Supporting Information

" σ - π -diauration as an alternative binding mode for digold intermediates in gold(I) catalysis"

Dieter Weber, Michel R. Gagné

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I. <u>General Information:</u>

Reactions were run under ambient conditions in air using solvents, gold chloride precursors, phosphine ligands, NBu₄Br, acetic acid, HCl (conc.), and HNTf₂ as purchased from Aldrich, Fisher Scientific, or Strem. NMR data were acquired using a BRUKER AVANCE 600 MHz spectrometer. Spectra were referenced to TMS (0.00 ppm) using residual proton or carbon signals of the deuterated solvent. ³¹P spectra were referenced to P(OPh)₃ in CDCl₃ (-18.0 ppm) or concentrated H₃PO₃ (0 ppm) as external standards. ESI high resolution mass spectra (HRMS-ESI+) were obtained on a BRUKER APEX-QE.

II. <u>Synthesis and Characterization of Gold-Complexes:</u>

Synthesis of (o-Tol)₃PAuCl:

A 1:1 mixture of $(o-Tol)_3P$ (121 mg, 0.40 mmol) and Me₂SAuCl (119 mg, 0.40 mmol) were dissolved in dichloromethane and stirred for 4 h. The solvent was removed under reduced pressure and a white powder of $(o-Tol)_3PAuCl$ (212 mg, 0.39 mmol) was isolated in a quantitative yield (> 95%).

¹H-NMR (CD₂Cl₂, 600 MHz, δ in ppm): 7.50 (t, $J_{HH} = 7.8$ Hz, 1H), 7.40 (apparent t, $J_{PH} = 7.2$ Hz, $J_{HH} = 7.2$ Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.12 (dd, $J_{PH} = 13.2$ Hz, $J_{HH} = 7.8$ Hz, 1H), 2.68 (s, 3H). ¹³C {¹H} (CD₂Cl₂, 150 MHz, δ in ppm): 143.5 (d, $J_{PC} = 12.0$ Hz), 134.1 (d, $J_{PC} = 9.0$ Hz), 132.9 (d, $J_{PC} = 9.0$ Hz), 132.5 (s), 127.2 (d, $J_{PC} = 10.5$ Hz), 125.7 (d, $J_{PC} = 60.0$ Hz), 23.5 (d, $J_{PC} = 10.5$ Hz). ³¹P {¹H} (CD₂Cl₂, 242 MHz, δ in ppm): 8.2 (s). Coupling constants were assigned using ¹H {³¹P}. The synthesis of this gold complex was reported earlier.¹

Synthesis of (o-Tol)₃PAuNTf₂ (4b):

A 1:1 mixture of $(o\text{-Tol})_3$ PAuCl (326 mg, 0.61 mmol) and AgNTf₂ (236 mg, 0.61 mmol) were dissolved in 20 mL of dichloromethane and stirred for 1 h. The reaction mixture was filtered through a plug of celite The solvent was removed under reduced pressure and a white powder of $(o\text{-Tol})_3$ PAuNTf₂ was isolated in a quantitative yield (> 95%, 466 mg, 0.60 mmol).²

¹H-NMR (CD₂Cl₂, 600 MHz, δ in ppm): 7.55 (t, J = 7.8 Hz, 1H), 7.44 (apparent t, $J_{HH} = 7.8$ Hz, $J_{PH} = 6.6$ Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 6.92 (dd, $J_{PH} = 13.8$ Hz, $J_{HH} = 7.8$ Hz, 1H), 2.67 (s, 3H). ¹³C {¹H} (CD₂Cl₂, 150 MHz, δ in ppm): 143.5 (d, $J_{PC} = 10.5$ Hz), 134.1 (d, $J_{PC} = 9.0$ Hz), 133.2 (d, $J_{PC} = 3.0$ Hz), 133.1 (m), 127.5 (d, $J_{PC} = 10.5$ Hz), 124.0 (d, $J_{PC} = 64.5$ Hz), 120.0 (q, $J_{FC} = 321.0$ Hz), 23.0 (d, $J_{PC} = 12.0$ Hz). ³¹P {¹H} (CD₂Cl₂, 242 MHz, δ in ppm): -0.7 (s). HRMS-ESI+: m/z 501.1041 calculated for [M–NTf₂]⁺, found m/z 501.1034. Coupling constants were assigned using ¹H {³¹P}.

Trapping of σ - π -diaurated vinyl intermediate **6**:

Method 1: In a 20 dram vial was suspended 88 mg of $(o\text{-Tol})_3$ PAuNTf₂ (**4b**, 0.11 mmol) and 122 mg of polymer bound 2,6-di-*tert*-butyl pyridine (0.22 mmol, Aldrich 1.8 mmol/g) in 5 mL dichloromethane. A solution of 19 mg of **1** (0.056 mmol) in 5 mL dichloromethane was added and stirred for 24 h. The suspension was filtered through a plug of glass wool. The solvent was removed *in vacuo* to obtain an enriched sample of **6**. Minor impurities of **2** (< 10 % based on integration of proton signals) were detected by ¹H NMR. (*o*-Tol)₃PAuNTf₂ and {(*o*-Tol)₃P}₂AuNTf₂ (< 25 % based on integration of phosphorous signals) were additionally detected as impurities.

Method 2: In an NMR tube 3.5 mg of **1** (0.01 mmol) was dissolved in 0.5 mL CD_2Cl_2 and 5.3 mg of 2,6di-*tert*-butyl pyridine (DTBP, 0.028 mmol) were added. After adding 1.6 mg of (*o*-Tol)₃PAuNTf₂ (**4b**, 0.002 mmol, 0.2 equiv) the reaction was monitored by ¹H and ³¹P NMR, which indicated full conversion **4b** to **6** within 13 h. Then, a second portion of **4b** (11.2 mg, 0.014 mmol, to increase the total of **4b** to 1.6 equiv) was added, which again took 13 h to fully convert **4b** to **6**. NMR data obtained from these experiments were significantly cleaner and showed less by-products than samples from method 1, however DTBP and DTBP•HNTf₂ could not be separated. See Figure S1 for sections of the corresponding ¹H and ³¹P NMR spectra.

Single crystals of **6** suitable for X-ray analysis (see also section V): In a 20 dram vial 10 mg of an enriched sample of **6** was dissolved with a minimum quantity of dichloromethane. This solution was layered with pentane and slowly evaporated for 2-3 weeks. Single crystals of **6** and $\{(o-Tol)_3P\}_2AuNTf_2$ were obtained. The third crystal mounted gave a data set for the structure of **6**. The first two crystals revealed the structure of $\{(o-Tol)_3P\}_2AuNTf_2$.



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NMR data of a sample obtained through method 1. These samples were used in the reactivity studies mentioned in section IV: ¹H (CD₂Cl₂, 600 MHz, δ in ppm): 7.57-6.81 (m, 24H, *o*-Tol; integration was always >24H because of other ligated gold species as impurities), 6.16 (d, ⁴J_{HH} = 2.4 Hz, 1H, H^{8/10}), 6.14 (apparent q, $J_{PH} = 3.0$ Hz, $J_{PH} = 3.0$ Hz, ² $J_{HH} = 3.0$ Hz, ¹H, H¹_{syn}), 6.11 (d, J = 2.4 Hz, 1H, H^{8/10}), 5.81 (dd, ⁴ $J_{PH} = 9.6$ Hz, ² $J_{HH} = 3.0$ Hz, 1H, H¹_{anti}), 4.21 (apparent q, $J_{PH} = 7.8$ Hz, ³ $J_{HH} = 7.8$ Hz (with both H⁴), 1H, H³), 3.68 (s, 3H, OMe), 3.52 (s, 3H, OMe), 3.50 (s, 3H, OMe), 3.49 (s, 3H, OMe), 3.05 (dd, J = 15.6 Hz, J = 2.4 Hz, 1H, H⁶), 2.92 (d, J = 15.6 Hz, 1H, H⁶), 2.81 (ddd, J = 11.4 Hz, J = 8.4 Hz, J = 3.0 Hz, 1H, H⁴, 2.45 (dd, J = 13.2 Hz, J = 8.4 Hz, 1H, H⁴), 2.40 (s, 9H, *o*-Tol), 2.23 (s, 9H, *o*-Tol). ³¹P {¹H} (CD₂Cl₂, 242 MHz, δ in ppm): 22.6 (s), 16.1 (s). HRMS-ESI+: m/z 1335.3425 calculated for [M–NTf₂]⁺, found m/z 1335.3450. ¹H signals and coupling constants were assigned using ¹H {³¹P}, COSY, and NOESY experiments. ¹³C data was not conclusive due to the presence of multiple (*o*-Tol)₃PAu-species.

III. <u>Catalytic Experiments:</u>

Monitoring the reaction of **1** with 10 mol% of **4b**:

In an NMR tube 42 mg of **1** (0.126 mmol) was dissolved in 0.65 mL CD_2Cl_2 . To this solution was added 9.3 mg of **4b** (0.012 mmol) as a solid. The reaction was followed by ³¹P NMR. Broad signals corresponding to **4b** and intermediate **6** were detected by ³¹P NMR (see Figure 3 in the manuscript).

Monitoring the reaction of 1 with 10 mol% of other catalysts (general procedure):

In an NMR tube a sample of **1** was dissolved in CD_2Cl_2 . To this solution, 5-10 mol% of catalyst were added as a solid. The reaction was followed by ¹H and ³¹P NMR. Sharp signals in a 1:1 ratio (typically in the 36 ppm region) were detected by ³¹P NMR, which were indicative of a digold species (see Figure S2 and S3).

IV. <u>Reactivity Studies of σ - π -Diaurated Complex 6:</u>

Reaction with excess (o-Tol)₃P:

In an NMR tube 3.5 mg of an enriched sample of **6** (approx. 0.0022 mmol) was dissolved in 0.5 mL CD₂Cl₂. To this solution was added 7.4 mg of $(o\text{-Tol})_3P$ (0.024 mmol) as a solid. Immediate conversion (< 5 minutes) to gold-vinyl **3b** and { $(o\text{-Tol})_3P_2AuNTf_2$ were observed by NMR. The formation of **3b** was indicated by characteristic ¹H NMR signals that favorably compare to **3a**³: Section of ¹H NMR data (CD₂Cl₂, 600 MHz, δ in ppm): 5.42 (dd, $J_{PH} = 16.2$ Hz, $J_{HH} = 4.2$ Hz, 1H, H^1_{anti}), 5.42 (dd, $J_{PH} = 9.0$ Hz, $J_{HH} = 4.2$ Hz, 1H, H^1_{syn}), 3.84 (ddd apparent q, $J_{PH} = 8.4$ Hz, $J_{HH} = 8.4$ Hz, $J_{HH} = 8.4$ Hz, 1H, H³), 3.71 (s, OMe), 3.67 (s, OMe), 3.66 (s, OMe), 3.53 (s, OMe), 3.02 (d, $J_{HH} = 15.0$ Hz, H^6), 2.96 (dd, $J_{HH} = 15.6$ Hz, $J_{HH} = 2.4$ Hz, H^6), 2.55 (ddd, $J_{HH} = 13.8$ Hz, $J_{HH} = 8.4$ Hz, $J_{HH} = 2.4$ Hz, H^4). ³¹P {¹H} (CD₂Cl₂, 242 MHz, δ in ppm): 31.8 (s); other signals for { $(o\text{-Tol})_3P_2AuNTf_2$ [21.3 ppm (s)] and ($o\text{-Tol})_3P$ [30.5 ppm (s)] were also detected. Coupling constants were assigned using ¹H {³¹P} data.

Reaction with excess NBu₄Br:

In an NMR tube 3.3 mg of an enriched sample of **6** (approx. 0.0020 mmol) was dissolved in 0.5 mL CD_2Cl_2 . To this solution was added 4.7 mg of NBu₄Br (0.015 mmol) as a solid. Immediate conversion (< 5 minutes) to gold-vinyl **3b** and (*o*-Tol)₃PAuBr was observed by NMR. ³¹P {¹H} (CD₂Cl₂, 242 MHz, δ in ppm): 31.8 (s); a signal for (*o*-Tol)₃PAuBr [11.6 ppm (s)] was also observed.

Reaction with excess AcOH:

In an NMR tube 4.4 mg of an enriched sample of **6** (approx. 0.0027 mmol) was dissolved in 0.5 mL CD_2Cl_2 . To this solution was added 1 drop of glacial acetic acid. No conversion of **6** was observed by NMR within 30 min.

Reaction with excess HCl:

In an NMR tube 3.6 mg of an enriched sample of **6** (approx. 0.0022 mmol) was dissolved in 0.5 mL CD_2Cl_2 . To this solution was added 1 drop of conc. HCl. Instant conversion of **6** to **2** and (*o*-Tol)₃PAuCl were observed by NMR (< 5 min).

Reaction with excess HNTf₂:

In a vial 28.8 mg of $HNTf_2$ (0.10 mmol) was dissolved in 0.4 mL CD_2Cl_2 . To this solution was added 3.4 mg of an enriched sample of **6** (approx. 0.0021 mmol) dissolved in 0.4 mL CD_2Cl_2 and shaken for 10 minutes. The reaction mixture was transferred to an NMR tube and sequential ¹H NMR spectra indicated no significant conversion of **6** for another 90 minutes at RT. Monitoring this solution for reaction for an additional 11 h by ¹H NMR indicated complete consumption of **6** but no formation of **2**. Instead, decomposition of **6** to other unidentified compounds was observed.

In a control experiment, a vial was charged with 29.5 mg of HNTf₂ and dissolved in 0.4 mL CD₂Cl₂. To this solution was added 4.1 mg of the previously reported digold-vinyl 5^3 (0.0027 mmol) dissolved in 0.4 mL CD₂Cl₂. The reaction mixture was immediately transferred to an NMR tube. NMR data showed instant conversion of 5 to 2 (< 5 minutes).



V. <u>Analytic Data and Supplementary Figures:</u>



CDCC 873041 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Empirical formula	$C_{63}H_{65}Au_{2}Cl_{2}F_{6}NO_{10}P_{2}S_{2} \\$
Formula weight	1701.05
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	12.9063(2)
b/Å	14.0711(2)
c/Å	20.7385(4)

α/°	101.1780(10)	
β/°	99.8060(10)	
γ/°	113.1430(10)	
Volume/Å ³	3268.14(9)	
Ζ	2	
$\rho_{calc} mg/mm^3$	1.729	
m/mm ⁻¹	10.764	
F(000)	1676	
Crystal size/mm ³	$0.236 \times 0.208 \times 0.112$	
Theta range for data collection	4.52 to 139.78°	
Index ranges	$-15 \le h \le 15, -17 \le k \le 16, -23 \le l \le 24$	
Reflections collected	48793	
Independent reflections	11834[R(int) = 0.0322]	
Data/restraints/parameters	11834/0/803	
Goodness-of-fit on F ²	1.080	
Final R indexes [I>2 σ (I)]	$R_1 = 0.0276, wR_2 = 0.0706$	
Final R indexes [all data]	$R_1 = 0.0302, wR_2 = 0.0720$	
Largest diff. peak/hole / e Å ⁻³	1.418/-0.763.	

<u>NMR spectra of **4b**</u>: ¹H NMR:







Figure S1. ³¹P (top) and ¹H NMR (bottom) data after addition of aliquots of $(o-Tol)_3$ PAuNTf₂ to allene 1 in the presence of 2,6-di-*tert*-butyl pyridine.

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