Electronic Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

María J. López-Gómez, David Martin and Guy Bertrand

UCSD-CNRS Joint Research Laboratory (UMI 3555)

Department of Chemistry and Biochemistry, University of California, San Diego,

La Jolla, CA 92093-0343, USA

E-mail: guybertrand@ucsd.edu.

General considerations: All reactions were performed under an atmosphere of argon by using standard Schlenk or dry box techniques; solvents were dried over sodium or CaH_2. Compounds **1•H**$^+$, **3**[1] and (tetrahydrothiophene)gold(I) chloride[2] were synthesized according to the literature procedures. ^{1}H NMR, and ^{13}C NMR spectra were obtained with a Bruker Advance 300 and Varian Mercury 400 spectrometers at 298K. ^{1}H NMR, ^{19}F and ^{13}C NMR chemical shifts (δ) are reported in parts per million (ppm) relative to TMS and were referenced to the residual solvent peak. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Melting points were measured with a Büchi melting point apparatus system. A Bruker X8-APEX X-ray diffraction instrument with Mo-radiation was used for data collection.

Complex 2: A solution of **1•H**$^+$ (400 mg, 0.92 mmol) in 6 mL of THF was added dropwise to a stirred solution of KHMDS (202.1 mg, 1.01 mmol) in THF (5 mL) at -78 º C. After 5 min (tetrahydrothiophene)gold(I) chloride (147.7 mg, 0.46 mmol) was added in the absence of light, and the mixture was allowed to reach room temperature overnight. The volatiles were removed *in vacuo* and the remaining dark precipitate was washed with benzene until the washes became colorless. The remaining solid was extracted with CH_2Cl_2. This colorless solution was slowly concentrated under in vacuo and hexane was layered affording a white microcrystalline solid; 650 mg, 85 % yield. Colorless single crystals were obtained by layering pentane on a solution of **2** in $CHCl_3$. mp (dec.) 231°C. MS (m/z): $[M]^+$ calcd. for $C_{38}H_{56}N_4Au$, 765.4165; found, 765.4167. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (m, 2H), 7.16 (m, 4H), 3.44 (m, 2H), 3.30 (m, 4H), 3.14 (m, 2H), 2.90 (m, 5H), 2.68 (m, 7H), 2.00 (m, 2H), 1.69 (m, 4H), 1.31 (d, 6H, *J* = 7 Hz), 1.23 (d, 6H, *J* = 7 Hz), 1.16 (d, 6H, *J* = 7 Hz), 0.94 (d, 6H, *J* = 7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.9 (CH_3), 24.7 (CH_3), 25.0 (2 CH_3), 26.4 (CH_2), 26.5 (CH_2), 28.2 (CH), 28.6 (CH), 29.7 (CH), 49.7 (CH_2), 51.7 (CH_2), 59.3 (CH_2),

124.6 (CH_{aro}), 124.9 (CH_{aro}), 129.9 (CH_{aro}), 139.0 (C_{aro}), 144.2 (C_{aro}), 146.1 (C_{aro}), 223.5 (CAu).

Complex 1•AuCl: A solution of **1•H**$^+$ (400 mg, 1.05 mmol) in THF (6 mL) was added dropwise to a solution of KHMDS (202.5 mg, 1.16 mmol) in THF (5 mL) at -78 ºC. The mixture was stirred 15 min, then warmed to room temperature and added to a suspension of (tetrahydrothiophene)gold(I) chloride (295.3 mg, 1.05 mmol) in THF (5 mL) at -78 °C in the absence of light. The mixture was stirred and allowed to reach room temperature overnight. The volatiles were removed *in vacuo* and the resulting dark precipitate was extracted with benzene. Removal of the volatiles *in vacuo*, followed by trituration with pentane afforded **1•AuCl** as a powder; 307 mg, 57 % yield. Eventual colored impurities can be removed by filtration on neutral alumina (eluent: dichloromethane). Colorless single crystals were obtained by layering hexanes on a solution of **1•AuCl** in dichloromethane. mp (dec.): 240°C. MS (m/z): $[M+Na]^+$ calcd. for $C_{19}H_{28}N_2AuClNa$, 539.1499; found, 539.1495. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (m, 1H), 7.16 (m, 2H), 4.6 (m, 1H), 3.48 (m, 1H), 3.39 (m, 1H), 3.16 (m, 3H), 2.85 (m, 2H), 2.67 (m, 1H), 2.03 (m, 1H), 1.81 (m, 3H), 1.48 (d, 3H, J = 7 Hz), 1.26 (d, 3H, J = 7 Hz), 1.24 (d, 3H, J = 7 Hz), 1.22 (d, 3H, J = 7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.1 (CH_3), 25.1 (CH_3), 25.3 (2×CH_3), 26.4 (CH_2), 27.3 (CH_2), 28.5 (CH), 28.9 (CH), 30.3 (CH), 49.8 (CH_2), 53.1 (CH_2), 59.2 (CH_2), 124.5 (CH_{aro}), 125.6 (CH_{aro}), 130.1 (CH_{aro}), 139.6 (C_{aro}), 144.6 (C_{aro}), 145.2 (C_{aro}), 209.3 (CAu).

General procedure for the hydroamination of alkynes: Complex **1•AuCl** (12.9 mg, 0.025 mmol) and $KB_{Ar}^{F}{}_4$ ($B_{Ar}^{F}{}_4$: $B[C_6H_3(CF_3)_2]_4^-$) (17.9 mg, 0.025 mmol) were introduced in a J Young NMR tube. The solvent (0.4 mL), 1,4-di-*tert*-butylbenzene (10 mg, 0.05 mmol), the desired alkyne, (0.5 mmol) and anhydrous NH_2NH_2 (15.7 µL, 0.5 mmol) were added in this

order. The reaction was monitored by ^{1}H and ^{13}C NMR spectroscopy. After completion of the reaction, the reaction mixture was promptly passed under a stream of argon through a short pad of well dried florisil® silica gel.

2- hydrazonohexane[3] (Table 2, entry 1): ^{1}H NMR (400 MHz, C_6D_6): δ = 4.47 (br s, 2H), 2.20 (t, J = 7.5 Hz, 2H), 1.6-1.4 (m, 2H), 1.45 (s, 3H), 1.4-1.2 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 149.0 (C), 38.4 (CH_2), 28.9 (CH_2), 22.4 (CH_2), 13.9 (CH_3), 12.8 (CH_3).

1-cyclohexylhydrazonoethane[3] (Table 2, entry 2): ^{1}H NMR (400 MHz, C_6D_6): δ = 4.3 (br s, 2H), 2.13-2.09 (m, 1H), 1.9-1.6 (m, 6H), 1.45 (s, 3H), 1.4-1.2 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6): δ = 152.7 (C), 46.8 (CH), 30.5 (CH_2), 26.4 (CH_2), 26.1 (CH_2), 11.5 (CH_3).

1-phenylhydrazonopropane[3] (Table 2, entry 3): ^{1}H NMR (400 MHz, C_6D_6): δ = 7.3-7.1 (m, 5H), 4.6 (br s, 2H), 3.47 (s, 2H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 148.3 (C), 139.0 (C), 129.3 (CH), 128.7 (CH), 126.6 (CH), 45.6 (CH_2), 12.7 (CH_3).

2-hydrazono-3,3-dimethylbutane[4] (Table 2, entry 5): ^{1}H NMR (400 MHz, C_6D_6): δ = 4.1 (br s, 2H), 1.28 (s, 3H), 1.02 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6): δ = 155.1 (C), 46.1 (C), 28.0 (CH_3), 9.5 (CH_3).

1-phenylhydrazonoethane[5] (Table 2, entry 7): ^{1}H NMR (400 MHz, C_6D_6) δ 7.8–7.7 (m, 2H); 7.2–7.1 (m, 2H), 7.1–7.0 (m, 1H), 4.69 (br, 2H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 145.1 (C), 140.1 (C), 128.4 (CH), 127.9 (CH), 125.7 (CH), 10.6 (CH_3).

1-anisylhydrazonoethane[6] (Table 2, entry 8): ^{1}H NMR (400 MHz, C_6D_6): δ = 7.57 (d, J = 8.9 Hz, 2H), 6.70 (d, J = 8.9 Hz, 2H), 3.27 (s, 3H), 2.74 (br s, 2H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 159.9 (C), 145.2 (C), 133.0 (C), 127.0 (CH), 113.9 (CH), 54.9 (CH_3), 11.1 (CH_3).

1-cyclohexenylhydrazonoethane[3] (Table 2, entry 9): ^{1}H NMR (100 MHz, C_6D_6): δ 5.81 (s, 1H), 4.65 (br s, 2H), 2.56 (m, 2H), 2.00 (m, 2H), 1.58(m, 2H), 1.51 (s, 3H), 1.48 (m, 2H); ^{13}C

NMR (100 MHz, C_6D_6): δ150.3 (C), 138.0 (C), 125.6 (CH), 26.3 (CH_2), 25.2 (CH_2), 23.3 (CH_2), 22.9 (CH_2), 9.2 (CH_3).

1-hydrazono-1,2-diphenylethane[7] (Table 2, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (m, 2H), 7.4-7.3 (m, 3H), 7.2-7.1 (m, 5H), 6.11 (br s, 2H), 4.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3 (C), 137.6 (2C), 130.0 (CH), 129.3 (CH), 128.9 (CH), 128.8 (CH), 128.6 (CH), 127.7 (CH), 126.3 (C), 35.0 (CH_2).

Crystallographic Data

Crystal data for 2: $C_{41}H_{58}AuCl_6F_3N_4O_3S$, M = 1153.64, triclinic, a = 11.8363(11)Å, b = 13.7890(13) Å, c = 16.121(2)Å, α = 110.5960(10)°, β = 91.5170(10)°, γ = 104.5830(10)°, V = 2364.3(4) Å^3, T = 293(2) K, space group *P-1*, Z = 2, μ(MoKα) = 0.71073 mm^{-1}, 15826 reflections measured, 10419 independent reflections (R_{int} = 0.0158). The final R_1 values were 0.0291 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0728 ($I > 2\sigma(I)$). The final R_1 values were 0.0313 (all data). The final $wR(F^2)$ values were 0.0743 (all data). The goodness of fit on F^2 was 1.028. CCDC 924514.

Table S1. Bond lengths [Å] and angles [°] for 2.

Au(1)-C(1)	2.040(3)	Au(1)-C(8)	2.044(3)
N(1)-C(1)	1.381(4)	N(1)-C(2)	1.475(4)
N(1)-C(7)	1.475(4)	N(2)-C(1)	1.328(4)
N(2)-C(15)	1.449(4)	N(2)-C(6)	1.488(4)
N(3)-C(8)	1.369(4)	N(3)-C(14)	1.470(4)
N(3)-C(13)	1.484(4)	N(4)-C(8)	1.329(4)
N(4)-C(21)	1.450(4)	N(4)-C(9)	1.493(4)
C(2)-C(3)	1.537(5)	C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700	C(3)-C(4)	1.546(5)
C(3)-H(3A)	0.9700	C(3)-H(3B)	0.9700
C(4)-C(5)	1.536(5)	C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700	C(5)-C(7)	1.514(4)
C(5)-C(6)	1.529(4)	C(5)-H(5)	0.9800
C(6)-H(6A)	0.9700	C(6)-H(6B)	0.9700
C(7)-H(7A)	0.9700	C(7)-H(7B)	0.9700
C(9)-C(10)	1.529(4)	C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700	C(10)-C(14)	1.522(4)

C(10)-C(11)	1.538(5)	C(10)-H(10)	0.9800
C(11)-C(12)	1.541(4)	C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700	C(12)-C(13)	1.539(4)
C(12)-H(12A)	0.9700	C(12)-H(12B)	0.9700
C(13)-H(13A)	0.9700	C(13)-H(13B)	0.9700
C(14)-H(14A)	0.9700	C(14)-H(14B)	0.9700
C(15)-C(16)	1.402(5)	C(15)-C(20)	1.406(5)
C(16)-C(17)	1.402(4)	C(16)-C(27)	1.520(5)
C(17)-C(18)	1.383(5)	C(17)-H(17)	0.9300
C(18)-C(19)	1.391(5)	C(18)-H(18)	0.9300
C(19)-C(20)	1.392(4)	C(19)-H(19)	0.9300
C(20)-C(30)	1.521(5)	C(21)-C(26)	1.402(4)
C(21)-C(22)	1.404(5)	C(22)-C(23)	1.385(5)
C(22)-C(33)	1.525(5)	C(23)-C(24)	1.386(5)
C(23)-H(23)	0.9300	C(24)-C(25)	1.386(5)
C(24)-H(24)	0.9300	C(25)-C(26)	1.402(5)
C(25)-H(25)	0.9300	C(26)-C(36)	1.523(5)
C(27)-C(29)	1.534(5)	C(27)-C(28)	1.536(5)
C(27)-H(27)	0.9800	C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600	C(28)-H(28C)	0.9600
C(29)-H(29A)	0.9600	C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600	C(30)-C(31)	1.520(5)
C(30)-C(32)	1.530(5)	C(30)-H(30)	0.9800
C(31)-H(31A)	0.9600	C(31)-H(31B)	0.9600
C(31)-H(31C)	0.9600	C(32)-H(32A)	0.9600
C(32)-H(32B)	0.9600	C(32)-H(32C)	0.9600
C(33)-C(35)	1.519(5)	C(33)-C(34)	1.533(5)
C(33)-H(33)	0.9800	C(34)-H(34A)	0.9600
C(34)-H(34B)	0.9600	C(34)-H(34C)	0.9600
C(35)-H(35A)	0.9600	C(35)-H(35B)	0.9600
C(35)-H(35C)	0.9600	C(36)-C(38)	1.534(4)
C(36)-C(37)	1.536(5)	C(36)-H(36)	0.9800
C(37)-H(37A)	0.9600	C(37)-H(37B)	0.9600
C(37)-H(37C)	0.9600	C(38)-H(38A)	0.9600
C(38)-H(38B)	0.9600	C(38)-H(38C)	0.9600
C(39)-F(1)	1.283(5)	C(39)-F(2)	1.328(5)
C(39)-F(3)	1.359(6)	C(39)-S(1)	1.813(4)
O(1)-S(1)	1.409(3)	O(2)-S(1)	1.431(3)
O(3)-S(1)	1.450(4)	C(40)-Cl(3)	1.758(3)
C(40)-Cl(1)	1.760(4)	C(40)-Cl(2)	1.769(4)
C(40)-H(40)	0.9800	C(41)-Cl(4)	1.759(4)
C(41)-Cl(6)	1.759(4)	C(41)-Cl(5)	1.767(4)
C(41)-H(41)	0.9800		

C(1)-Au(1)-C(8)	179.54(12)	C(1)-N(1)-C(2)	112.5(3)
C(1)-N(1)-C(7)	116.7(2)	C(2)-N(1)-C(7)	111.2(2)
C(1)-N(2)-C(15)	119.9(2)	C(1)-N(2)-C(6)	124.7(2)
C(15)-N(2)-C(6)	115.0(2)	C(8)-N(3)-C(14)	117.2(3)
C(8)-N(3)-C(13)	112.9(2)	C(14)-N(3)-C(13)	110.9(2)
C(8)-N(4)-C(21)	120.2(2)	C(8)-N(4)-C(9)	124.6(3)
C(21)-N(4)-C(9)	114.8(2)	N(2)-C(1)-N(1)	116.2(3)
N(2)-C(1)-Au(1)	122.8(2)	N(1)-C(1)-Au(1)	121.0(2)
N(1)-C(2)-C(3)	107.9(3)	N(1)-C(2)-H(2A)	110.1
C(3)-C(2)-H(2A)	110.1	N(1)-C(2)-H(2B)	110.1
C(3)-C(2)-H(2B)	110.1	H(2A)-C(2)-H(2B)	108.4
C(2)-C(3)-C(4)	112.9(3)	C(2)-C(3)-H(3A)	109.0
C(4)-C(3)-H(3A)	109.0	C(2)-C(3)-H(3B)	109.0
C(4)-C(3)-H(3B)	109.0	H(3A)-C(3)-H(3B)	107.8
C(5)-C(4)-C(3)	116.2(3)	C(5)-C(4)-H(4A)	108.2
C(3)-C(4)-H(4A)	108.2	C(5)-C(4)-H(4B)	108.2

C(3)-C(4)-H(4B)	108.2	H(4A)-C(4)-H(4B)	107.4
C(7)-C(5)-C(6)	104.3(2)	C(7)-C(5)-C(4)	108.8(3)
C(6)-C(5)-C(4)	117.6(3)	C(7)-C(5)-H(5)	108.6
C(6)-C(5)-H(5)	108.6	C(4)-C(5)-H(5)	108.6
N(2)-C(6)-C(5)	112.7(2)	N(2)-C(6)-H(6A)	109.1
C(5)-C(6)-H(6A)	109.1	N(2)-C(6)-H(6B)	109.1
C(5)-C(6)-H(6B)	109.1	H(6A)-C(6)-H(6B)	107.8
N(1)-C(7)-C(5)	107.0(3)	N(1)-C(7)-H(7A)	110.3
C(5)-C(7)-H(7A)	110.3	N(1)-C(7)-H(7B)	110.3
C(5)-C(7)-H(7B)	110.3	H(7A)-C(7)-H(7B)	108.6
N(4)-C(8)-N(3)	116.4(3)	N(4)-C(8)-Au(1)	121.7(2)
N(3)-C(8)-Au(1)	121.9(2)	N(4)-C(9)-C(10)	112.5(3)
N(4)-C(9)-H(9A)	109.1	C(10)-C(9)-H(9A)	109.1
N(4)-C(9)-H(9B)	109.1	C(10)-C(9)-H(9B)	109.1
H(9A)-C(9)-H(9B)	107.8	C(14)-C(10)-C(9)	104.5(2)
C(14)-C(10)-C(11)	108.1(3)	C(9)-C(10)-C(11)	118.0(3)
C(14)-C(10)-H(10)	108.6	C(9)-C(10)-H(10)	108.6
C(11)-C(10)-H(10)	108.6	C(10)-C(11)-C(12)	115.9(3)
C(10)-C(11)-H(11A)	108.3	C(12)-C(11)-H(11A)	108.3
C(10)-C(11)-H(11B)	108.3	C(12)-C(11)-H(11B)	108.3
H(11A)-C(11)-H(11B)	107.4	C(13)-C(12)-C(11)	112.8(3)
C(13)-C(12)-H(12A)	109.0	C(11)-C(12)-H(12A)	109.0
C(13)-C(12)-H(12B)	109.0	C(11)-C(12)-H(12B)	109.0
H(12A)-C(12)-H(12B)	107.8	N(3)-C(13)-C(12)	107.0(3)
N(3)-C(13)-H(13A)	110.3	C(12)-C(13)-H(13A)	110.3
N(3)-C(13)-H(13B)	110.3	C(12)-C(13)-H(13B)	110.3
H(13A)-C(13)-H(13B)	108.6	N(3)-C(14)-C(10)	106.9(2)
N(3)-C(14)-H(14A)	110.3	C(10)-C(14)-H(14A)	110.3
N(3)-C(14)-H(14B)	110.3	C(10)-C(14)-H(14B)	110.3
H(14A)-C(14)-H(14B)	108.6	C(16)-C(15)-C(20)	123.3(3)
C(16)-C(15)-N(2)	119.5(3)	C(20)-C(15)-N(2)	117.2(3)
C(15)-C(16)-C(17)	116.9(3)	C(15)-C(16)-C(27)	122.9(3)
C(17)-C(16)-C(27)	120.2(3)	C(18)-C(17)-C(16)	121.1(3)
C(18)-C(17)-H(17)	119.5	C(16)-C(17)-H(17)	119.5
C(17)-C(18)-C(19)	120.5(3)	C(17)-C(18)-H(18)	119.7
C(19)-C(18)-H(18)	119.7	C(18)-C(19)-C(20)	120.9(3)
C(18)-C(19)-H(19)	119.5	C(20)-C(19)-H(19)	119.5
C(19)-C(20)-C(15)	117.2(3)	C(19)-C(20)-C(30)	121.1(3)
C(15)-C(20)-C(30)	121.6(3)	C(26)-C(21)-C(22)	122.9(3)
C(26)-C(21)-N(4)	119.4(3)	C(22)-C(21)-N(4)	117.7(3)
C(23)-C(22)-C(21)	117.4(3)	C(23)-C(22)-C(33)	120.1(3)
C(21)-C(22)-C(33)	122.5(3)	C(22)-C(23)-C(24)	121.2(3)
C(22)-C(23)-H(23)	119.4	C(24)-C(23)-H(23)	119.4
C(23)-C(24)-C(25)	120.5(3)	C(23)-C(24)-H(24)	119.8
C(25)-C(24)-H(24)	119.8	C(24)-C(25)-C(26)	120.7(3)
C(24)-C(25)-H(25)	119.7	C(26)-C(25)-H(25)	119.7
C(21)-C(26)-C(25)	117.2(3)	C(21)-C(26)-C(36)	123.3(3)
C(25)-C(26)-C(36)	119.5(3)	C(16)-C(27)-C(29)	111.5(3)
C(16)-C(27)-C(28)	111.3(3)	C(29)-C(27)-C(28)	110.1(3)
C(16)-C(27)-H(27)	108.0	C(29)-C(27)-H(27)	108.0
C(28)-C(27)-H(27)	108.0	C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5	H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5	H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5	C(27)-C(29)-H(29A)	109.5
C(27)-C(29)-H(29B)	109.5	H(29A)-C(29)-H(29B)	109.5
C(27)-C(29)-H(29C)	109.5	H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5	C(31)-C(30)-C(20)	110.1(3)
C(31)-C(30)-C(32)	111.0(3)	C(20)-C(30)-C(32)	112.1(3)
C(31)-C(30)-H(30)	107.8	C(20)-C(30)-H(30)	107.8
C(32)-C(30)-H(30)	107.8	C(30)-C(31)-H(31A)	109.5

C(30)-C(31)-H(31B)	109.5	H(31A)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31C)	109.5	H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5	C(30)-C(32)-H(32A)	109.5
C(30)-C(32)-H(32B)	109.5	H(32A)-C(32)-H(32B)	109.5
C(30)-C(32)-H(32C)	109.5	H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5	C(35)-C(33)-C(22)	111.4(3)
C(35)-C(33)-C(34)	111.0(4)	C(22)-C(33)-C(34)	111.0(3)
C(35)-C(33)-H(33)	107.8	C(22)-C(33)-H(33)	107.8
C(34)-C(33)-H(33)	107.8	C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5	H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5	H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5	C(33)-C(35)-H(35A)	109.5
C(33)-C(35)-H(35B)	109.5	H(35A)-C(35)-H(35B)	109.5
C(33)-C(35)-H(35C)	109.5	H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5	C(26)-C(36)-C(38)	111.1(3)
C(26)-C(36)-C(37)	110.7(3)	C(38)-C(36)-C(37)	110.4(3)
C(26)-C(36)-H(36)	108.2	C(38)-C(36)-H(36)	108.2
C(37)-C(36)-H(36)	108.2	C(36)-C(37)-H(37A)	109.5
C(36)-C(37)-H(37B)	109.5	H(37A)-C(37)-H(37B)	109.5
C(36)-C(37)-H(37C)	109.5	H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5	C(36)-C(38)-H(38A)	109.5
C(36)-C(38)-H(38B)	109.5	H(38A)-C(38)-H(38B)	109.5
C(36)-C(38)-H(38C)	109.5	H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5	F(1)-C(39)-F(2)	110.8(4)
F(1)-C(39)-F(3)	104.2(4)	F(2)-C(39)-F(3)	106.0(4)
F(1)-C(39)-S(1)	113.3(3)	F(2)-C(39)-S(1)	112.4(3)
F(3)-C(39)-S(1)	109.6(3)	O(1)-S(1)-O(2)	118.3(2)
O(1)-S(1)-O(3)	112.2(3)	O(2)-S(1)-O(3)	113.5(2)
O(1)-S(1)-C(39)	104.9(2)	O(2)-S(1)-C(39)	103.5(2)
O(3)-S(1)-C(39)	102.4(2)	Cl(3)-C(40)-Cl(1)	109.8(2)
Cl(3)-C(40)-Cl(2)	110.16(18)	Cl(1)-C(40)-Cl(2)	110.72(19)
Cl(3)-C(40)-H(40)	108.7	Cl(1)-C(40)-H(40)	108.7
Cl(2)-C(40)-H(40)	108.7	Cl(4)-C(41)-Cl(6)	110.5(2)
Cl(4)-C(41)-Cl(5)	110.3(2)	Cl(6)-C(41)-Cl(5)	110.2(2)
Cl(4)-C(41)-H(41)	108.6	Cl(6)-C(41)-H(41)	108.6
Cl(5)-C(41)-H(41)	108.6		

Crystal data for 1•AuCl: : $C_{19}H_{28}AuClN_2$, M = 516.85, monoclinic, a = 9.8369(11)Å, b = 17.341(2)Å, c = 11.3162(13)Å, α = 90.00°, β = 100.9140(10) °, γ = 90.00°, V = 1895.4(4)Å^3, T = 296(2) K, space group *P21/n*, Z = 4, μ(MoKα) = 0.71073mm^{-1}, 10885 reflections measured, 4078 independent reflections (R_{int} = 0.0283). The final R_1 values were 0.0246 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0785 ($I > 2\sigma(I)$). The final R_1 values were 0.0294 (all data). The final $wR(F^2)$ values were 0.0883 (all data). The goodness of fit on F^2 was 0.789. CCDC 924515.

Table S2. Bond lengths [Å] and angles [°] for 1•AuCl.

Au(1)-C(1)	1.983(3)	C(9)-C(17)	1.530(4)
Au(1)-Cl(1)	2.2994(7)	C(10)-C(11)	1.390(4)
N(1)-C(1)	1.330(3)	C(10)-H(21)	0.9300
N(1)-C(8)	1.445(3)	C(11)-C(12)	1.392(4)
N(1)-C(2)	1.491(3)	C(11)-H(20)	0.9300
N(2)-C(1)	1.376(4)	C(12)-C(13)	1.396(4)
N(2)-C(4)	1.472(4)	C(12)-H(19)	0.9300
N(2)-C(5)	1.474(4)	C(13)-C(14)	1.518(4)
C(2)-C(3)	1.516(4)	C(14)-C(16)	1.526(4)
C(2)-H(11)	0.9700	C(14)-C(15)	1.532(4)
C(2)-H(10)	0.9700	C(14)-H(15)	0.9800
C(3)-C(4)	1.526(4)	C(15)-H(12)	0.9600
C(3)-C(7)	1.559(4)	C(15)-H(14)	0.9600
C(3)-H(1)	0.9800	C(15)-H(13)	0.9600
C(4)-H(8)	0.9700	C(16)-H(17)	0.9600
C(4)-H(9)	0.9700	C(16)-H(16)	0.9600
C(5)-C(6)	1.540(4)	C(16)-H(18)	0.9600
C(5)-H(7)	0.9700	C(17)-C(18)	1.532(5)
C(5)-H(6)	0.9700	C(17)-C(19)	1.536(4)
C(6)-C(7)	1.541(5)	C(17)-H(22)	0.9800
C(6)-H(5)	0.9700	C(18)-H(23)	0.9600
C(6)-H(4)	0.9700	C(18)-H(25)	0.9600
C(7)-H(2)	0.9700	C(18)-H(24)	0.9600
C(7)-H(3)	0.9700	C(19)-H(27)	0.9600
C(8)-C(9)	1.392(4)	C(19)-H(28)	0.9600
C(8)-C(13)	1.407(4)	C(19)-H(26)	0.9600
C(9)-C(10)	1.395(4)		
		C(3)-C(2)-H(10)	108.9
C(1)-Au(1)-Cl(1)	177.95(8)	H(11)-C(2)-H(10)	107.7
C(1)-N(1)-C(8)	122.7(2)	C(2)-C(3)-C(4)	104.4(2)
C(1)-N(1)-C(2)	123.5(2)	C(2)-C(3)-C(7)	117.9(2)
C(8)-N(1)-C(2)	113.4(2)	C(4)-C(3)-C(7)	108.0(2)
C(1)-N(2)-C(4)	117.3(2)	C(2)-C(3)-H(1)	108.7
C(1)-N(2)-C(5)	114.0(2)	C(4)-C(3)-H(1)	108.7
C(4)-N(2)-C(5)	110.9(2)	C(7)-C(3)-H(1)	108.7
N(1)-C(1)-N(2)	116.0(2)	N(2)-C(4)-C(3)	106.0(2)
N(1)-C(1)-Au(1)	123.1(2)	N(2)-C(4)-H(8)	110.5
N(2)-C(1)-Au(1)	120.88(19)	C(3)-C(4)-H(8)	110.5
N(1)-C(2)-C(3)	113.4(2)	N(2)-C(4)-H(9)	110.5
N(1)-C(2)-H(11)	108.9	C(3)-C(4)-H(9)	110.5
C(3)-C(2)-H(11)	108.9	H(8)-C(4)-H(9)	108.7
N(1)-C(2)-H(10)	108.9	N(2)-C(5)-C(6)	106.8(2)

N(2)-C(5)-H(7)	110.4	C(13)-C(14)-C(15)	111.4(2)
C(6)-C(5)-H(7)	110.4	C(16)-C(14)-C(15)	109.9(2)
N(2)-C(5)-H(6)	110.4	C(13)-C(14)-H(15)	108.2
C(6)-C(5)-H(6)	110.4	C(16)-C(14)-H(15)	108.2
H(7)-C(5)-H(6)	108.6	C(15)-C(14)-H(15)	108.2
C(5)-C(6)-C(7)	112.5(3)	C(14)-C(15)-H(12)	109.5
C(5)-C(6)-H(5)	109.1	C(14)-C(15)-H(14)	109.5
C(7)-C(6)-H(5)	109.1	H(12)-C(15)-H(14)	109.5
C(5)-C(6)-H(4)	109.1	C(14)-C(15)-H(13)	109.5
C(7)-C(6)-H(4)	109.1	H(12)-C(15)-H(13)	109.5
H(5)-C(6)-H(4)	107.8	H(14)-C(15)-H(13)	109.5
C(6)-C(7)-C(3)	116.0(2)	C(14)-C(16)-H(17)	109.5
C(6)-C(7)-H(2)	108.3	C(14)-C(16)-H(16)	109.5
C(3)-C(7)-H(2)	108.3	H(17)-C(16)-H(16)	109.5
C(6)-C(7)-H(3)	108.3	C(14)-C(16)-H(18)	109.5
C(3)-C(7)-H(3)	108.3	H(17)-C(16)-H(18)	109.5
H(2)-C(7)-H(3)	107.4	H(16)-C(16)-H(18)	109.5
C(9)-C(8)-C(13)	122.5(3)	C(9)-C(17)-C(18)	109.6(2)
C(9)-C(8)-N(1)	118.1(3)	C(9)-C(17)-C(19)	112.2(2)
C(13)-C(8)-N(1)	119.2(2)	C(18)-C(17)-C(19)	111.2(3)
C(8)-C(9)-C(10)	118.2(3)	C(9)-C(17)-H(22)	107.9
C(8)-C(9)-C(17)	122.4(3)	C(18)-C(17)-H(22)	107.9
C(10)-C(9)-C(17)	119.4(3)	C(19)-C(17)-H(22)	107.9
C(11)-C(10)-C(9)	120.5(3)	C(17)-C(18)-H(23)	109.5
C(11)-C(10)-H(21)	119.8	C(17)-C(18)-H(25)	109.5
C(9)-C(10)-H(21)	119.8	H(23)-C(18)-H(25)	109.5
C(10)-C(11)-C(12)	120.4(3)	C(17)-C(18)-H(24)	109.5
C(10)-C(11)-H(20)	119.8	H(23)-C(18)-H(24)	109.5
C(12)-C(11)-H(20)	119.8	H(25)-C(18)-H(24)	109.5
C(11)-C(12)-C(13)	120.7(3)	C(17)-C(19)-H(27)	109.5
C(11)-C(12)-H(19)	119.7	C(17)-C(19)-H(28)	109.5
C(13)-C(12)-H(19)	119.7	H(27)-C(19)-H(28)	109.5
C(12)-C(13)-C(8)	117.7(3)	C(17)-C(19)-H(26)	109.5
C(12)-C(13)-C(14)	119.5(3)	H(27)-C(19)-H(26)	109.5
C(8)-C(13)-C(14)	122.9(3)	H(28)-C(19)-H(26)	109.
C(13)-C(14)-C(16)	110.9(2)		

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