

Electronic Supplementary Information for

**Isolation and characterization of gem-diaurated species having two
C–Au σ bonds in gold(I)-activated amidiniumation of alkyne**

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General Information:

Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. NMR spectra were recorded by using a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (^1H NMR CDCl_3 : 7.26 ppm; ^{13}C NMR CDCl_3 : 77.0 ppm; ^{13}C NMR DMSO: 39.43 ppm). Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods. X-ray diffraction analysis was performed by using a Bruker Smart-1000X-ray diffractometer.

Propiolic acid is commercially available and was used as received without further purification. Compound **1** was synthesized by the procedure we previously reported.¹

Preparation and characterization

Synthesis of complex **2b**

The mixture of **1** (50 mg, 0.12 mmol) and $\text{AuCl}\cdot\text{Me}_2\text{S}$ (35 mg, 0.12 mmol) was stirred in the DCE (1 ml) at 25 °C for 30 min. All volatiles were removed under vacuum, and the crude product was washed twice with diethyl ether to afford pure **2b** as a white solid (63 mg, 81%). ^1H NMR (400 MHz, CDCl_3) δ = 10.05 (d, J = 1.6 Hz, 1H), 8.49 (d, J = 1.6 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.42-7.35 (m, 4H), 2.75-2.71 (m, 2H), 2.64-2.60 (m, 2H), 1.42 (d, J = 6.8 Hz, 6H), 1.31 (d, J = 6.8 Hz, 6H), 1.25-1.18 (m, 18H); ^{13}C NMR (100 MHz, DMSO) δ = 173.65, 157.20, 154.16, 145.74, 137.68, 131.62, 128.30, 126.11, 124.56, 64.84, 45.02, 28.83, 24.76, 23.85, 23.48, 23.00, 22.77, 15.09; HRMS (ESI): m/z $[\text{2M}-\text{Cl}]^+$ calcd. for $\text{C}_{56}\text{H}_{72}\text{Au}_2\text{ClN}_4\text{O}_2^+$: 1261.4675; found: 1261.4663.

Synthesis of complex **2c**

The mixture of PPh_3AuCl (50 mg, 0.10 mmol) and silver triflate (26 mg, 0.10 mmol) was stirred in the DCE (1 mL) at 25 °C for 15 minutes, then the solid components were filtered off and the filtrate was added to the solution of **1** (42 mg, 0.10 mmol) in the DCE (0.5 mL). After stirring for 30 min at 25 °C, all volatiles were removed under vacuum. The crude product was washed twice with diethyl ether to afford pure **2c** as a yellow solid (77 mg, 75%). ^1H NMR

(400 MHz, CDCl₃) δ = 10.48 (d, J = 2.0 Hz, 1H), 9.28 (t, J = 2.0 Hz, 1H), 7.61-7.54 (m, 4H), 7.53-7.45 (m, 7H), 7.35-7.26 (m, 8H), 7.05-6.99 (m, 2H), 2.73-2.59 (m, 4H), 1.30-1.21 (m, 24H); ¹³C NMR (100 MHz, CDCl₃) δ = 158.09, 157.41, 145.71, 139.58, 134.09, 131.93, 131.65, 129.13, 128.48, 128.12, 125.92, 124.56, 65.80, 29.69, 29.45, 24.49, 23.98, 23.63, 15.22; ³¹P NMR (162 MHz, CDCl₃) δ = 42.30; HRMS (ESI): m/z [M-OTf]⁺ calcd. for C₄₆H₅₁AuN₂OP⁺: 875.3405; found: 875.3408.

Synthesis of digold complex **3**

The mixture of **2c** (30 mg, 0.03 mmol) and H₂O (50 μ l) was stirred in the DCM (1 ml) at 25 °C. After stirred for 2 days, a 37.5% NMR yield of digold complex **3** was observed by NMR spectroscopy. ¹H NMR (400 MHz, CDCl₃) δ = 7.49-7.27 (m, 32H), 7.26-7.16 (m, 4H), 7.04 (d, J = 5.4 Hz, 1H), 6.76 (s, 1H), 4.06 (s, 1H), 3.27-3.17 (m, 2H), 2.88-2.78 (m, 2H), 1.39-1.16 (m, 18H), 0.95-0.87 (m, 6H); ³¹P NMR (162 MHz, CDCl₃) δ = 37.60, 37.52; HRMS (ESI): m/z [M-OTf]⁺ calcd. for C₆₄H₆₇Au₂N₂O₂P₂⁺: 1351.4009; found: 1351.4247; ¹³C NMR data was not conclusive due to the presence of considerable PPh₃AuOTf and unreacted monogold complex **3**.

Acidolysis of complex **2c** in the presence of HOTf:

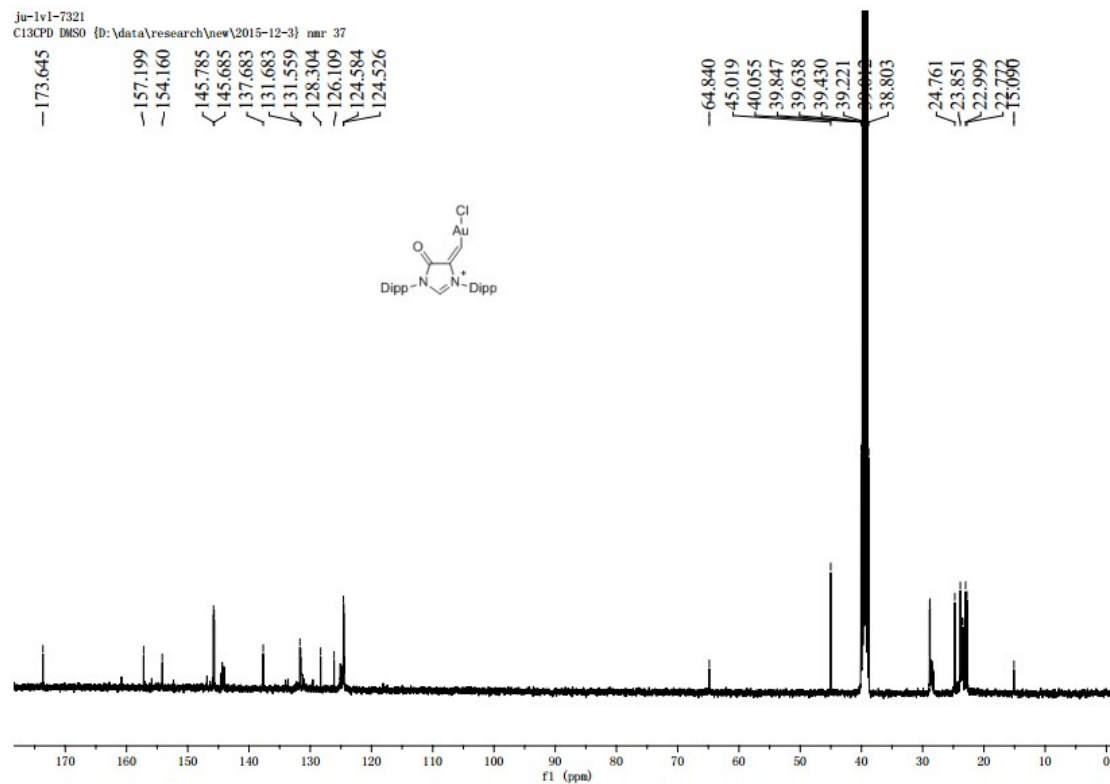
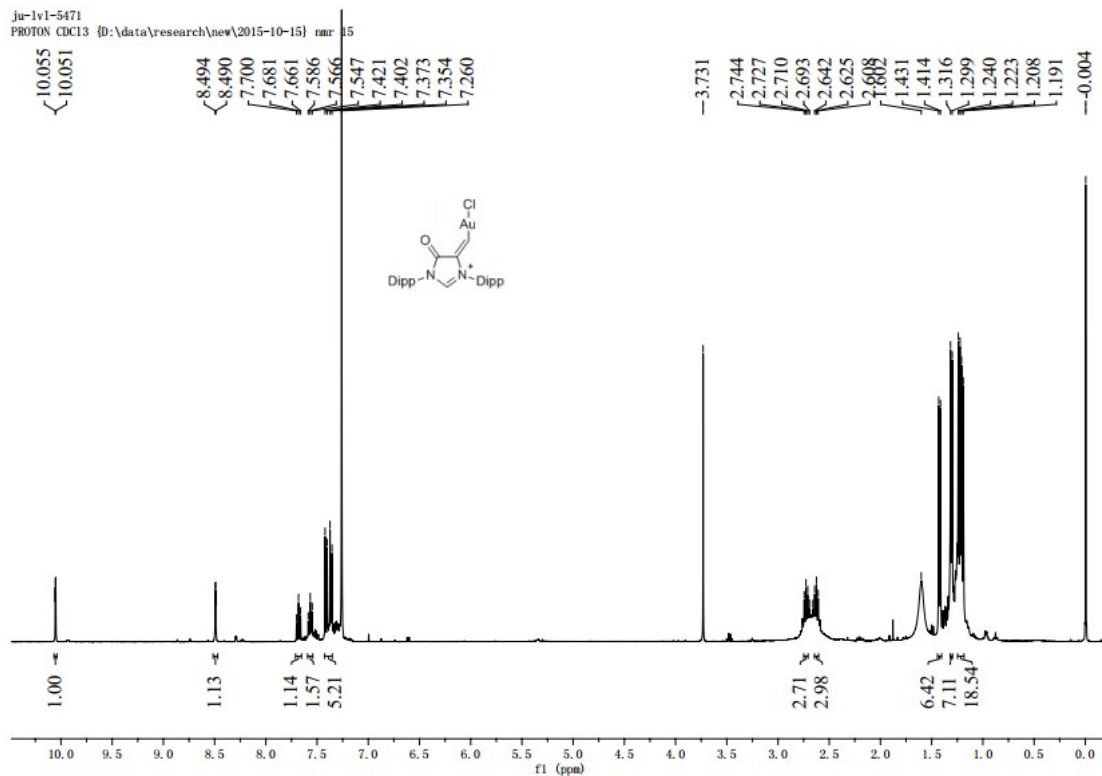
The mixture of **2c** (100 mg, 0.09 mmol) and trifluoromethanesulfonic acid (14 mg, 0.09 mmol) was stirred in the DCE (1.5 ml) at 25 °C for 3 h. All volatiles were removed under vacuum, a 35 % NMR yield of complex **4** was observed by NMR spectroscopy. The NMR analysis data of **4** are in full agreement with those reported in the literature.¹

Reference:

1. Lv, S.; Wang, J.; Zhang, C.; Xu, S.; Shi, M.; Zhang, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 14941.

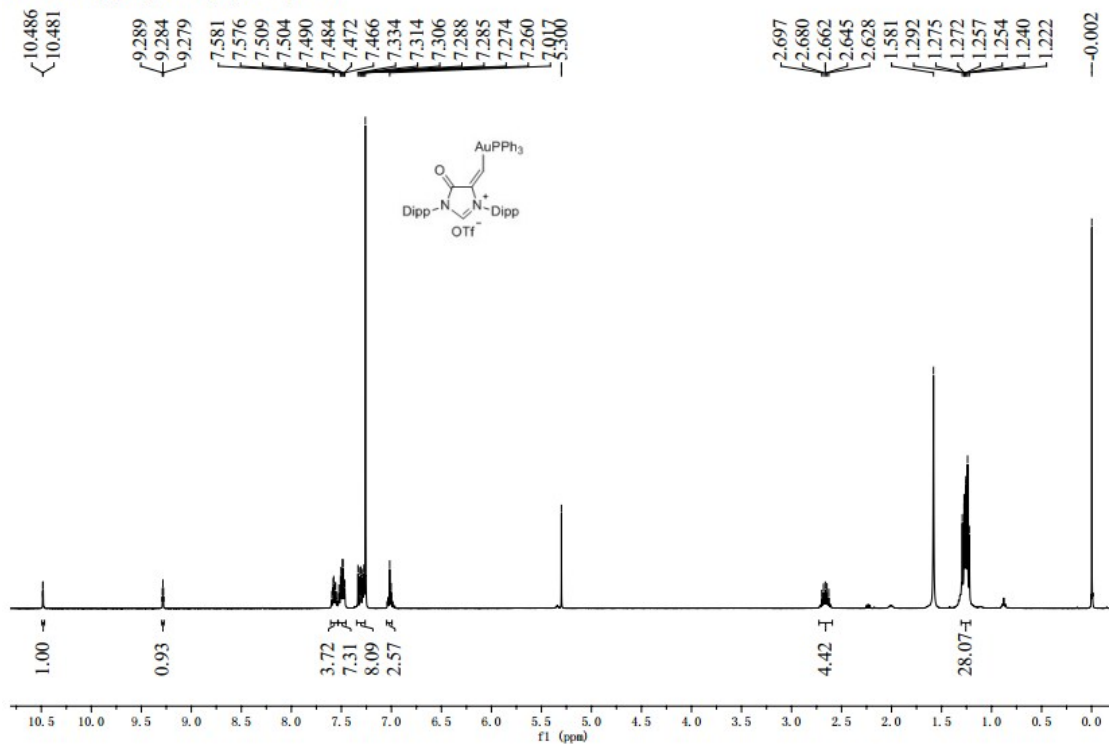
NMR Spectra:

Complex 2b

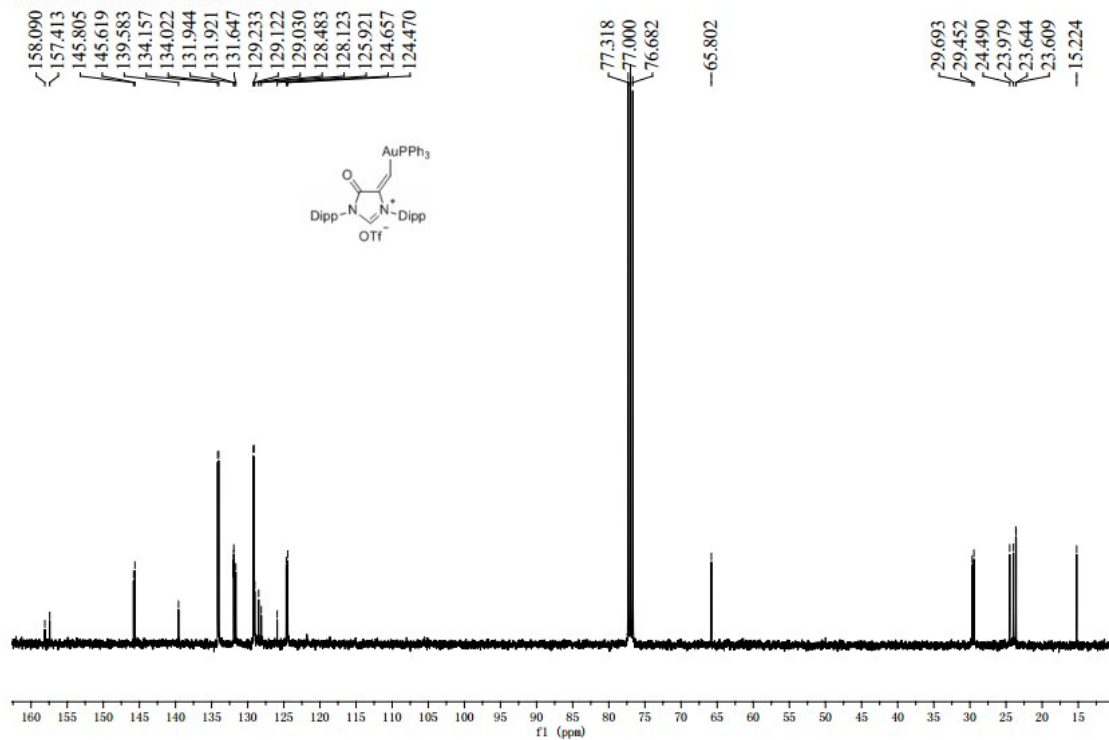


Complex 2c

ju-lvl-1338
 PROTON CDCl3 {D:\data\research\new\2015-5-6} nmr 42



ju-lvl-1335
 C13CPD CDCl3 {D:\data\research\new\2015-4-30} nmr 19



X-Ray Crystallography. Each crystal was mounted on a glass fiber. Crystallographic measurements were made on a Bruker Smart Apex 100 CCD area detector using graphite monochromated Mo-K α radiation ($\lambda_{\text{Mo-K}\alpha} = 0.71073 \text{ \AA}$). The structures were solved by direct methods (SHELXS-97) and refined on F^2 by full-matrix least squares (SHELX-97) using all unique data. All the calculations were carried out with the SHELXTL18 program.

Key details of the crystal and structure refinement data are summarized in Table S1-S2. Further crystallographic details may be found in the respective CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK [CCDC 1440087 (3)].

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

| 3 | |
|---|--|
| Identification code | mo_50521aa |
| Formula | C ₆₅ H ₆₇ Au ₂ F ₃ N ₂ O ₅ P ₂ S |
| Formula weight | 1501.14 |
| <i>T</i> , K | 203(2) |
| crystal system | Triclinic |
| space group | P -1 |
| <i>a</i> , Å | 13.7513(10) |
| <i>b</i> , Å | 16.025(2) |
| <i>c</i> , Å | 17.1415(12) |
| α , deg | 109.0540(10) |
| β , deg | 110.9850(10) |
| γ , deg | 96.8090(10) |
| Volume, Å ³ | 3212.7(5) |
| <i>Z</i> | 2 |
| <i>D</i> _{calc} , Mg / m ³ | 1.552 |
| absorption coefficient, mm ⁻¹ | 4.700 |
| F(000) | 1484 |
| crystal size, mm | 0.260 x 0.170 x 0.150 |
| 2 θ range, deg | 1.395 to 26.999 |
| reflections collected /unique | 22748/13794 [R(int) = 0.0237] |
| data / restraints/ parameters | 13794 / 60 / 729 |
| goodness of fit on F ² | 1.084 |
| final R indices [<i>I</i> > 2 σ (<i>I</i>)] ^a | R1 = 0.0388, wR2 = 0.1113 |
| R indices (all data) | R1 = 0.0540, wR2 = 0.1283 |
| lgst diff peak and hole, e/Å ³ | 1.631 and - 0.958 |