Electronic Supplementary Information for

Catalytic domino amination and oxidative coupling of gold acetylides and isolation of key vinylene digold intermediates as a new class of ditopic N-heterocyclic carbene complexes

Haifeng Chen,^a Jiwei Wang,^a Zejun Hu,^a Sheng Xu,^{*,a} Min Shi,^{a,b} and Jun Zhang^{*,a}

^a Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Mei Long Road, Shanghai 200237, China.

^b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China.

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 CDCl₃: 7.26 ppm; ¹³C NMR CDCl₃: 77.0 ppm; ¹³C 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. Compounds **1a**, **1b** were synthesized by the procedures we previously reported.¹ IPrAuOH² was prepared according to literature methods.

Preparation and characterization

Synthesis of complex 4a

The mixture of **1a** (100 mg, 0.24 mmol) and ethyldiisopropylamine (31 mg, 0.24 mmol) was stirred in the DCE (3 mL) at 25 °C, and then AuCl·Me₂S (141 mg, 0.48 mmol) was added. After stirring for 20 min, all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. The rude product was washed twice with diethyl ether to afford pure **4a** as a yellow-green solid (218 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ = 8.47 (s, 1H), 8.27 (s, 1H), 7.47-7.40 (m, 2H), 7.26-7.20 (m, 4H), 3.95-3.86 (m, 2H), 3.31-3.23 (m, 2H), 2.91-2.82 (m, 2H), 2.73-2.65 (m, 2H), 1.54 (d, *J* = 6.4 Hz, 12H), 1.49-1.43 (m, 12H), 1.22 (d, *J* = 6.4 Hz, 6H), 1.18-1.15 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 184.28, 156.96, 151.09, 146.79, 145.15, 144.43, 139.07, 132.23, 130.84, 124.46, 54.75, 42.95, 28.91, 28.70, 24.57, 24.30, 24.00, 19.05, 17.71, 12.48; HRMS (ESI): m/z [2M-AuCl-2[N(Pr)₂Et·HCl]+H]⁺ calcd. for C₅₆H₇₁Au₃ClN₄O₂⁺: 1457.4262; found: 1457.4268. Anal. Calcd. For C₃₆H₅₅Au₂Cl₂N₃O·0.5(CH₂Cl₂): C, 41.63; H, 5.36; N, 3.99; Found: C, 41.83; H, 5.46; N, 3.97 %.

Synthesis of complex 4b

Following a similar procedure to that described for **4a**, the mixture of **1b** (100 mg, 0.30 mmol), ethyldiisopropylamine (39 mg, 0.30 mmol) and AuCl·Me₂S (176 mg, 0.60 mmol) was stirred in the DCE (3 mL) at 25 °C to afford pure **4b** as a green solid (255 mg, 92%). ¹H NMR (400 MHz, CDCl₃) δ = 8.46 (s, 1H), 8.12 (s, 1H), 6.95 (d, *J* = 6.4 Hz, 4H), 3.99-3.86 (m, 2H), 3.34-3.23 (m, 2H), 2.29 (d, *J* = 4.4 Hz, 6H), 2.24 (s, 6H), 2.12 (s, 6H), 1.59-1.56 (m, 9H), 1.46 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ = 183.43, 156.46, 151.99, 147.26, 140.19, 139.89, 139.58, 134.16, 133.44, 132.82, 129.57, 54.76, 43.49, 42.99, 21.07, 19.08, 17.98, 17.67, 12.56; HRMS (ESI): m/z [2M-2[N(ⁱPr)₂Et·HCl]-Cl+CH₃OH]⁺ calcd. for C₄₅H₅₀Au₄ClN₄O₃⁺: 1517.2234; found: 1517.2990. Anal. Calcd. For C₃₀H₄₃Au₂Cl₂N₃O·0.5 (CH₂Cl₂): C, 37.81; H, 4.58; N, 4.34; Found: C, 38.05; H, 4.97; N, 4.27 %.

Synthesis of complex 4c

The mixture of 4a (100 mg, 0.1 mmol) and PPh₃AgOTf (103 mg, 0.2 mmol) was stirred in the DCE (2.5 mL) at 25 °C for 3 h. All volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water (2 mL) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford pure 4c as a yellow solid (108 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ = 8.60 $(d, J = 1.6 \text{ Hz}, 1\text{H}), 7.68-7.64 \text{ (m}, 1\text{H}), 7.63-7.57 \text{ (m}, 4\text{H}), 7.52 \text{ (q}, J = 6.4, 4\text{H}), 7.45-7.35 \text{ (m}, 7.45-7.35 \text{ (m}, 7.45), 7.45-7.35 \text{ (m}, 7.45-7.35 \text{ (m}, 7.45-7.35), 7.45-7.35 \text{ (m}, 7.45-7.35), 7.45-7.35 \text{ (m}, 7.45-7.35 \text{ (m}, 7.45-7.35), 7.45-7.35 \text{ (m}, 7.45-7.35 \text{ (m}, 7.45-7.35), 7.45-7.35), 7.45-7.35 \text{ (m}, 7.45-7.35), 7.45-7.35 \text$ 9H), 7.34-7.31 (m, 4H), 7.30-7.27 (m, 4H), 7.21 (td, *J* = 7.8, 2.3 Hz, 5H), 7.04 (dd, *J* = 12.8, 7.2 Hz, 5H), 2.96-2.85 (m, 2H), 2.77-2.65 (m, 2H), 1.29 (d, J = 6.8 Hz, 6H), 1.27-1.18 (m, 18H); ¹³C NMR (100 MHz, CDCl₃) δ = 201.15 (d, ²J_{P-C} = 133.2 HZ), 167.89 (d, ²J_{P-C} = 116.7 HZ), 157.67, 157.37, 149.77, 144.81, 138.28, 134.20, 133.44, 132.92, 131.86, 131.44, 130.02, 129.54, 129.10, 128.37, 127.08, 126.78, 125.12, 124.73, 29.14, 28.83, 24.30; ³¹P NMR (162 MHz, CDCl₃) δ = 41.70 (s), 40.65 (s). HRMS (MALDI): m/z [M-OTf]⁺ calcd. for $C_{64}H_{65}Au_2N_2OP_2^+$: 1333.3903; found: 1333.3723. Anal. Calcd. For C₆₅H₆₅Au₂F₃N₂O₄P₂S·CH₂Cl₂: C, 50.55; H, 4.31; N, 1.79; Found: C, 50.29; H, 4.45; N, 1.72 %.

Synthesis of complex 5a

From the reaction of 4a with AgOTf:

The mixture of **4a** (100 mg, 0.10 mmol) and silver triflate (26 mg, 0.10 mmol) was stirred in the DCE (1.5 mL) at 25 °C. After stirring for 8 h, all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water (2 mL) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford pure **5a** as a yellow solid (49 mg, 76%). ¹H NMR (400 MHz, CDCl₃) δ = 8.60 (s, 1H), 7.52-7.45 (m, 2H), 7.36-7.28 (m, 3H), 7.25-7.21 (m, 1H), 3.18-3.08 (m, 1H), 2.94-2.84 (m, 1H), 2.84-2.70 (m, 2H), 1.55 (d, *J* = 6.7 Hz, 3H), 1.40 (d, *J* = 6.7 Hz, 3H), 1.28-1.20 (m, 18H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.83, 154.33, 150.39, 146.26, 145.74, 144.81, 143.46, 138.98, 132.45, 131.62, 130.11, 125.54, 125.19, 124.36, 43.45, 29.45, 29.37, 29.14, 24.51, 23.97; HRMS (ESI): m/z [M-Cl]⁺ calcd. for C₅₆H₇₀Au₂ClN₄O₂⁺: 1259.4518; found: 1259.4514. Anal. Calcd. For C₅₆H₇₀Au₂Cl₂N₄O₂: C, 51.90; H, 5.44; N, 4.32; Found: C, 51.96; H, 5.64; N, 4.33 %.

From the reaction of 4c in the presence of AuCl·Me₂S:

The mixture of 4c (50 mg, 0.034 mmol) and AuCl·Me₂S (20 mg, 0.068 mmol) was stirred in the DCE (1 mL) at 25 °C for 24 h. All volatiles were then removed under vacuum, and afford 5a in a 68% NMR yield.

From the AuCl·Me₂S-catalyzed reaction of 1a in the presence of ethyldiisopropylamine and PhI(OAc)₂:

The mixture of **1a** (100 mg, 0.24 mmol), ethyldiisopropylamine (31 mg, 0.24 mmol), AuCl·Me₂S (78 mg, 0.26 mmol) and PhI(OAc)₂ (77 mg, 0.24 mmol) was stirred in the DCE (3 mL) at 80 °C. After stirring for 3 h, all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water (2 mL) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford pure **5a** as a yellow solid (106 mg, 68%).

From the reaction of 1a with AuCl·Me₂S in the presence of ethyldiisopropylamine:

The mixture of **1a** (100 mg, 0.24 mmol), ethyldiisopropylamine (31 mg, 0.24 mmol) and AuCl·Me₂S (141 mg, 0.48 mmol) was stirred in the DCE (3 mL) at 80 °C. After stirring for 8 h, all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water (2 mL) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford a mixture of **5a** and **6a** in the ratio of 5:1 with a conversion of one hundred percent.

From heating 4a in the DCE at 80 °C:

4a (100 mg, 0.10 mmol) was stirred in the DCE (1.5 mL) at 80 °C. After stirring for 8 h, all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water (2 mL) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford mixture of **5a** and **6a** in the ratio of 5:1 with a conversion of one hundred percent.

From heating 7 in the presence of AuCl·Me₂S at 60 °C:

The mixture of 7 (50 mg, 0.05 mmol) and AuCl·Me₂S (18 mg, 0.06 mmol) was stirred in the DCE (1 mL) at 60 °C. After stirring for 8 h, all volatiles were then removed under vacuum, and afford **5a** in a 67% NMR yield.

Synthesis of complex 5b

From the reaction of 4b with AgOTf:

Following a similar procedure to that described for **5a**, the mixture of **4b** (100 mg, 0.11 mmol) and silver triflate (28 mg, 0.11 mmol) was stirred in the DCE (3 mL) at 25 °C to afford pure **5b** as a yellow solid (58 mg, 94%). ¹H NMR (400 MHz, CDCl₃) δ = 8.36 (s, 1H), 7.03-6.93 (m, 4H), 2.43 (s, 3H), 2.32-2.21 (m, 12H), 2.14 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.34, 153.49, 151.18, 141.30, 140.96, 139.62, 134.56, 134.27, 133.37, 132.70, 130.81,

130.20, 129.83, 43.46, 21.15, 18.93, 18.21, 17.85, 17.55; HRMS (ESI): m/z [M-Cl]⁺ calcd. for C₄₄H₄₆Au₂ClN₄O₂⁺: 1091.2640; found: 1091.2635. Anal. Calcd. For C₄₄H₄₆Au₂Cl₂N₄O₂·CH₂Cl₂: C, 44.57; H, 3.99; N, 4.62; Found: C, 44.89; H, 4.09; N, 4.51 %.

From the AuCl·Me₂S-catalyzed reaction of 1b in the presence of ethyldiisopropylamine and PhI(OAc)₂:

The mixture of **1b** (100 mg, 0.30 mmol), ethyldiisopropylamine (39 mg, 0.30 mmol), AuCl·Me₂S (97 mg, 0.33 mmol) and PhI(OAc)₂ (97 mg, 0.30 mmol) was stirred in the DCE (3.5 mL) at 80 °C. After stirring for 3 h, all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water (2 mL) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford pure **5b** as a yellow solid (128 mg, 76%).

From the oxidation reaction of 4b in the presence of PhI(OAc)₂:

The mixture of **4b** (100 mg, 0.11 mmol) and PhI(OAc)₂ (35 mg, 0.11 mmol) was stirred in the DCE (1.5 mL) at 25 °C. After stirring for 12 h, all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water (2 mL) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford pure **5b** as a yellow solid (102 mg, 82%).

From the reaction of 1b with AuCl·Me₂S in the presence of ethyldiisopropylamine:

The mixture of **1b** (100 mg, 0.30 mmol), ethyldiisopropylamine (39 mg, 0.30 mmol) and AuCl·Me₂S (176 mg, 0.60 mmol) was stirred in the DCE (3 mL) at 80 °C. After stirring for 8 h, all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water (2 mL) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford a mixture of **5b** and **6b** in the ratio of 3:1 with a conversion of one hundred percent.

From heating 4b in the DCE at 80 °C:

4b (100 mg, 0.11 mmol) was dissolved in the DCE (1.5 mL) and stirred at 80 °C. After stirring for 8 h, all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water (2 mL) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford a mixture of **5b** and **6b** in the ratio of 3:1 with a conversion of one hundred percent.

Synthesis of complex 6a and 6b

Scheme S1 Formation of 6a or 6b by heating 4a or 4b under neat condition

From the reaction of heated 4a under neat condition to synthesis 6a:

4a (100 mg, 0.10 mmol) was heated at 150 °C under neat condition. After stirring for 8 h, the resultant solid was solvents in DCM, and filtered through a pad of Celite. After washing the solid several times with DCM, and the solvents in the filtrate were evaporated. The rude product was washed twice with diethyl ether to afford pure **6a** as a gray solid (58 mg, 89%). ¹H NMR (400 MHz, CDCl₃) δ = 8.48 (s, 1H), 7.56-7.49 (m, 2H), 7.36-7.27 (m, 4H), 6.88 (s, 1H), 2.81-2.69 (m, 2H), 2.67-2.56 (m, 2H), 1.50 (d, *J* = 6.8 Hz, 6H), 1.28-1.18 (m, 18H); ¹³C NMR (100 MHz, DMSO) δ = 185.06, 154.96, 144.50, 143.65, 139.19, 131.11, 124.53, 54.84, 28.61, 23.52; HRMS (ESI): m/z [2M-Cl]⁺ calcd. for C₅₆H₇₂Au₂ClN₄O₂⁺: 1261.4675; found: 1261.4677. Anal. Calcd. For C₂₈H₃₆AuClN₂O·0.5(CH₂Cl₂): C, 49.50; H, 5.39; N, 4.05; Found: C, 49.49; H, 5.48; N, 4.11 %.

From the reaction of heated 5b under neat condition to synthesis 6b:

Following a similar procedure to that described for **6a**, **4b** (130 mg, 0.14 mmol) afford **6b** as a gray solid (71 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ = 8.33 (s, 1H), 7.04 (s, 2H), 7.00 (s, 2H), 6.91 (s, 1H), 2.33 (d, *J* = 8.4 Hz, 6H), 2.24 (s, 6H), 2.16 (s, 6H); ¹³C NMR (100 MHz, DMSO) δ = 183.65, 155.32, 153.49, 139.96, 139.62, 134.18, 133.29, 131.02, 129.23, 123.88, 20.56, 17.39, 17.08; HRMS (ESI): m/z [2M-Cl]⁺ calcd. for C₄₄H₄₈Au₂ClN₄O₂⁺: 1093.2797;

found: 1093.2794. Anal. Calcd. For C₂₂H₂₄AuClN₂O·CH₂Cl₂: C, 42.51; H, 4.03; N, 4.31; Found: C, 42.79; H, 4.14; N, 4.52 %.

Synthesis of complex 7

The mixture of **1a** (60 mg, 0.14 mmol) and IPrAuOH (84 mg, 0.14 mmol) was stirred in the toluene (1.5 mL) at 25 °C for 8 h. All volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. The rude product was washed twice with pentane and dried under vacuum to afford pure **7** as a white microcrystalline solid (125 mg, 89%). ¹H NMR (400 MHz, CDCl₃) δ = 8.98 (s, 1H), 7.51-7.44 (m, 2H), 7.35-7.28 (m, 1H), 7.25-7.16 (m, 6H), 7.12 (s, 2H), 7.04 (s, 3H), 2.92-2.78 (m, 4H), 2.52-2.38 (m, 4H), 1.22-1.17 (m, 30H), 1.10-1.01 (m, 18H); ¹³C NMR (100 MHz, CDCl₃) δ = 175.32, 163.07, 147.12, 146.84, 146.28, 145.55, 133.94, 130.71, 129.59, 124.42, 123.76, 123.50, 123.04, 28.73, 28.27, 24.44, 23.97, 23.02; HRMS (ESI): m/z [M+H]⁺ calcd. for C₅₅H₇₂AuN₄O⁺: 1001.5372; found: 1001.5368. Anal. Calcd. For C₅₅H₇₁AuN₄O·0.5(CH₂Cl₂): C, 63.87; H, 6.95; N, 5.37; Found: C, 63.75; H, 7.00; N, 5.33 %.

Reference:

- Lv, S.; Wang, J.; Zhang, C.; Xu, S.; Shi, M.; Zhang, J. Angew. Chem., Int. Ed. 2015, 54, 14941.
- 2. Nahra, F.; Patrick, S. R.; Collado, A.; Nolan, S. P. Polyhedron 2014, 84, 59.

NMR Spectra:

Complex 4a



Complex 4b



Complex 4c

¥30150179-1011-525







PPh₃ Dipp^{-N} ^N Dipp ⁻OTf



Complex 5a

151030-JU-WJW-0707



Complex 5b



Complex 6a



100 90 f1 (ppm)

Complex 6b



100 90 f1 (ppm)

Complex 7



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-Karadiation ($\lambda_{Mo-Ka} = 0.71073$ Å). The structures were solved by directed 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-S3. Further crystallographic details may be found in the respective CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK [CCDC 1440090 (4a); 1514554 (4c); 1440089 (5a)].



Figure S1. Molecular structures of **4c** with 20% probability. The counterion (OTf^{-}) in **4c**, and H atoms in anyl rings have been omitted for clarity.

	4 a	4 c	5a
Identification code	mo_51016b	mo_dm16665_0m	mo_51010b
Formula	$C_{36}H_{55}Au_2Cl_2$	$C_{66}H_{67}Au_2Cl_2F_3$	$C_{58}H_{74}Au_2Cl_4$
Formula	N_3O	$N_2O_4P_2S$	$N_4 O_2$
Formula weight	1010.66	1568.05	1394.94
Т, К	296(2)	130 K	296(2)
crystal system	Orthorhombic	Monoclinic	Trigonal
space group	P 21 21 21	P 1 21/n 1	P 32 2 1
<i>a</i> , Å	12.7762(14)	18.1480(12)	15.803(2)
b, Å	17.0556(19)	18.4838(12)	15.803(2)
<i>c</i> , Å	18.581(2)	19.8362(14)	21.901(3)
α , deg	90	90	90
β , deg	90	108.0470(10)	90
γ , deg	90	90	120
Volume, Å ³	4048.9(8)	6326.6(7)	4736.5(15)
Ζ	4	4	3
D_{calc} , Mg / m ³	1.658	1.646	1.467
absorption coefficient, mm ⁻¹	7.399	4.858	4.850
F(000)	1968	3096	2076
crystal size, mm	0.180 x 0.100 x 0.070	0.3 x 0.25 x 0.2	0.500 x 0.240 x 0.220
2θ range, deg	1.934 to 26.612	1.614 to 25.999	1.755 to 27.357
reflections	35920/8474	45853/12444	34011/7149
collected /unique	[R(int) = 0.0487]	[R(int) = 0.0241]	[R(int) = 0.0393]
data / restraints/ parameters	8474 / 26 / 416	12444 / 0 / 747	7149 / 1 / 328
goodness of fit on F ²	0.998	1.034	1.052
final R indices	R1 = 0.0264,	R1 = 0.0251,	R1 = 0.0270, WR
$[I > 2\sigma(I)]^a$	wR2 = 0.0479	wR2 = 0.0547	= 0.0620
R indices	R1 = 0.0395,	R1 = 0.0327,	R1 = 0.0380, WR
(all data)	wR2 = 0.0514	wR2 = 0.0582	= 0.0669
lgst diff peak and hole, $e/Å^3$	0.512 and -0.577	3.320 and -1.888	0.883 and -0.388

Table S1. Crystal Data, Data Collection, and Structure Refinement for 4a, 4c and 5a.