.49, 128.88, 128.35, 126.35, 60.86, 59.84, 30.16, 12.53. MS (ESI): m/z 663.20 (100, $[AuL_2]^+$), 232.27 (30), calcd for dimer $[C_{13}H_{15}NOS]_2Au^+$: 663.62; elemental analysis calcd (%) for $C_{13}H_{15}AuClNOS^+$ (465.02) C 33.52, H 3.25, Au 42.29, Cl 7.61, N 3.01, O 3.44, S 6.88; found C 33.63, H 3.39, Cl 7.73, N 3.01, S 6.81.



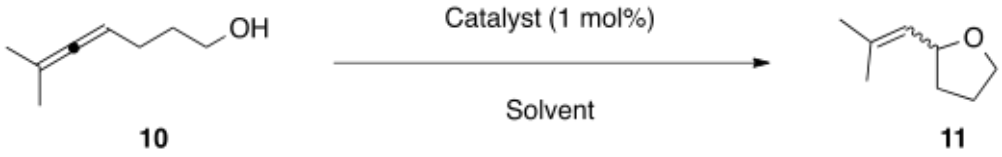
3-Benzyl-5-(2-((hydroxy(phosphonooxy)phosphoryl)oxy)ethyl)-4-methylthiazol-3-ium gold(I) chloride (7). In a 25 mL round bottom flask equipped with a magnetic stir bar, benthylthiazolium pyrophosphate (**6**) (100 mg; 0.253 mmol; 1 equivalent) and dimethylsulfide gold(I) chloride (82.2 mg; 0.279 mmol; 1.1 equivalents) were dissolved in 50 mM Tris-HCl / potassium phosphate buffer (1:1) pH 9 (20 mL; 13 mM). After quick sonication, the reaction mixture was stirred at 45 °C in the absence of light for 3 h. The purple reaction was supplemented with an additional equivalent of dimethylsulfide gold(I) chloride and stirred at 45 °C for an additional 2 h. The reaction mixture was filtered through 0.22 µm filters to remove gold nanoparticules. The product was purified by preparative-HPLC (column: VP250/21 NUCLEODUR 100-7 C_{18} (Macherey-Nagel), gradient: acetonitrile 0.08% TFA/H2O 0.1% TFA from 5:95 to 60:40 in 95 min). After removal of the solvent under high vacuum, a white powder was obtained in 21% yield (33 mg). Other products included acetonitrile activated carbene and the bis-carbene. ^{1}H NMR (400 MHz, D_2O) δ 7.57 (q, J = 7.3, 6.3 Hz, 3H), 7.30 (d, J = 6.5 Hz, 2H), 5.87 (s, 2H), 4.36 (s, 2H), 3.38 (s, 2H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, D_2O) δ 205.05, 143.76, 134.22, 129.31, 128.63, 126.69, 65.15, 59.05, 28.15, 12.17; MS (MALDI): m/z 983.322 (100, $[AuL_2]^+$), calcd for dimer $[C_{13}H_{17}NO_7P_2S]_2Au^+$: 983.54.

5. GOLD-CATALYZED REACTIONS



8 **9**

Carbocyclization of tert-butyl 2-acetylhept-5-ynoate. In a glass vial, tert-butyl 2-acetylhept-5-ynoate (**8**) (0.4 M) was mixed with benzylthiazolium gold(I)-carbene (**5**) (1 mol%) and silver triflate (1 mol%) in dichloromethane at 25 °C. After 45 min, full conversion was observed by TLC (hexane:EtOAc 7:1); a 63% isolated yield was calculated after purification. For comparison, an authentic sample of product **9** was synthesized with dimethylsulfide gold(I) chloride (1 mol%) as catalyst in dichloromethane, isolated and characterized by NMR. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.65 (tq, J = 2.3, 1.5 Hz, 1H), 2.63 - 2.51 (m, 1H), 2.44 - 2.19 (m, 2H), 2.15 (s, 3H), 2.14 - 2.03 (m, 1H), 1.80 (td, J = 2.2, 1.5 Hz, 3H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.02, 170.56, 137.53, 131.54, 81.73, 75.17, 32.46, 30.08, 27.80, 26.72, 14.76.



10 **11**

Hydroalkoxylation of 6-methylhepta-4,5-dien-1-ol.

Organic solvent procedure: In a glass vial, 6-methylhepta-4,5-dien-1-ol (**10**) (30 mg; 0.24 mmol; 1 equivalent) and benzylthiazolium gold(I)-carbene (**5**) (1.1 mg; 2.4 µmol; 1 mol%) were dissolved in DCM (594 µL, 0.4 M). The reaction was stirred at room temperature in the dark overnight. The reaction was monitored by TLC (pentane/diethyl ether, 8:2, $KMnO_4$) R_f: starting material **10** = 0.23, product **11** = 0.70. The solvent was evaporated and a conversion of 94% was determined by NMR analysis. For comparison, an authentic sample of product **11** was synthesized with dimethylsulfide gold(I) chloride (1 mol%) as catalyst in dichloromethane, isolated and characterized by NMR. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.19 (dp, *J* = 8.6, 1.4 Hz, 1H), 4.49 (td, *J* = 8.3, 6.2 Hz, 1H), 3.94 - 3.69 (m, 2H), 2.06 - 1.95 (m, 1H), 1.95 - 1.83 (m, 2H), 1.71 (d, *J* = 1.4 Hz, 3H), 1.69 (d, *J* = 1.4 Hz, 3H), 1.50 (dq, *J* = 11.8, 8.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.00, 125.96, 75.95, 67.79, 32.58, 26.34, 25.94, 18.28.

Aqueous buffer procedure: A solution of 6-methylhepta-4,5-dien-1-ol (**10**) in DMSO (25 µL, 0.4M) was added to a glass vial containing 283 µL of 50 mM potassium phosphate buffer at pH 7 and 1 mM $MgCl_2$, followed by a solution of benzyl-thiazolium pyrophosphate gold(I)-carbene (**7**) in DMSO (25 µL; 0.004M; 1mol%). The reaction mixture was shaken at room temperature in the dark for 24h and finally extracted with diethyl ether, concentrated and the ratio starting material/product characterized by ^{1}H NMR. The conversion reached 99%.

6. CRYSTALLOGRAPHIC DATA

Crystals of compounds **5** and **6** were measured on a Bruker/Nonius Kappa APEX-II diffractometer with Mo-Kα radiation (λ = 0.71073 Å). All measurements were carried out at 100K using an Oxford Cryosystems Cryostream 700 sample cryostat. Data were integrated using SAINT from Bruker Apex-II program suite and corrected for absorption effects using the multi-scan method (SADABS). The structures were solved using SHELXS and refined by full-matrix least-squares analysis (SHELXL) using the program package OLEX2. Unless otherwise indicated, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters (in terms of riding model). CCDC 1470873 and CCDC 1470874 contain the supplementary crystallographic data for this paper, and can be obtained free of charge from The Cambridge Crystallographic Data Center (12 Union Road, Cambridge CB2 +EZ, UK; email: deposit@ccdc.cam.ac.uk) or via htpps://www.ccdc.cam.ac.uk/getstructures. Compound **5** was crystallized by slow diffusion of pentane in EtOAc, whereas compound **6** was crystallized by slow diffusion of acetone in water.

7. REFERENCES

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Table S1. Crystal data and structure refinement for **5** (CCDC 1470873).

Identification code	H200316_1_1
Empirical formula	$C_{13}H_{15}AuClNOS$
Formula weight	465.74
Temperature/K	100.0(2)
Crystal system	triclinic
Space group	P -1
a/Å	8.7017(7)
b/Å	8.8040(7)
c/Å	10.7083(9)
α/°	108.863(3)
β/°	91.805(3)
γ/°	114.116(3)
Volume/Å^3	695.72(10)
Z	2
ρ_{calc}g/cm^3	2.223
μ/mm^{-1}	10.901
F(000)	440.0
Crystal size/mm^3	0.12 x 0.1 x 0.025
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.224 to 61.206
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 11, -15 ≤ l ≤ 15
Reflections collected	22080
Independent reflections	4232 [R(int) = 0.0256, R(sigma) = 0.0182]
Data/restraints/parameters	4232 / 1 / 167
Goodness-of-fit on F^2	1.112
Final R indexes [I>=2σ (I)]	R1 = 0.0166, wR2 = 0.0421
Final R indexes [all data]	R1 = 0.0182, wR2 = 0.0428
Largest diff. peak/hole / e Å^{-3}	2.24 and -1.37

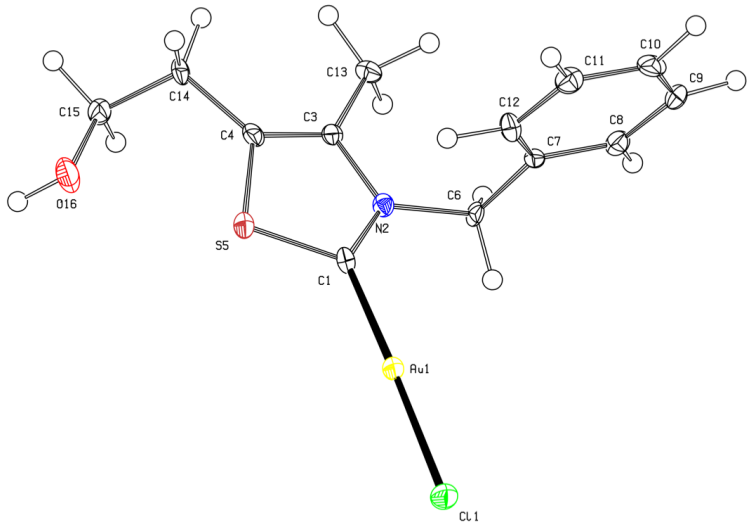

Figure S1. ORTEP representation of the molecular structure of **5** (100K, crystallized by slow diffusion of pentane in a solution of ethyl acetate). Selected bond lengths [Å] and bond angles [°]: Au1-C1 1.980(2), Au1-Cl1 2.2867(6), C1-Au1-Cl1 178.06(6).

Table S2. Crystal data and structure refinement for **6** (CCDC 1470874).

Identification code	h040811
Empirical formula	$C_{13}H_{17}NO_7P_2S$
Formula weight	393.27
Temperature/K	100.0(2)
Crystal system	triclinic
Space group	P -1
a/Å	7.6460(6)
b/Å	8.5134(8)
c/Å	12.6646(11)
α/°	85.150(3)
β/°	83.269(3)
γ/°	87.675(3)
Volume/Å^3	815.38(12)
Z	2
ρ_{calc}g/cm^3	1.602
μ/mm^{-1}	0.432
F(000)	408
Crystal size/mm^3	0.16 x 0.12 x 0.035
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.368 to 55.114
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -16 ≤ l ≤ 16
Reflections collected	13597
Independent reflections	3718 [R(int) = 0.0262, R(sigma) = 0.0307]
Data/restraints/parameters	3718 / 2 / 284
Goodness-of-fit on F^2	1.103
Final R indexes [I>=2σ (I)]	R1 = 0.0378, wR2 = 0.0878
Final R indexes [all data]	R1 = 0.0459, wR2 = 0.0912
Largest diff. peak/hole / e Å^{-3}	0.340 and -0.45

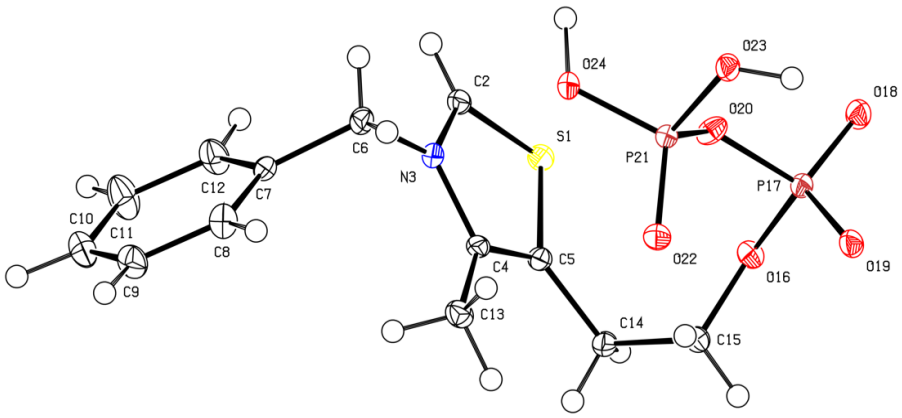

Figure S2. ORTEP representation of the molecular structure of **6** (100K, crystallized by slow diffusion of acetone in an aqueous solution).