Identification of (Phosphine)gold(I) Hydrates and Their Equilibria in Wet Solutions

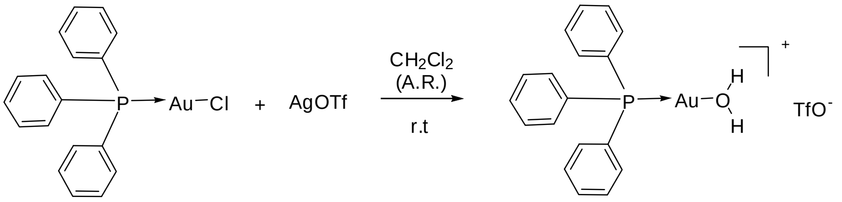
Yu Tang and Biao Yu*
State Key Laboratory of Bioorganic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China. *e-mail: byu@mail.sioc.ac.cn

Table of Contents

General Information

All experiments were carried out under ambient atmosphere unless otherwise noted. All solvents were of analytical grade and used as received. The water content in CH_2Cl_2 used was about 100 ppm. Methylene chloride-d2 (D 99.9 %) was obtained from Cambridge Isotope Laboratories and used as received. Silver trifluoromethanesulfonate (99 %) was purchased from Acros Organics (New Jersey, USA) and was used as received. Chloro(triphenylphosphine)gold(I), chloro[tri(*o*-tolyl)phosphine]gold(I), [bis(trifluoromethanesulfonyl)imidate](triphenylphosphine)gold(I) were prepared according to the literature methods.[S1-3] Commercially available 5Å molecular sieves were ground to pass through a 100 mush sieve, and then directly used without further activation. Elemental analysis was conducted on a Vario EL III elemental analyzer. The infrared spectra were recorded using KBr pellet technique in Nicolet 380 FT-IR spectrometer in the region 4000–400 cm^{-1}. ^1H, ^{13}C, and ^{31}P NMR experiments were performed on a Bruker DRX 400 instrument and were calibrated to the residual proton resonance of the solvent (CD_2Cl_2: $\delta_H = 5.32$ ppm; $\delta_C = 54.00$ ppm). ^{31}P NMR chemical shifts were reported relative to external aqueous 85% phosphoric acid ($\delta = 0.0$ ppm). ^{19}F NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer at 282.5 MHz using trifluoroacetic acid as an external standard ($\delta = -76.5$ ppm). Single crystal X-ray data were collected on either a Bruker APEX CCD diffractometer operating at 50 kV and 30 mA with Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K, or a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo Kα radiation ($\lambda = 0.71073$ Å) at 133 K.

Synthesis of complex 1a.



To a mixture of chloro(triphenylphosphine)gold(I) (300 mg, 0.606 mmol) and silver trifluoromethane sulfonate (156 mg, 0.606 mmol) was added CH_2Cl_2 (5 mL). After being stirred for 15 minutes, the mixture was filtered through a sand core funnel (G4 type with 3-4 μm cores) to remove AgCl. The filtrate was evaporated on a rotary evaporator to provide a slurry. The slurry was cooled at -20 °C overnight. Colorless needles formed gradually, which melted immediately when being warmed to room temperature. These crystals were dissolved in CH_2Cl_2 (10 mL), followed by addition of cumene (20 mL). The solution was cooled to -20 °C, *n*-hexane (40 mL) was then added dropwise. **1a** was formed as a flocculent precipitate, which was washed several times with cold *n*-hexane, and dried under reduced pressure at 0 °C (305 mg, 80 %). Colorless needle-shaped crystals of complex **1a** could also obtained by low diffusion of hexane into a CH_2Cl_2-toluene solution at 0 °C. This compound is very hygroscopic and decomposes slowly at room temperature and should thus be stored in inert atmosphere at temperatures below -10 °C. ^1H NMR (400 MHz, CD_2Cl_2, 0.2 M, 298 K) $\delta = 7.74–7.28$ (m, 15H), 4.55 (s, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2, 0.2 M, 298 K) $\delta = 134.66$ (d, $J = 13.6$ Hz), 133.24 (d, $J = 2.8$ Hz), 130.08 (d, $J = 12.4$ Hz), 127.54 (d, $J = 68.0$ Hz), 120.81 (q, $J = 318.7$ Hz); ^{31}P NMR (162 MHz,

CD_2Cl_2, 0.200 M, 298 K) δ = 28.20 (s); ^{19}F NMR (282 MHz, CD_2Cl_2, 0.2 M, 298 K) δ = -76.60 (s); IR (KBr, cm^{-1}) 3431, 3050, 1617, 1481, 1437, 1291, 1234, 1168, 1102, 1028, 997, 752, 721, 692, 637, 550, 508; Anal. calcd. for $C_{19}H_{17}AuF_3O_4PS$ (626.02) C 36.43, H 2.74, found C 36.83, H 3.22.

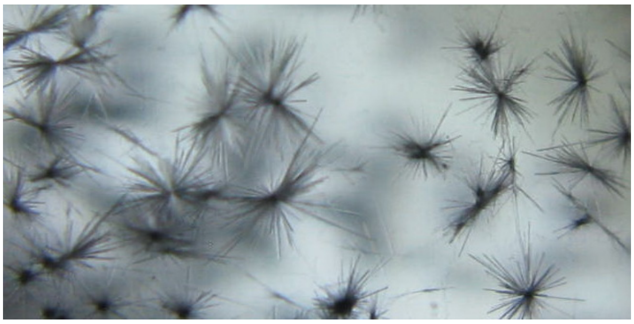


Figure S1. Crystals of **1a**

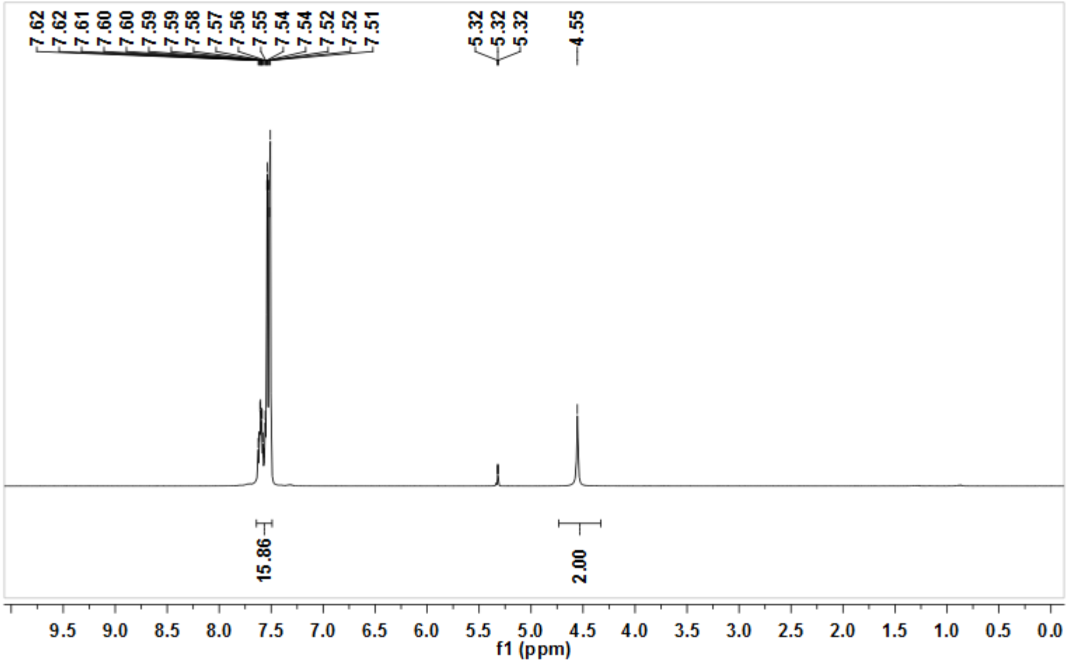


Figure S2. ^1H NMR spectrum of **1a** (400 MHz, CD_2Cl_2, 0.2 M, 298 K)

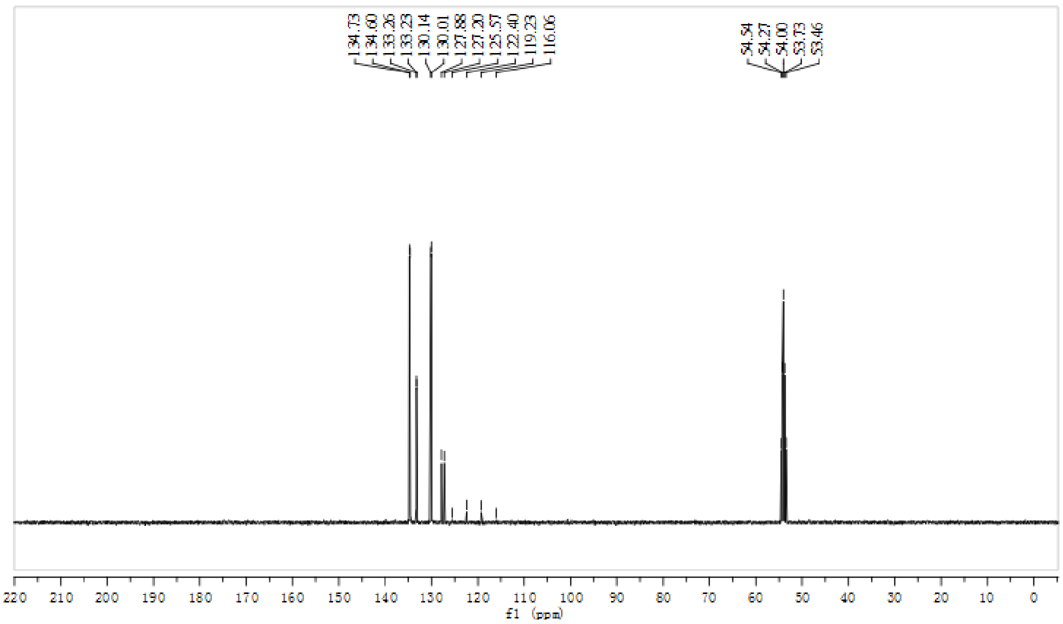
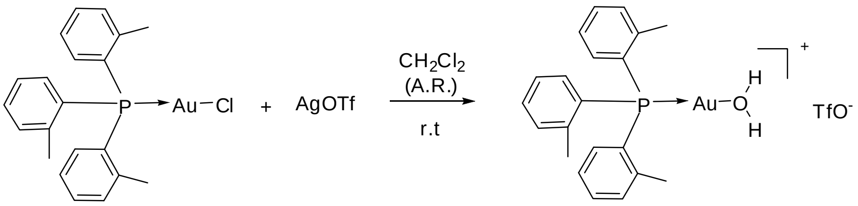


Figure S3. ^{13}C NMR spectrum of **1a** (101 MHz, CD_2Cl_2, 0.2 M, 298 K)

Synthesis of complex 1b



Silver trifluoromethanesulfonate (58 mg, 0.224 mmol) was added to a solution of chloro [tri(*o*-tolyl)phosphine]gold(I) (120 mg, 0.224 mmol) in wet CH_2Cl_2 (10 mL). The mixture was stirred for 15 minutes then filtered through a sand core funnel (G4 type with 3-4 μm cores) to remove AgCl. Evaporation of the solvent led to complex **1b** as a white powder (141 mg, 95 %). Single crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a CH_2Cl_2-toluene solution of complex **1b** at room temperature. This compound was quite stable at room temperature but quickly decomposes when heated to over 100 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 0.040 M, 298 K) $\delta = 7.55$ (t, $J = 7.5$ Hz, 3H), 7.48–7.39 (m, 3H), 7.25 (t, $J = 7.6$ Hz, 3H), 6.94 (dd, $J = 14.1$, 7.6 Hz, 3H), 2.67 (s, 9H), 1.94 (s, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2, 0.040 M, 298 K) $\delta = 143.44$ (d, $J = 11.3$ Hz), 134.13 (d, $J = 10.3$ Hz), 133.28 (d, $J = 12.8$ Hz), 133.25 (s), 127.56 (d, $J = 11.3$ Hz), 123.75 (d, $J = 67.4$ Hz), 120.77 (q, $J = 318.3$ Hz), 23.44 (s); ^{31}P NMR (162 MHz, CD_2Cl_2, 0.04 M, 298 K): $\delta = -2.89$ (s); ^{19}F NMR (282 MHz, CD_2Cl_2, 0.04 M, 298 K) $\delta = -76.26$ (s); IR (KBr, cm^{-1}) 3054, 1590, 1566, 1470, 1449, 1381, 1300, 1228, 1201, 1174, 1132, 1073, 1027, 804, 762, 712, 683, 669, 636, 579, 559, 513, 475; Anal. calcd. for $C_{22}H_{23}AuF_3O_4PS$ (668.07) C 39.53, H 3.47, found C 39.45, H 3.42.

X-ray structure analysis of 1b: $C_{22}H_{23}AuF_3O_4PS$, $M_r = 668.40$ g·mol^{-1}, colorless prismatic, crystal size 0.212 x 0.145 x 0.101 mm, triclinic, space group P-1, a = 10.7896(12) Å, b = 11.7019(13) Å, c = 11.8546(14) Å, α = 107.733(2)°, β = 96.492(2)°, γ = 116.338(2)°, V = 1222.4(2) Å^3, T = 293 K, Z = 2, D_{calc} = 1.816 g·cm^3, λ = 0.71073 Å, μ(Mo-Kα) = 6.216 mm^{-1}. Empirical absorption correction (T_{min} = 0.20513, T_{max} = 1.00000), Bruker APEX CCD diffractometer, 1.88 < θ < 26.00°, 7427 measured reflections, 4790 independent reflections, 3971 reflections with I > 2σ(I). Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0557 [I > 2σ(I)], wR_2 = 0.1532, 367 parameters, H atoms riding, S = 1.190, residual electron density 2.613/-1.376 Å^{-3}.

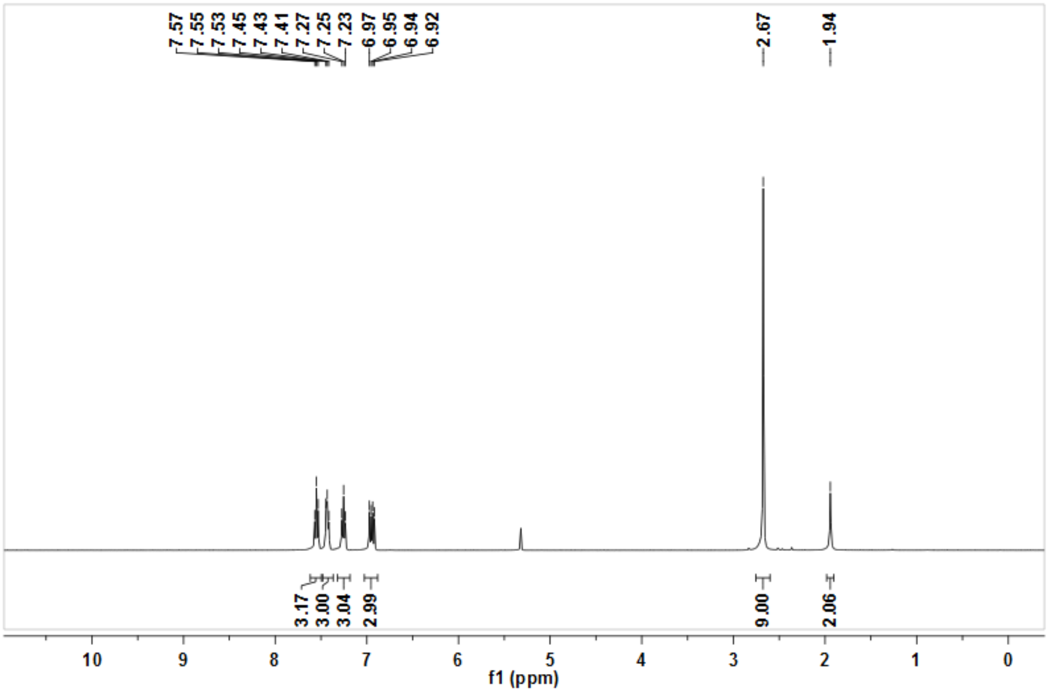


Figure S4. ^{1}H NMR spectrum of **1b** (400 MHz, CD_2Cl_2, 0.040 M, 298 K)

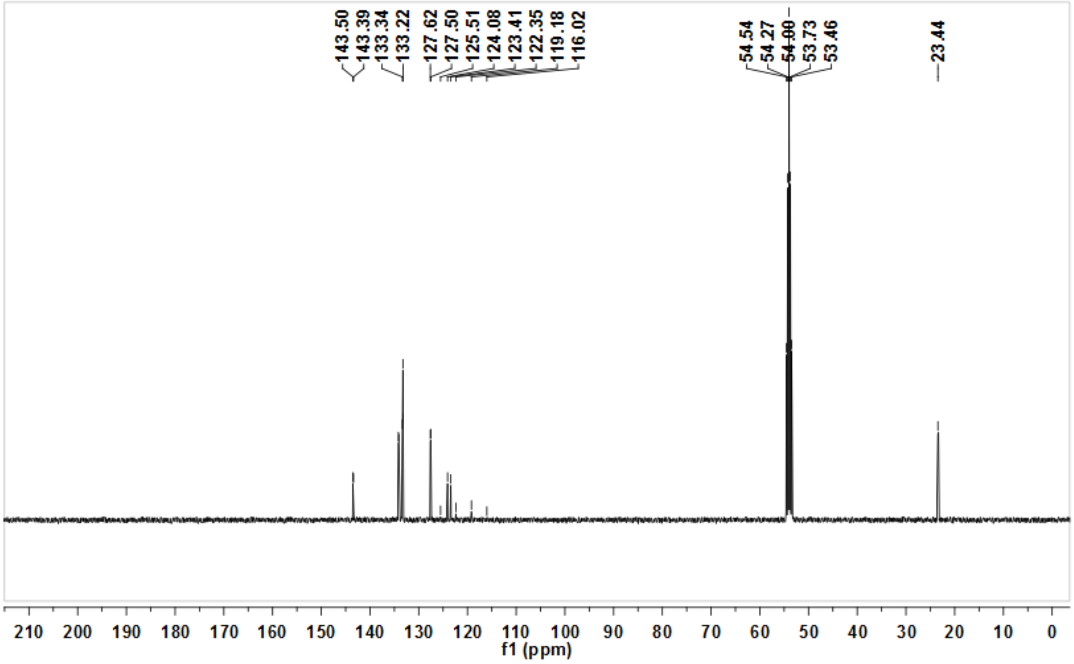
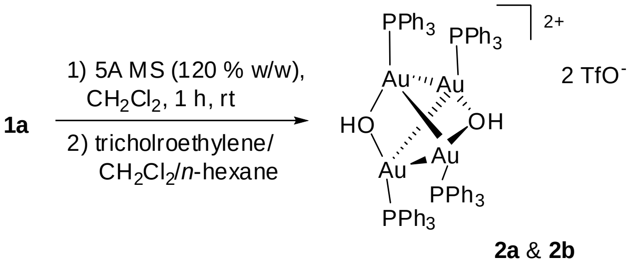


Figure S5. ^{13}C NMR spectrum of **1b** (400 MHz, CD_2Cl_2, 0.040 M, 298 K)

Synthesis of complexes 2a & 2b



To a solution of complex **1a** (60 mg, 0.121 mmol) in CH_2Cl_2 (5 mL) was added 5Å molecular sieves (90 mg, 150 % w/w). The mixture was stirred for 1 h, then filtered through a sand core funnel (G4 type with 3-4 μm cores). The filtrate was evaporated to a volume of about 2 mL, then was added trichloroethylene (5 mL). The resulting solution was slowly diffused with *n*-hexane (50 mL) at 0 °C (Fig. S6). After 1 week, colorless tetragonal dipyramid-shaped crystals of **2a** and colorless rectangular shaped crystals of **2b** were formed. These crystals were separated manually to afford pure **2a** (26 mg, 39 %) and **2b** (17 mg, 26 %).

2a: ^{1}H NMR (400 MHz, CD_2Cl_2, 0.015M, 298 K) δ = 7.60–7.53 (m, 12H), 7.52–7.44 (m, 24H), 7.42–7.34 (m, 24H), 1.69 (s, 4H, water signal); ^{13}C NMR (101 MHz, CD_2Cl_2, 0.015M, 298 K) δ = 134.53 (d, J = 13.3 Hz), 133.23 (d, J = 2.7 Hz), 130.08 (d, J = 12.2 Hz), 127.90 (d, J = 66.2 Hz) (The carbon signal of the CF_3 group was not detected); ^{31}P NMR (162 MHz, CD_2Cl_2, 0.015 M, 298 K) δ = 25.72 (s); ^{19}F NMR (282 MHz, CD_2Cl_2, 0.015 M, 298 K) δ = -77.54 (s); IR (KBr, cm^{-1}) 3425, 3226, 3071, 3053, 1480, 1436, 1291, 1241, 1218, 1165, 1101, 1023, 997, 751, 712, 692, 635, 542, 501; Anal. calcd. for $C_{74}H_{62}Au_4F_6O_8P_4S_2$ (2169.16) C 40.97, H 2.88, found C 40.72, H 3.18.

X-ray structure analysis of 2a: $C_{74}H_{60}Au_4F_6O_8P_4S_2$, M_r = 2167.09 g·mol^{-1}, colorless block, crystal size 0.20 x 0.15 x 0.10 mm. Tetragonal, space group I4(1)/a, a = 20.4779(15) Å, b = 20.4779(15) Å, c = 34.934(3) Å, α = 90°, β = 90°, γ = 90°, V = 14649.4(19) Å^3, T = 133 K, Z = 8, D_{calc} = 1.965 g·cm^3, λ = 0.71073 Å, μ(Mo-Kα) = 8.200 mm^{-1}. Semi-empirical absorption correction (T_{min} = 0.2908, T_{max} = 0.4944), Bruker APEX-II CCD diffractometer, 1.83 < θ < 30.53°, 71755 measured reflections, 11209 independent reflections, 8179 reflections with I > 2σ(I). Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0547 [I > 2σ(I)], wR_2 = 0.1713, 443 parameters, H atoms riding, S = 1.057, residual electron density 3.688/-2.117 Å^{-3}.

2b: ^{1}H NMR (400 MHz, CD_2Cl_2, 0.015M, 298K) δ = 7.61–7.53 (m, 12H), 7.52–7.44 (m, 24H), 7.39 (td, *J* = 7.9, 2.8 Hz, 24H), 1.71 (s, 4H, water signal); ^{13}C NMR (101 MHz, CD_2Cl_2, 0.015M, 298K) δ = 134.53 (d, *J* = 13.3 Hz), 133.23 (d, *J* = 2.7), 130.08 (d, *J* = 12.2 Hz), 127.81 (d, *J* = 66.3 Hz) (The carbon signal of the CF_3 group was not detected); ^{31}P NMR (162 MHz, CD_2Cl_2, 0.015 M, 298 K) δ = 25.71 (s); ^{19}F NMR (282 MHz, CD_2Cl_2, 0.015 M, 298 K) δ = -77.60 (s); IR(KBr, cm^{-1}) 3199, 3071, 3047, 1483, 1435, 1289, 1242, 1221, 1166, 1102, 1023, 997, 751, 712, 692, 635, 540, 504; Anal. calcd. for $C_{74}H_{62}Au_4F_6O_8P_4S_2$ (2169.16) C 40.97, H 2.88, found C 41.16, H 3.03.

X-ray structure analysis of 2b: $C_{74}H_{62}Au_4F_6O_8P_4S_2$, M_r = 2169.10 g·mol^{-1}, colorless block, crystal size 0.30 x 0.20 x 0.15 mm. Triclinic, space group P-1, a = 11.7057(9) Å, b = 13.5981(11) Å, c = 23.7768(19) Å, α = 81.7100(10)°, β = 82.2150(10)°, γ = 73.7290(10)°, V = 3577.1(5) Å^3, T = 133 K, Z = 2, D_{calc} = 2.014 g·cm^3, λ = 0.71073 Å, μ(Mo-Kα) = 8.396 mm^{-1}. Semi-empirical absorption correction (T_{min} = 0.1873, T_{max} = 0.3657), Bruker APEX-II CCD diffractometer, 1.82 < θ < 30.49°, 34935 measured reflections, 21437 independent reflections, 18352 reflections with I > 2σ(I). Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0313 [I > 2σ(I)], wR_2 = 0.0727, absolute structure parameter = 0.059(16), 883 parameters, H atoms riding, S = 0.948, residual electron density 3.215/-3.708 Å^{-3}.

Figure S6. Apparatus for crystallization of **2a** & **2b**

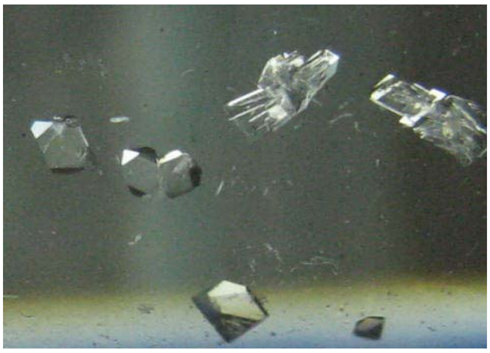


Figure S7. Crystals of **2a** (tetragonal dipyramid shaped) and **2b** (rectangular shaped)

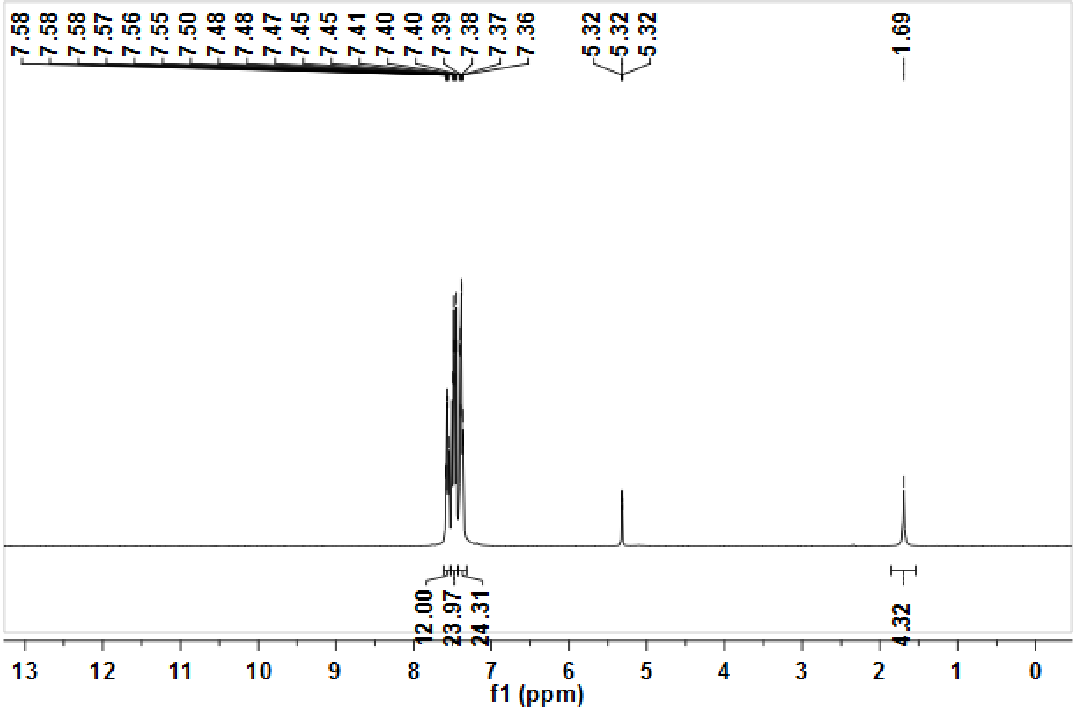


Figure S8. ^{1}H NMR spectrum of **2a** (400 MHz, CD_2Cl_2, 0.015M, 298K)

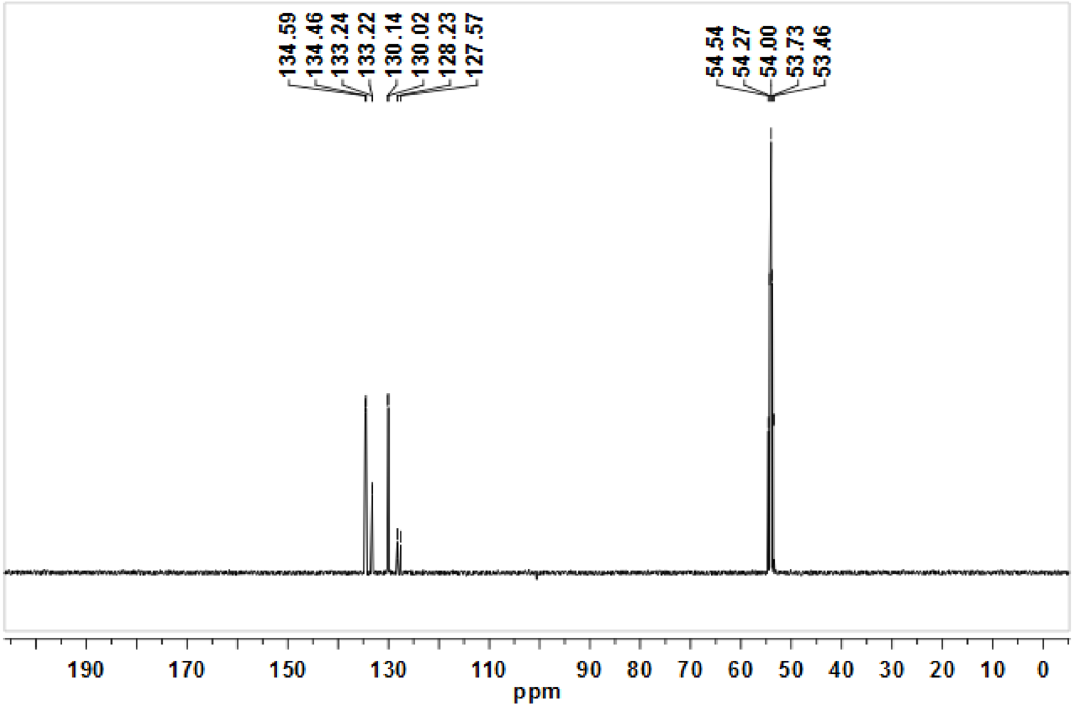


Figure S9. ^{13}C NMR spectrum of **2a** (400 MHz, CD_2Cl_2, 0.015M, 298K)

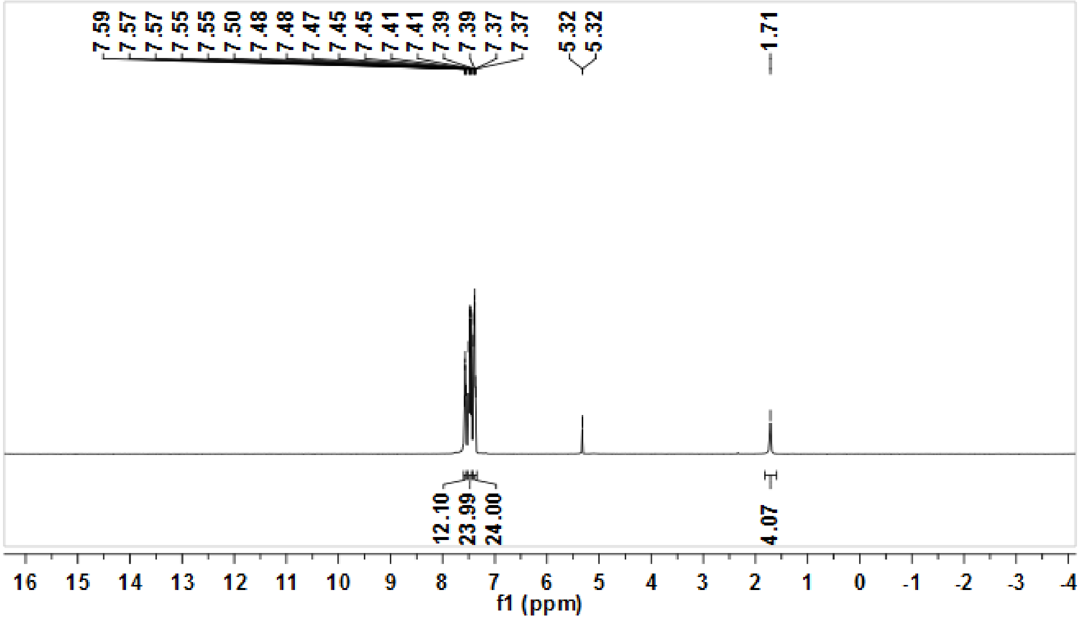


Figure S10. ^{1}H NMR spectrum of **2b** (400 MHz, CD_2Cl_2, 0.015M, 298K)

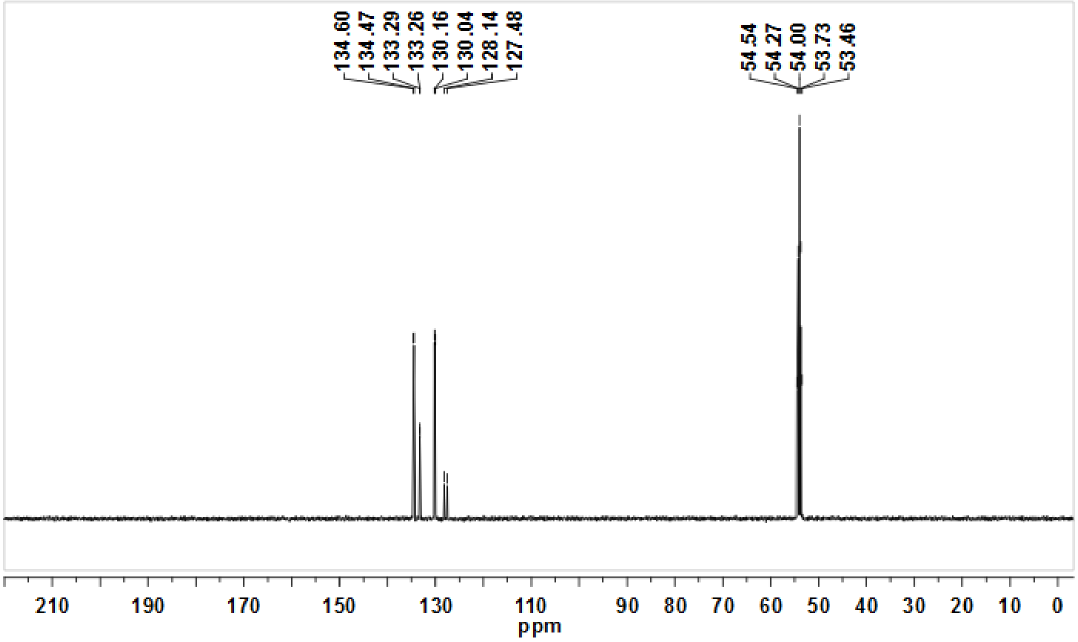
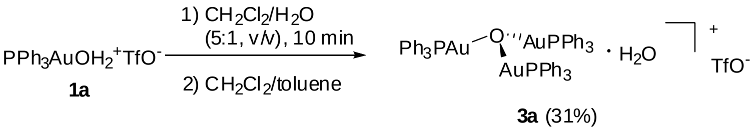


Figure S11. ^{13}C NMR spectrum of **2b** (400 MHz, CD_2Cl_2, 0.015M, 298K)

Synthesis of complex 3

A. 3a: $[(AuPPh_3)_3O^+ \cdot H_2O \cdot TfO^-]$

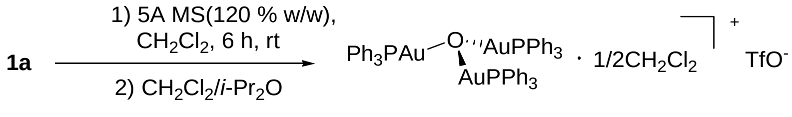


Water (0.4 mL) was added to a solution of complex **1a** (130 mg, 0.208 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred for 10 minutes, then cooled to -78 °C, and filtered through a precooled sand core funnel (G4 type with 3-4 µm cores). The ice was washed with cold CH_2Cl_2 (5 mL), and the combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. CH_2Cl_2 (15 mL) and toluene (40 mL) were successively added and the solution was slowly diffused with toluene at 0 °C. After 1 week, colorless rectangular shaped crystals of complex **3a** were formed (33 mg, 31 %). ^{1}H NMR (400 MHz, CD_2Cl_2, 0.020 M, 298 K) δ = 7.83–7.46 (m, 27H), 7.37 (ddd, J = 8.0, 5.8, 2.5 Hz, 18H), 1.67 (s, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2, 0.020 M, 273 K) δ = 134.53 (d, J = 13.4 Hz), 132.69 (d, J = 2.6 Hz), 129.84 (d, J = 11.9 Hz), 129.13 (d, J = 63.5 Hz) (The carbon signal of the CF_3 group was not detected); ^{31}P NMR (162 MHz, CD_2Cl_2, 0.020 M, 298 K) δ = 24.44 (s); ^{19}F NMR (282 MHz, CD_2Cl_2, 0.020 M, 298 K) δ = -77.75 (s); IR (KBr, cm^{-1}) 3048, 1480, 1435, 1266, 1223, 1183, 1149, 1101, 1031, 997, 755, 711, 692, 637, 544, 505, 468, 435; Anal. calcd. for $C_{74}H_{62}Au_4F_6O_8P_4S_2$ (1560.84) C 42.32, H 3.04, found C 42.80, H 3.33.

X-ray structure analysis of 3a: $C_{110}H_{94}Au_6F_6O_{10}P_6S_2$, M_r = 3121.59 g·mol^{-1}, colorless prism, crystal size 0.25 x 0.08 x 0.05 mm. Triclinic, space group P-1, a = 12.6600(13) Å, b = 14.4505(15) Å, c =

16.2267(17) Å, α = 64.226(2)°, β = 81.660(2)°, γ = 89.732(2)°, V = 2639.3(5) Å^3, T = 133 K, Z = 1, D_{calc} = 1.964 g·cm^3, λ = 0.71073 Å, μ(Mo-Kα) = 8.505 mm^{-1}. Semi-empirical absorption correction (T_{min} = 0.2249, T_{max} = 0.6757), Bruker APEX-II CCD diffractometer, 1.98 < θ < 30.56°, 26028 measured reflections, 15857 independent reflections, 12453 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0350 [$I > 2\sigma(I)$], wR_2 = 0.1007, 631 parameters, H atoms riding, S = 0.994, residual electron density 2.779/-1.461 Å^{-3}.

B. **3b:** $[(AuPPh_3)_3O^+ \cdot 0.5\ CH_2Cl_2 \cdot TfO^-]$



3b

To a solution of complex **1a** (145 mg, 0.232 mmol) in CH_2Cl_2 (5 mL) was added 5Å molecular sieves (150 mg). The mixture was stirred for 6 h, then filtered through a sand core funnel (G4 type with 3-4 μm cores). The filtrate was evaporated to a volume of about 1 mL, diisopropyl ether (5 mL) was added to form a white precipitate, which was then filtrated and dried to afford a white solid (66 mg).

The white solid (6.0 mg) was dissolved in CH_2Cl_2 (1 mL), diisopropyl ether (0.8 mL) was added. The resulting solution was slowly evaporated at room temperature. After 1 week, yellow rectangular shaped crystals of **3b** (3.6 mg, 30%) were formed.

X-ray structure analysis of 3b: $C_{111}H_{92}Au_6Cl_2F_6O_{10}P_6S_2$, M_r = 3170.48 g·mol^{-1}, colorless prism, crystal size 0.143 x 0.121 x 0.089 mm. Triclinic, space group P-1, a = 12.7852(16) Å, b = 14.6023(19) Å, c = 16.363(2) Å, α = 64.009(3)°, β = 81.587(3)°, γ = 88.896(3)°, V = 2712.8(6) Å^3, T = 293 K, Z = 1, D_{calc} = 1.941 g·cm^3, λ = 0.71073 Å, μ(Mo-Kα) = 8.323 mm^{-1}. Empirical absorption correction (T_{min} = 0.316, T_{max} = 0.477), Bruker SMART APEX CCD diffractometer, 1.57 < θ < 26.00°, 16529 measured reflections, 10625 independent reflections, 8076 reflections with $I > 2\sigma(I)$. Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0403 [$I > 2\sigma(I)$], wR_2 = 0.1068, 623 parameters, H atoms riding, S = 0.978, residual electron density 1.512/-0.747 Å^{-3}.

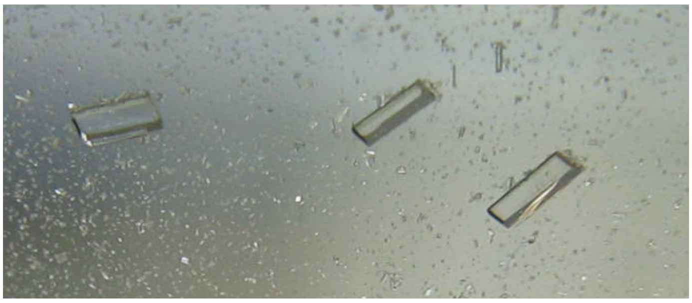


Figure S12. Crystals of **3a**

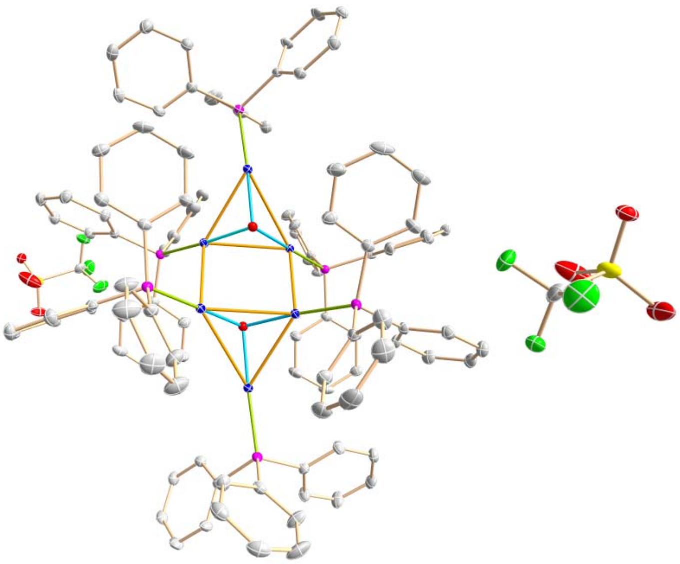


Figure S13. ORTEP plot (30% probability) of the crystal structure of **3a** (H atoms and co-crystallized solvent omitted for clarity).

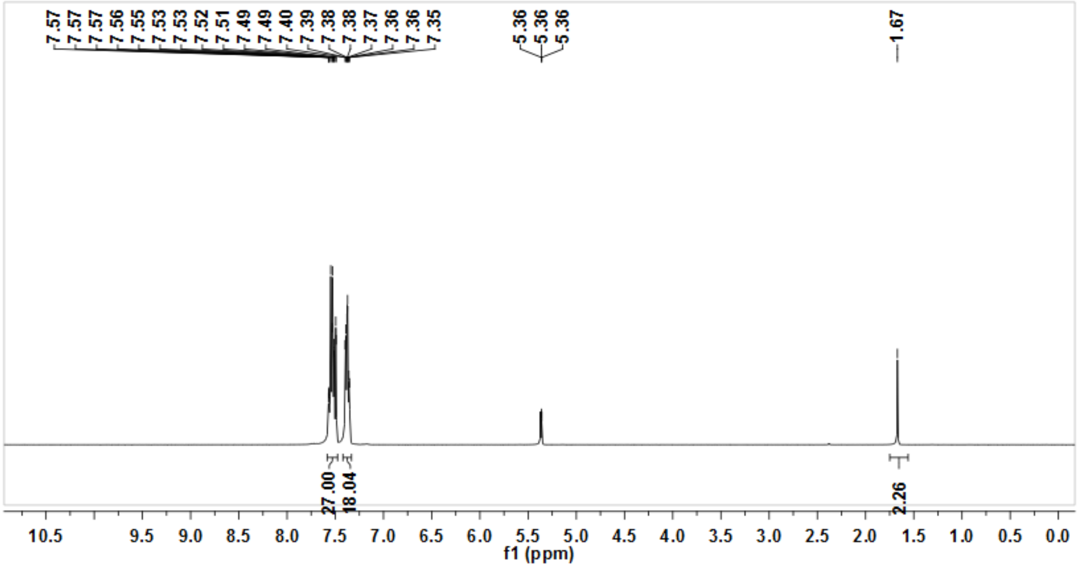


Figure S14. ^{1}H NMR spectrum of **3a** (400 MHz, CD_2Cl_2, 0.020 M, 298 K)

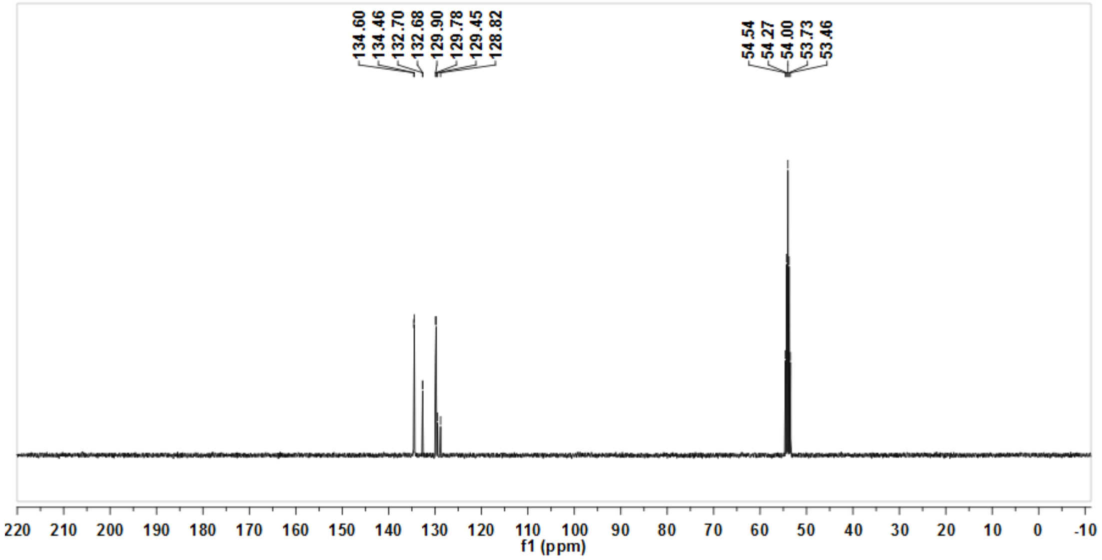


Figure S15. ^{13}C NMR spectrum of **3a** (400 MHz, CD_2Cl_2, 0.020 M, 298 K)

The analytical data of **3b** are identical to those of **3a**.

NMR analysis

a. NMR spectra of the gold(I) oxo species.

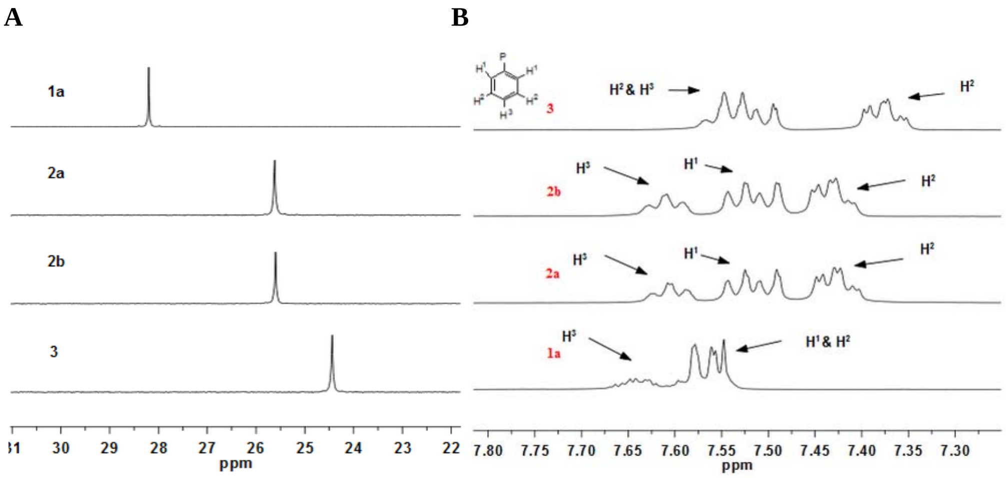


Figure S16. NMR spectra of the gold(I) oxo species. (A) ^{31}P NMR spectra of **1a**, **2a**, **2b** and **3** (162 MHz, CD_2Cl_2, 298 K). (B) The aromatic region of the ^{1}H NMR spectra of **1a**, **2a**, **2b** and **3** (400 MHz, CD_2Cl_2, 298 K).

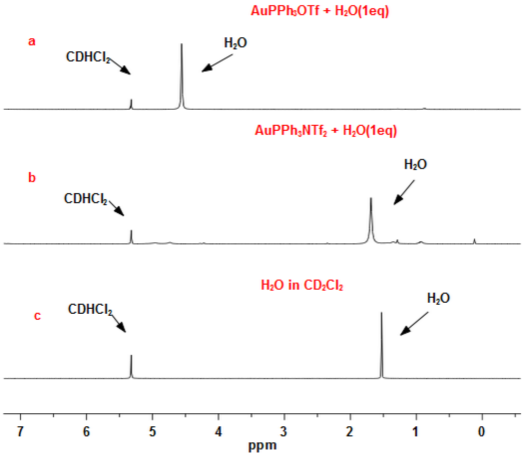


Figure S17. High field region of the ^{1}H NMR spectra of (a) AuPPh$_3$OTf (100 µM in 0.50 mL CD$_2$Cl$_2$ containing 1.0 eq water), (b) AuPPh$_3$NTf$_2$ (100 µM in 0.50 mL CD$_2$Cl$_2$ containing 1.0 eq water), and (c) water in CD$_2$Cl$_2$.

b. The reaction of Ph$_3$PAuOTf with water

To a mixture of chloro(triphenylphosphine)gold(I) (53 mg, 0.107 mmol) and silver trifluoromethane -sulfonate (28 mg, 0.107 mmol) in a dry NMR tube under argon atmosphere was added anhydrous CD$_2$Cl$_2$ (1.05 mL). The mixture was vigorously shaken for 15 minutes, then stayed in dark for 15 minutes. The solution turned clear, and the supernatant (0.50 mL) was transferred carefully to another dry NMR tube under argon atmosphere. Water was gradually added to the solution, followed by vigorously shaken for 5 minutes, and ^{31}P and ^{1}H NMR spectra were then recorded.

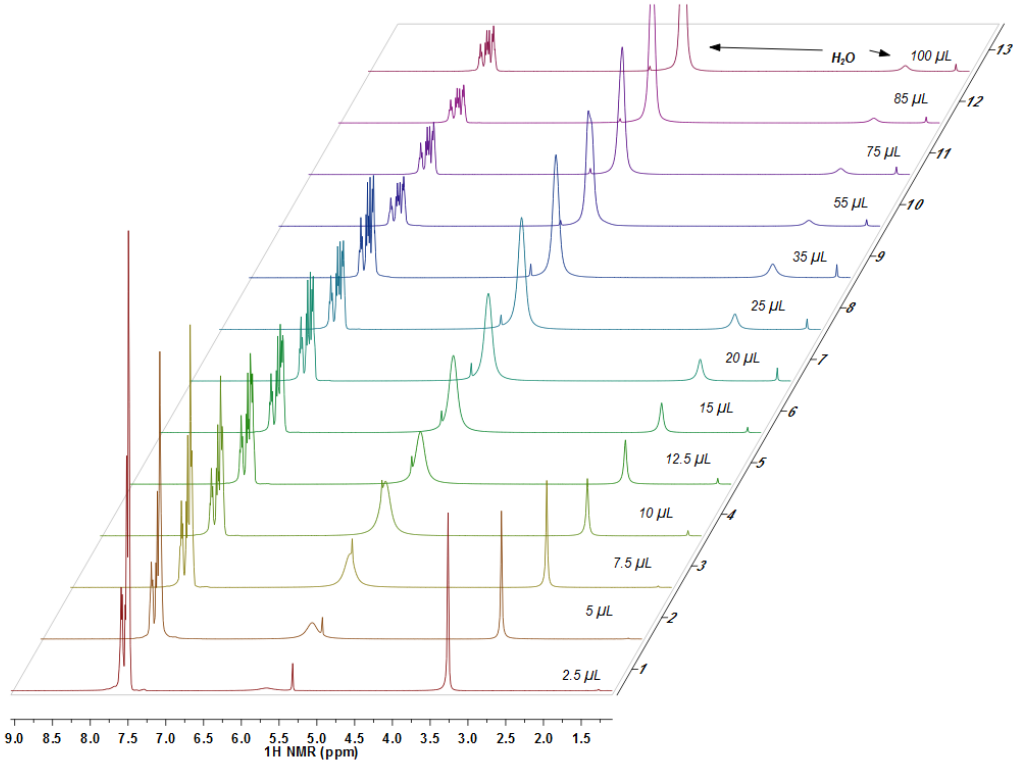


Figure S18. ^{1}H NMR spectra of the resulting gold(I) oxo species against the gradually increased volume of water in CD_2Cl_2 at rt.

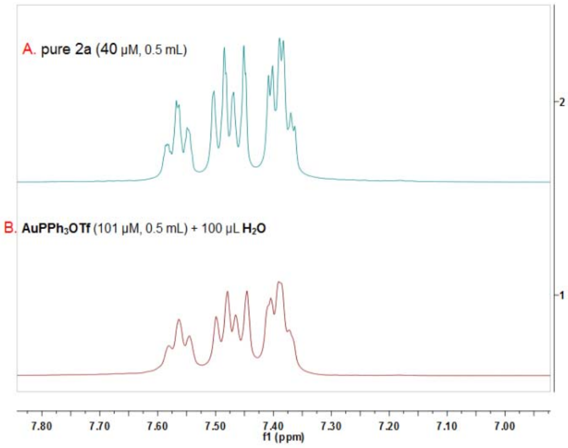


Figure S19. Aromatic region of the ^{1}H NMR (400 MHz) spectra of (A) pure **2a** and (B) the resulting gold(I) oxo species after 100 µL of water was added.

a. The reaction of $Ph_3PAuNTf_2$ with water

To a dry NMR tube under argon atmosphere was added $Ph_3PAuNTf_2$ (21.0 mg, 28.4 mmol) and anhydrous CD_2Cl_2 (0.50 mL). Water was gradually added to the solution, followed by vigorously shaken for 5 minutes, and ^{31}P and ^{1}H NMR spectra were then recorded.

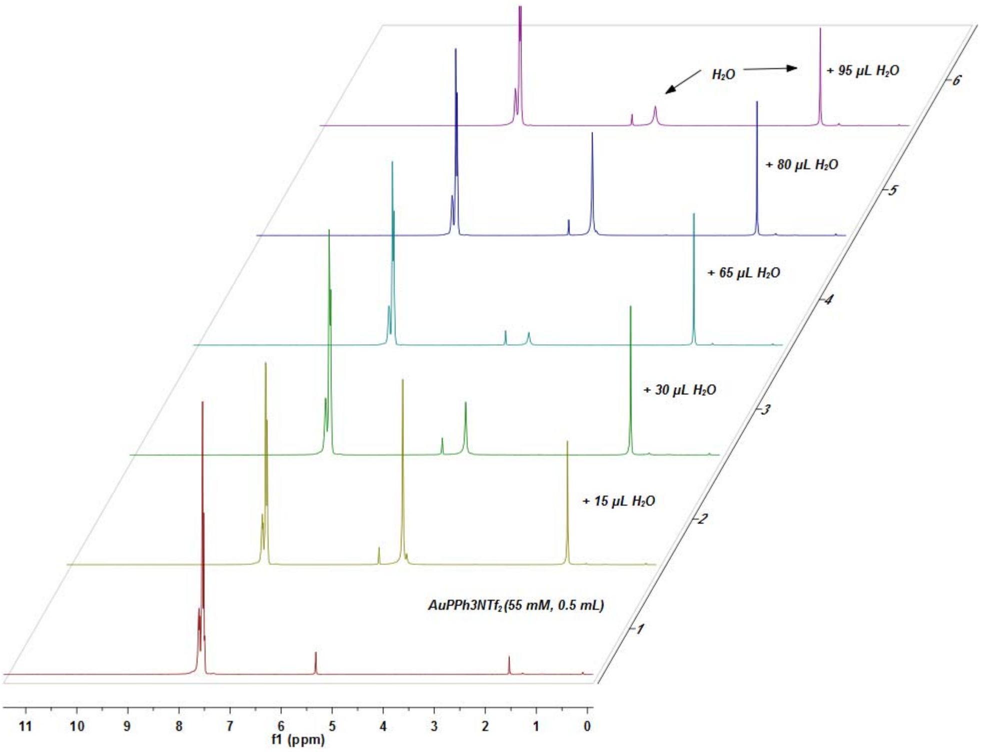


Figure S20. ^{1}H NMR spectra of $Ph_3PAuNTf_2$ in CD_2Cl_2 (55 µM) against the gradually increased volume of water at rt.

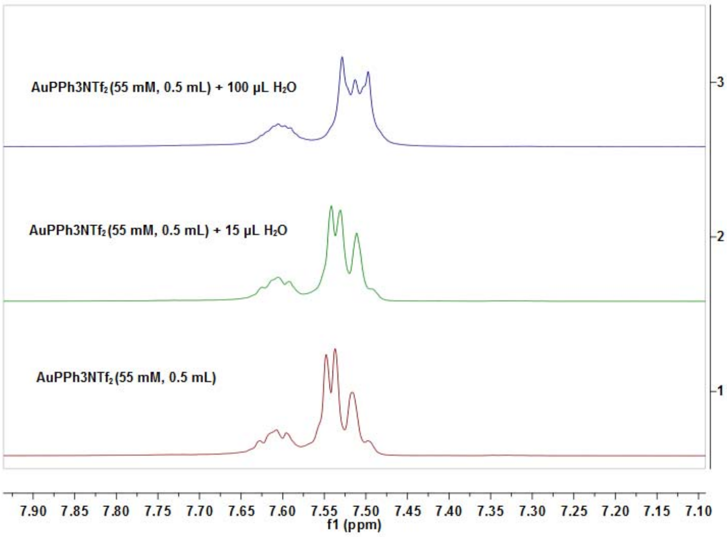


Figure S21. Aromatic region of the ^{1}H NMR (400 MHz) spectra of $Ph_3PAuNTf_2$ in CD_2Cl_2 after addition of water.

b. ^{31}P NMR spectra of gold oxo complexes after addition of molecular sieves

To a mixture of chloro(triphenylphosphine)gold(I) (55 mg, 0.111 mmol) and silver trifluoromethane -sulfonate (29 mg, 0.111 mmol) was added CH_2Cl_2 (5 mL A.R grade). After stirring for 15 minutes, the mixture was filtered through a sand core funnel (G4 type with 3-4 μm cores) to remove AgCl. The filtrate was evaporated on a rotary evaporator to a volume of about 3 mL. 5Å molecular sieves (90 mg) was added and the mixture was vigorously stirred. After a period of time, a small amount of the solution (~ 0.2 mL) was transferred to a clean tube, diluted with CH_2Cl_2, and filtered through a sand core funnel (G4 type with 3-4 μm cores). The filtrate was concentrated in vacuo, and ^{31}P NMR spectrum was recorded.

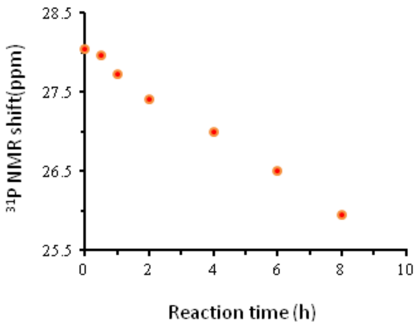


Figure S22. ^{31}P NMR chemical shift of the gold(I) oxo species after addition of molecular sieves.

Titration experiment

General procedure. To a solution of complex **1a** in CH_2Cl_2 (101 μM) was added water ($v_{H_2O}/v_{CH_2Cl_2} = 1/5$). The mixture was stirred for 10 minutes, then cooled to -78 °C, and filtered through a precooled sand core funnel (G4 type with 3-4 μm cores). The ice was washed with CH_2Cl_2 (5 mL). The filtrate was warmed to room temperature. The acid in the aqueous solution was titrated with standard NaOH solution (0.1 M) using cresol red as pH indictor.

$$4\ [(Ph_3PAu)OH_2]^+ \rightarrow \{[(Ph_3PAu)_2OH]_2\}^+ + 2\ H_3O^+$$

Entry	**1a** (μmol)	**V**$_{\text{water}}$ (mL)	**H$_3$O$^+$** (μmol)	**H$_3$O$^+$** (μmol)
			calculated	**found**
1	89.9	0.180	45.0	47.0
2	208	0.400	104	106

Table S1. Results of the titration experiment

Crystallization experiment

The crystallization experiments were performed under ambient atmosphere using different methods described below. Each experiment was independently repeated at least 3 times. The crystals obtained were manually separated and determined by either single-crystal X-ray crystallography or ^{31}P and ^{1}H NMR measurement.

1. Sample preparation

Sample A: To a mixture of chloro(triphenylphosphine) gold(I) (50.0 mg, 0.100 mmol) and silver trifluoromethanesulfonate (26.0 mg, 0.100 mmol) was added CH_2Cl_2 (5 mL). After stirring for 15 minutes, the mixture was filtered through a sand core funnel (G4 type with 3-4 μm cores) to remove AgCl. The solvent was slowly evaporated under reduced pressure to form sample **A** as a slurry, which was directly used for crystallization.

Sample B: To a solution of complex **1a** in CH_2Cl_2 (100 μM, 2 mL) was added water (0.5 mL). The mixture was stirred for 10 minutes, then cooled to -78 °C, and filtered through a precooled sand core funnel (G4 type with 3-4 μm cores). The ice was washed with cold CH_2Cl_2 (5 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo to afford sample **B** as a gelatinous solid.

Sample C: To a solution of complex **1a** in CH_2Cl_2 (50 μM, 2 mL) was added 5Å molecular sieves (75 mg, 150 % w/w). The mixture was stirred for 1 h, then filtered through a sand core funnel (G4 type with 3-4 μm cores). The filtrate was evaporated under reduced pressure to afford sample **C** as a white foam.

Sample D: To a solution of complex **1a** in CH_2Cl_2 (50 μM, 2 mL) was added 5Å molecular sieves (75 mg, 150 % w/w). The mixture was stirred for 6 h, then filtered through a sand core funnel (G4 type with 3-4 μm cores). The filtrate was evaporated under reduced pressure to afford sample **D** as a white solid.

Sample E: To a solution of complex **1a** in CH_2Cl_2 (50 μM, 2 mL) was added 5Å molecular sieves (75 mg, 150 % w/w). The mixture was stirred for 6 h, then filtered through a sand core funnel (G4 type with 3-4 μm cores). The filtrate was evaporated to a volume of about 1 mL, diisopropyl ether (5 mL) was added to form a white precipitate, which was then filtrated and dried to afford sample **E** as a white solid.

2. Crystallization methods

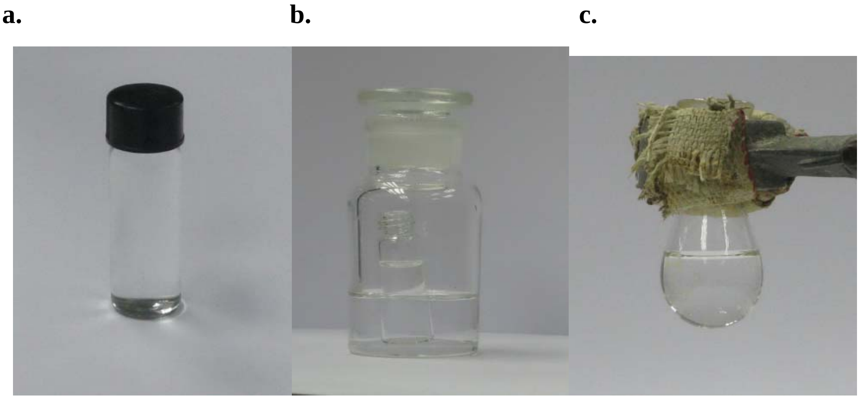


Figure S23. Apparatus for crystallization experiments: (a) for methods **A** and **D**, (b) for method **B**, and (c) for method **C**.

Method A: The sample (10 mg) was dissolved in solvent I (1.0 mL, red in Table S2) and transferred into a 5 mL sample bottle, then carefully layered with solvent II (4.0 mL, blue in Table S2) and sealed with a screw cap (Fig. S21). The solution was allowed to stand for several days.

Method B: To a 5 mL sample bottle was added the sample (10 mg) and solvent I (1.5 mL, red in Table S2). The sample bottle was then transferred into a 60 mL reagent bottle containing 20 mL of Solvent II (blue in Table S2). The solution was allowed to stand for several days.

Method C: The sample (10 mg) was dissolved in solvent I (1.5 mL, red in Table S2) and transferred into a 5 mL flask. Solvent II was carefully added until the solution became saturated. Solvent I (0.3 mL) was again added to form a clear solution. The flask was allowed to stand for several days.

Method D: The sample (15 mg) was dissolved in solvent I (1.0 mL, red in Table S2) and transferred into a 5 mL sample bottle, solvent II (4.0 mL, blue in Table S2) was added and the solution was shaken for 10 s. The bottle was sealed with a screw cap and the solution was allowed to stand for several days.

Table S2. Results of the crystallization experiments

Sample	^{31}P NMR	Solvent	T (°C)	Method	Product
A	28.12	CH_2Cl_2/benzene/*n*-pentane	0	**A**	**1a**
		CH_2Cl_2/toluene/*n*-pentane	0	**A**	**1a**
		CH_2Cl_2/cumene/*n*-pentane	0	**A**	**1a**
		CH_2Cl_2/*t*-butylbenzen/*n*-pentane	0	**A**	**1a**
		CH_2Cl_2/*p*-xylene/*n*-pentane	0	**A**	**1a**
		CH_2Cl_2/mesitylene/*n*-pentane	0	**A**	**1a**
		CH_2Cl_2/toluene	0	**B**	**2a/2b**
		CH_2Cl_2/Et_2O	0	**A**	**2a/2b**
		CH_2Cl_2/*i*-Pr_2O	0	**A**	**2a/2b**
		CH_2Cl_2/cumene	-25	**D**	**2b**
		acetone/*n*-pentane	0	**B**	**2a**

		methanol/Et_2O	0	**B**	**2a/2b**
		CH_2Cl_2/*i*-Pr_2O	20	**C**	**2a/2b**
		trichloroethylene/CH_2Cl_2/*n*-hexane	0	**A**	**2a/2b**
			0	**B**	**2a/2b**
B	26.16	CH_2Cl_2/toluene	0	**B**	**3a**
C	27.72	CH_2Cl_2/toluene/*n*-pentane	0	**A**	**2a/1a**
		CH_2Cl_2/toluene	0	**B**	**2a/2b**
		CH_2Cl_2/*i*-Pr_2O	0	**A**	**2a/2b**
		CH_2Cl_2/*i*-Pr_2O	20	**B**	**2a/2b**
		trichloroethylene/CH_2Cl_2/*n*-hexane	0	**A**	**2a/2b**
			0	**B**	**2a/2b**
D	26.51	CH_2Cl_2/toluene	0	**B**	**2a/2b**
		CH_2Cl_2/*i*-Pr_2O	0	**A**	**2a/2b**
		trichloroethylene/CH_2Cl_2/*n*-hexane	0	**B**	**2a/2b**
E	25.60	CH_2Cl_2/toluene	20	**C**	**3b**
		CH_2Cl_2/toluene	0	**B**	**3b**
		CH_2Cl_2/*i*-Pr_2O	20	**C**	**3b**

References:

S1. Al-Sa'Ady, A. K.; Mcauliffe, C. A.; Parish, R. V.; Sandbank, J. A.; Potts, R. A.; Schneider, W. F. *Inorg. Synth.* **1985**, *23*, 191.

S2. Yang, Y.; Ramamoorthy, V.; Sharp, P. R. *Inorg. Chem.* **1993**, *32,* 1946.

S3. Mezailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133.