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Synthesis and Characterization of a Gold(I) Bis(triazolylidene) Complex Featuring a Large $[(Tp^{Me2})_2K]$ anion

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Supporting information

Contents:

Experimental section

Commercially available reagents and solvents were used as received. Triazolium salt **1** and KTp^{Me2} were synthesized as reported in the literature.[1,2] All manipulations related to the synthesis of gold complexes was performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. NMR spectroscopy was obtained with a Bruker Ascend (400 MHz) spectrometer. Elemental analyses were obtained with a Thermo Finnegan CHNSO-1112 apparatus and a Perkin Elmer Series II CHNS/O 2400 instruments. X-Ray diffraction analyses were collected in an Agilent Gemini Diffractometer using Mo Kα radiation (l = 0.71073 Å). Data were integrated, scaled, sorted, and averaged using the CrysAlisPro software package. The structures we solved using direct methods, using SHELXT and refined by SHELXL full matrix least squares against F^2.[3,4] In the crystal structure of complex **3** highly disordered THF molecules were treated with the program SQUEEZE. PLATON/SQUEEZE estimated the solvent-accessible region void to occupy 875.6 Å^3 and contain 155 electrons. The electron density was modeled as 4 THF molecules (2 THF per asymmetric unit) which accounts for 160 electrons. In the crystal structure of complex **3´** highly disordered THF molecules were treated with the program SQUEEZE. PLATON/SQUEEZE estimated the solvent-accessible region void to occupy 569.4 Å^3 and contain 84 electrons. The electron density was modeled as 2 THF molecules (1 THF per asymmetric unit) which accounts for 80 electrons. All non hydrogen atoms were refined anisotropically. The position of the hydrogen atoms were kept fixed with common isotropic display parameters. The crystallographic data and some details of the data collection and refinement are given in Table 1.

Table 1. Crystallographic Data and Summary of Data Collection and Structure Refinement.

	2	**3·2THF**	**3´·THF**
Formula	$C_{18}H_{19}AuIN_3$	$C_{74}H_{98}O_2AuB_2KN_{18}$	$C_{70}H_{90}OAuB_2KN_{18}$
Fw	601.23	1529.41	1457.30
cryst syst	Monoclinic	Triclinic	Triclinic
Space group	P 21/c	P-1	P-1
T, K	293(2)	293(2)	293(2)
a, Å	9.6253(1)	14.1732(3)	14.7835(3)
b, Å	11.0961(2)	15.6010(3)	15.7197(3)
c, Å	17.7617(2)	19.7007(5)	16.7848(4)
α, deg	90	76.639(2)	82.050(2)
β, deg	94.060(1)	73.137(2)	83.870(2)
γ, deg	90	89.372(2)	87.964(2)
V, Å^3	1892.25(4)	4048.64(17)	3840.23(14)
Z	4	2	2
d_{calc} g.cm^{-3}	2.111	1.136	1.198
μ, mm^{-1}	27.428	4.223	2.017
refl collected	4003	17233	22024
$T_{\min}/T_{\max}$	0.807	0.899	0.912
N_{measd}	3424	15198	13247
$[R_{\text{int}}]$	0.0607	0.0459	0.0598
R [I > 2sigma(I)]	0.0318	0.0398	0.0370
R (all data)	0.0391	0.0455	0.0850
R_w[I > 2sigma(I)]	0.0813	0.1046	0.0755
R_w (all data)	0.0871	0.1089	0.0938
GOF	1.040	1.076	1.028

Synthesis of Complex **2**

Choloro(dimethylsulfide)gold (62 mg, 0.21 mmol), potassium hexamethyl disylazide (48 mg, 0.24 mmol) and triazolium **1** (81 mg, 0.2 mmol) were combined in a Schlenk flask and dissolved in THF

(7 mL) at -78°C. The resulting mixture was stirred for 16 h. The final clear suspension was dried under vacuum and the residue was washed with hexane (3 mL) and diethyl ether (3 mL) and further extracted with benzene. After cannula filtration and removal of the solvent the crude product is dissolved in 1 mL of DCM and precipitated by addition of 10 mL of petroleum ether. The solid is filtered and dried under vacuum yielding the title product in 87% yield (105 mg, 0.174 mmol) as white solid. Single crystals were obtained by pentane vapor diffusion into a concentrated DCM solution of the product. mp = 123-125 °C. ^{1}H-NMR ((CD_3)$_2$CO, 400 MHz): δ = 2.12 (s, 6H, CH_3), 2.38 (s, 3H, CH_3), 4.42 (s, 3H, NCH_3), 7.13 (s, 2H, CH_{ar}), 7.62 (m, 3H, CH_{ar}), 7.94-7.96 (m, 2H, C*H*ar). ^{13}C-NMR ((CD_3)$_2$CO, 100.6 MHz): δ = 16.7 (Ar*C*H$_3$), 20.3 (Ar*C*H$_3$), 38.1 (N*C*H$_3$), 126.9 (C_{ar}), 128.8 (*C*H$_{\mathrm{ar}}$), 129.1(*C*H$_{\mathrm{ar}}$), 129.8(*C*H$_{\mathrm{ar}}$), 130.1(*C*H$_{\mathrm{ar}}$), 134.4(*C*H$_{\mathrm{ar}}$), 135.9 (C_{ar}), 140.6 (C_{tz}), 146.8 (C_{ar}), 170.1 (Au=*C*). FT-IR/ATR ν_{max} cm^{-1}: 2920, 2870, 2852, 1648, 1595, 1491, 1453, 1431, 1407, 1375, 1327, 1258, 1213, 1149, 1049, 1015, 836. Found: C, 36.01; H, 3.22; N, 7.06; Calc for: $C_{18}H_{19}AuIN_3$ C, 35.96; H, 3.19; N, 6.99.

Synthesis of Complex **2a**

Potassium hexamethyl disylazide (48 mg, 0.24 mmol) and triazolium **1** (81 mg, 0.20 mmol) were combined in a Schlenk flask and dissolved in THF (7 mL) at -78°C. The resulting mixture was stirred for 30 min and then allowed to stir for 2h at room temperature. Choloro(dimethylsulfide)gold (31 mg, 0.11 mmol) in 5 mL of THF was then added and the final clear solution was stirred for 16 h. The final suspension was dried under vacuum and the residue was extracted with benzene. After removal of the solvent the crude product is dissolved in 1 mL of DCM and precipitated by addition of 10 mL of petroleum ether. The solid is filtered and dried under vacuum yielding the title product in 73% yield (71 mg, 0.081 mmol) as white solid. mp = 112-114 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ = 1.87 (s, 6H, CH_3), 2.09 (s, 6H, CH_3), 2.36 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 4.23 (s, 3H, NCH_3), 4.25 (s, 3H, NCH_3), 6.94 (s, 2H, CH$_{\mathrm{ar}}$), 7.00 (s, 2H, CH$_{\mathrm{ar}}$), 7.47-7.49 (m, 2H, CH_{ar}), 7.54-7.57 (m, 6H, CH_{ar}), 7.79-7.82 (m, 2H, CH_{ar}). ^{13}C-NMR (CDCl$_3$, 100.6 MHz): δ = 17.7 (Ar*C*H$_3$), 17.8 (Ar*C*H$_3$), 21.2 (Ar*C*H$_3$), 21.4 (Ar*C*H$_3$), 38.4 (N*C*H$_3$), 38.7, 125.8 (C$_{\mathrm{ar}}$), 126.1 (C_{ar}), 128.3 (*C*H$_{\mathrm{ar}}$), 129.16 (*C*H$_{\mathrm{ar}}$), 129.18 (*C*H$_{\mathrm{ar}}$), 129.2 (*C*H$_{\mathrm{ar}}$), 129.4 (*C*H$_{\mathrm{ar}}$), 129.5 (*C*H$_{\mathrm{ar}}$), 129.6 (*C*H$_{\mathrm{ar}}$), 130.39 (*C*H$_{\mathrm{ar}}$), 130.41 (*C*H$_{\mathrm{ar}}$), 134.2 (C_{ar}), 135.4 (C_{ar}), 140.3 (C_{tz}), 140.6 (C_{tz}), 146.7 (C_{ar}), 148.3 (C_{ar}), 173.8 (Au=*C*). FT-IR/ATR ν_{max} cm^{-1}: 2904, 2900, 2857, 1768, 1602, 1491, 1453, 1398, 1388, 1375, 1342, 1306, 1287, 1249, 1109, 1045, 934, 787. Found: C, 54.77; H, 4.61; N, 10.39; Calc for: $C_{36}H_{38}AuClN_6$ C, 54.93; H, 4.87; N, 10.68.

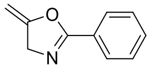
Synthesis of Complex **3**

Method A: Complex **2** (120 mg, 0.20 mmol) and KTp$^{\mathrm{Me2}}$ (70 mg, 0.20 mmol) were combined in a Schlenk flask and dissolved in THF (10 mL) at room temperature. The resulting mixture was stirred for 16 h. The final white suspension was filtered to remove the solids and the filtrate was dried under vacuum. The residue was recrystallized by pentane vapor diffusion into a concentrated THF solution of the crude providing the pure product as colorless crystals in 39% yield (54 mg, 0.039 mmol).

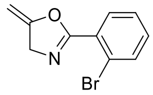
Method B: Complex **2a** (88 mg, 0.10 mmol) and KTp$^{\mathrm{Me2}}$ (70 mg, 0.20 mmol) were combined in a Schlenk flask and dissolved in THF (10 mL) at room temperature. The resulting mixture was stirred for 16 h. The final white suspension was filtered to remove the solids and the filtrate was dried under vacuum. The residue was recrystallized by pentane vapor diffusion into a concentrated THF solution of the crude providing the pure product as colorless crystals in 81% yield (112 mg, 0.081 mmol). mp = 178-180 °C. ^{1}H-NMR ($(CD_3)_2CO$, 400 MHz): δ = 1.89 (s, 12H, C*H*$_3$), 2.19 (s, 32H, NC*H*$_{3pyr}$), 2.47, (s, 6H, C*H*$_3$), 4.38 (s, 6H, NC*H*$_3$), 5.77 (s, 6H, C*H*), 7.11 (s, 4H, C*H*$_{ar}$), 7.53-7.57 (m, 3H, C*H*$_{ar}$), 7.61-7.63 (m, 3H, C*H*$_{ar}$), 7.73-7.76 (m, 4H, C*H*$_{ar}$). ^{13}C-NMR ($(CD_3)_2CO$, 100.6 MHz): δ = 11.3 (Ar*C*H$_3$), 16.5 (N*C*H$_{3pyr}$), 20.5 (Ar*C*H$_3$), 38.1 (NCH$_3$), 103.2 (*C*H$_{pyr}$), 126.7 (*C*$_{ar}$), 128.8 (*C*H$_{ar}$), 129.10 (*C*H$_{ar}$), 129.13 (*C*H$_{ar}$), 129.4 (*C*$_{ar}$), 129.6 (*C*H$_{ar}$), 129.8(*C*H$_{ar}$), 130.1 (*C*$_{pyr}$), 134.3 (*C*$_{tz}$), 140.4 (*C*$_{ar}$), 173.2 (Au=*C*). FT-IR/ATR ν_{max} cm^{-1}: 2907, 2900, 2876, 1712, 1695, 1518, 1503, 1472, 1424, 1381, 1367, 1300, 1243, 1249, 1197, 1015, 866. Found: C, 56.92; H, 5.75; N, 18.56; Calc for: $C_{66}H_{88}AuB_2KN_{18}$ C, 57.23; H, 5.97; N, 18.20.

General procedure for the catalytic cyclization of propargylated amides using complexes **2** and **3a**

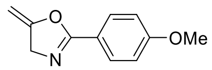
Complex **2** (1 mol%), $AgBF_4$ (1 mol%) (or solely complex **3**, 1 mol%) and 3 mL of dry dichloromethane were charged in a 5 ml screw capped scintillation vial. After the mixture was stirred 10 min, the proper propargylated amide was added (1 mmol) and the mixture stirred for 48 h ar room temperature. The solvent was removed under vaccum and the residue was extracted with diethyl ether, washed with brine, and dried with Na_2SO_4. The organic layer was evaporated and the crude product was purified by silica gel column using ethyl acetate/petroleum ether as eluent. NMR spectroscopic data is consistent with the literature reported values.[5]



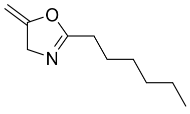
Isolated in 93% yield (148 mg, 0.093 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.37 (t, *J* = 2.7 Hz, 1H), 4.65 (t, *J* = 2.8 Hz, 2H), 4.82 (d, *J* = 2.9 Hz, 1H), 7.44 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.90-8.05 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz,) δ = 57.8, 83.8, 126.8, 128.0, 128.5, 131.8, 158.9, 163.7.



Isolated in 89% yield (212 mg, 0.089 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.39 (q, *J* =2.7 Hz, 1H), 4.72 (t, *J* = 2.9 Hz, 2H), 4.74-4.86 (m, 1H), 7.36 (dtd, *J* = 17.2, 7.5, 1.5 Hz, 2H), 7.69 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.78 (dd, *J* = 7.6, 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz,) δ 58.2, 84.1, 121.9, 127.2, 128.4, 131.5, 132.1, 134.3, 158.4, 162.6.



Isolated in 94% yield (178 mg, 0.094 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz,) δ = 3.86 (s, 3H), 4.34 (d, *J* = 2.6 Hz, 1H), 4.62 (t, *J* = 2.8 Hz, 2H), 4.79 (d, *J* = 2.9 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 7.92 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ = 55.4, 57.7, 83.4, 113.9, 119.3, 123.9, 127.6, 129.8, 159.0, 162.4, 163.5.



Isolated in 85% yield (142 mg, 0.085 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.64 (q, *J* = 3.0 Hz, 1H), 4.40 (dq, *J* = 4.3, 1.5 Hz, 2H), 4.24 (q, *J* = 2.6 Hz, 1H), 2.34 (dd, *J* = 10.9, 4.5 Hz, 2H), 1.76 – 1.64 (m, 2H), 1.35 - 1.26 (m, 6H), 0.92 - 0.83 (m, 5H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ = 14.0, 22.5, 25.5, 28.2, 28.8, 31.4, 57.2, 82.6, 159.6, 167.6.

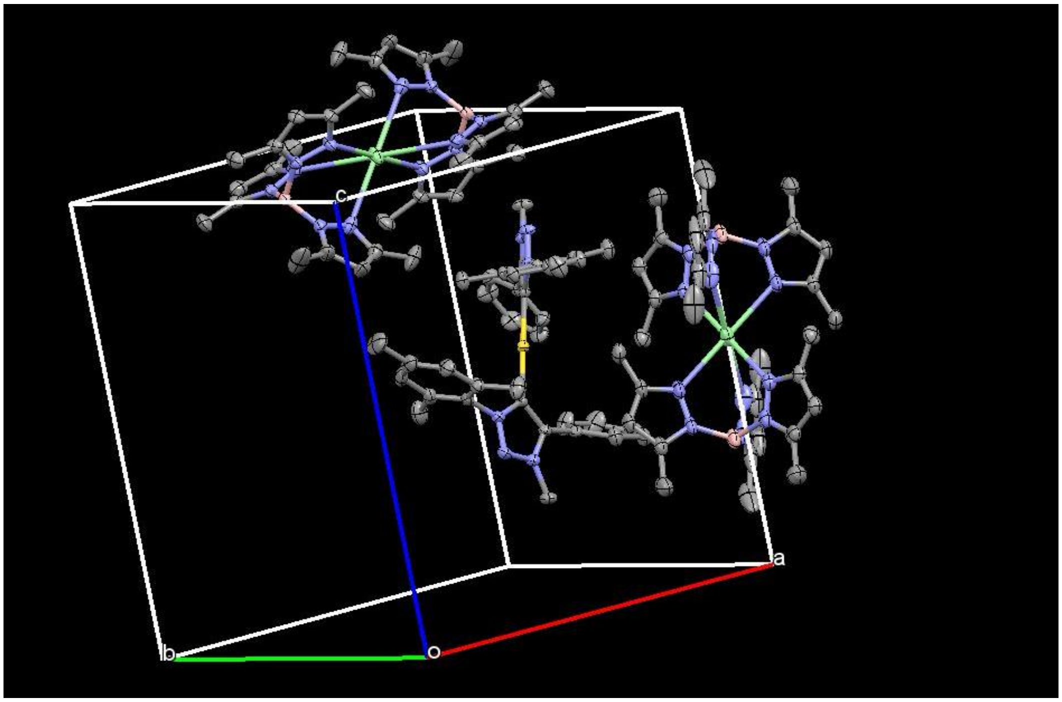


Figure S1. Molecular structure of complex **3´** (obtained from optimized procedure) showing cell axes. Ellipsoids shown at 30% probability. Hydrogen atoms ommited for clarity.

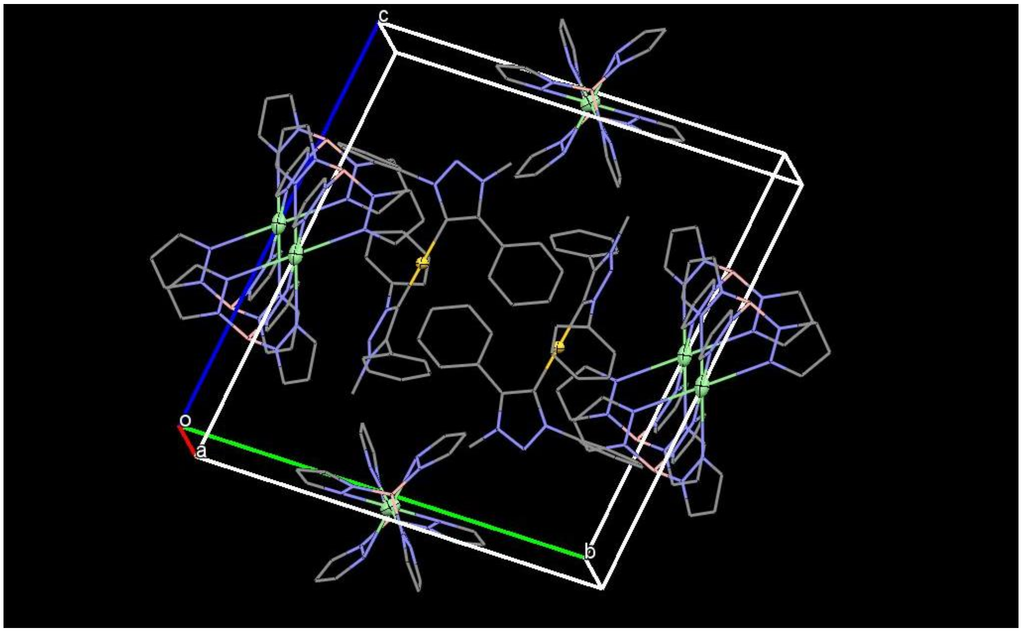


Figure S2. Packing of the crystal structure of complex **3´** (obtained from optimized procedure). Ellipsoids shown at 30% probability. Methyl groups on Tp and mesityl fragments ommited for clarity.

References:

1) S. C. Sau, S. R. Roy and S. K. Mandal, *Chem. Asian J.*, 2014, **10**, 2806.
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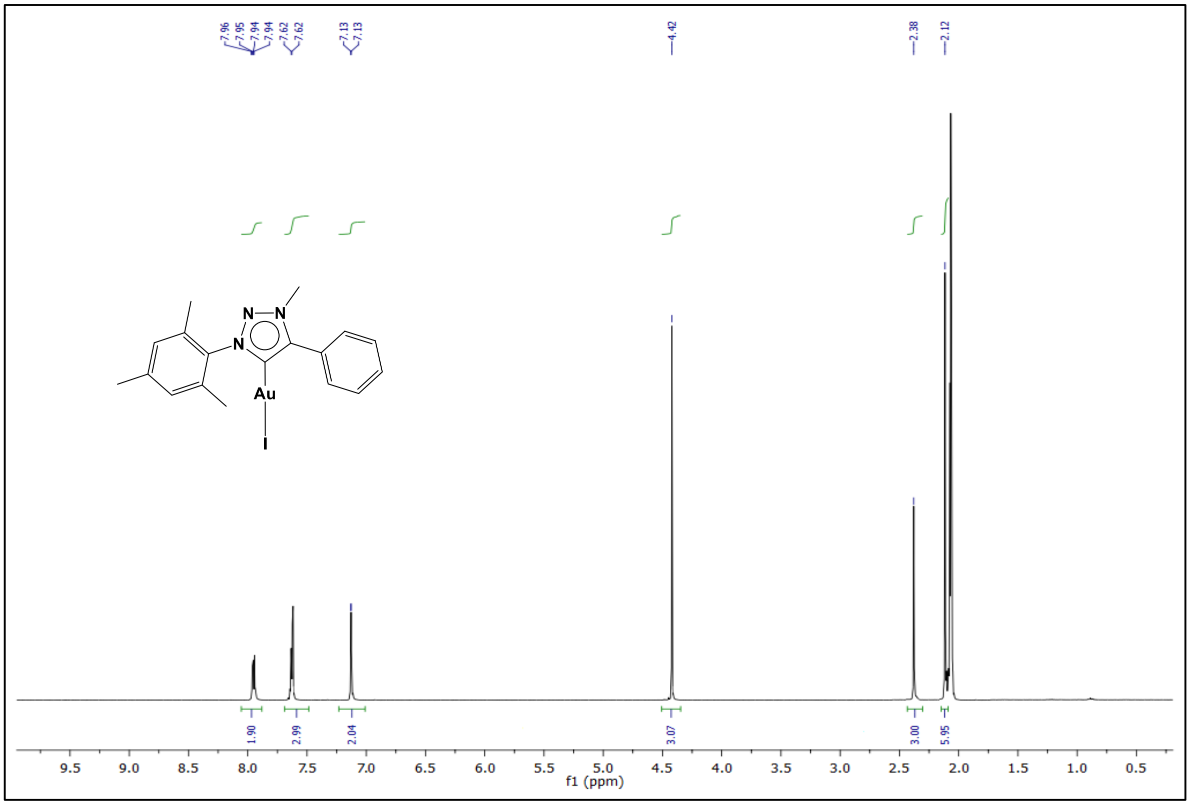
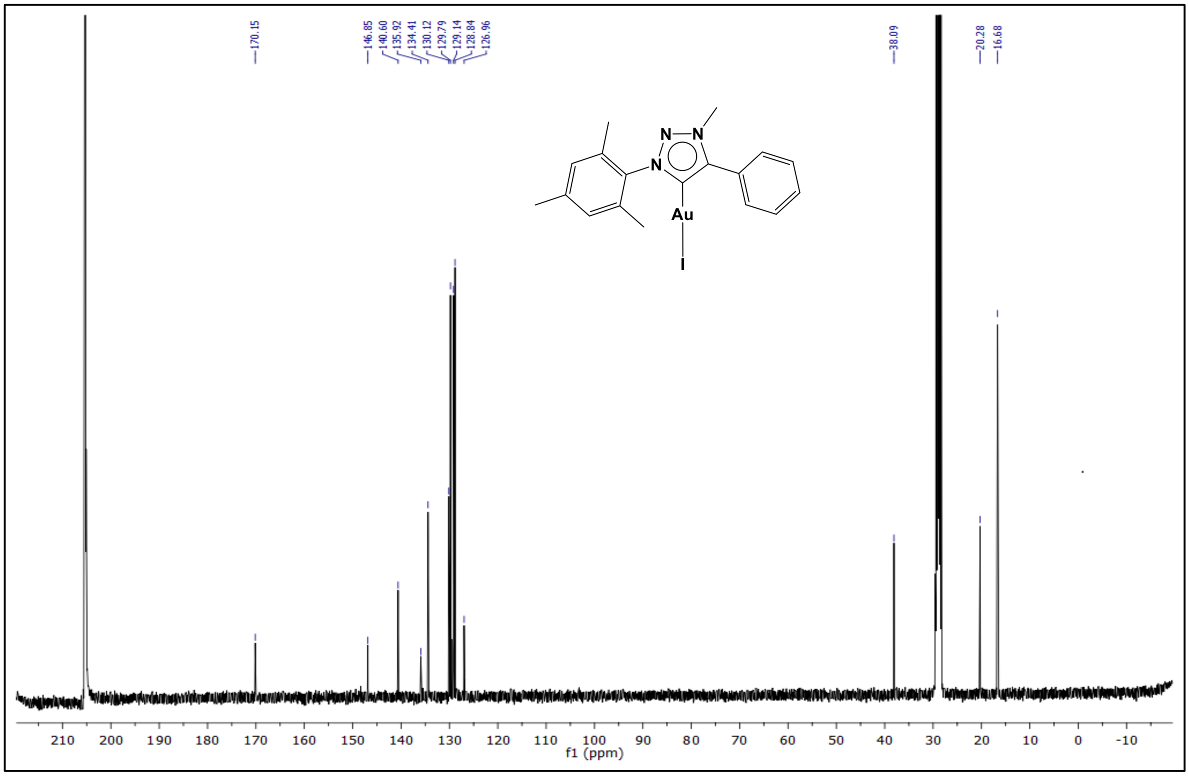
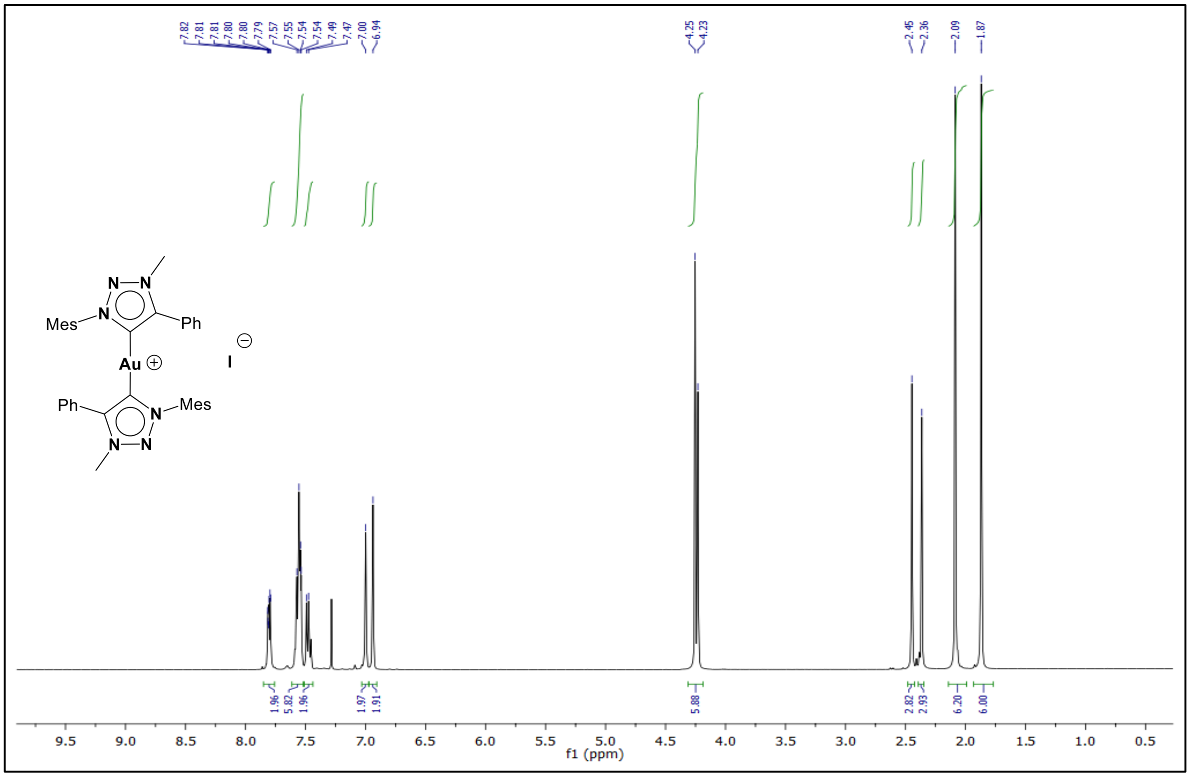


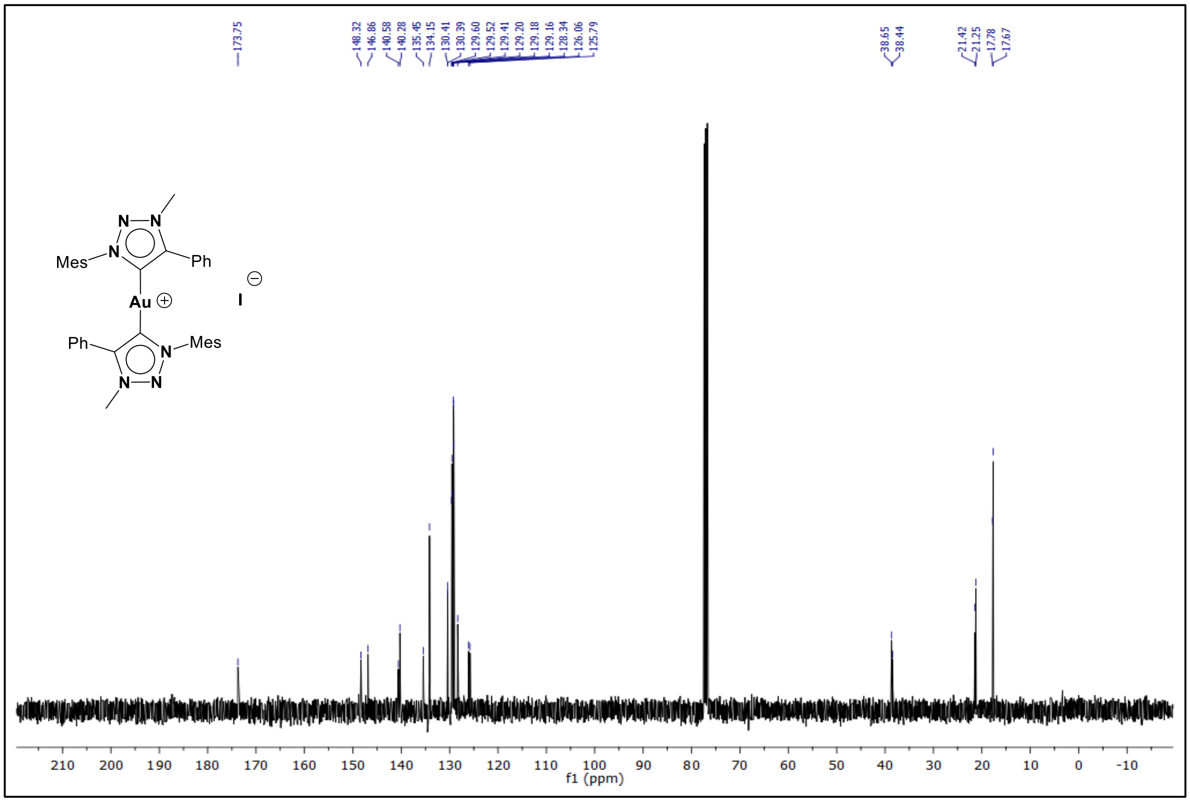
^{1}H-NMR (400 MHz) spectra for complex **2** in $(CD_3)_2CO$



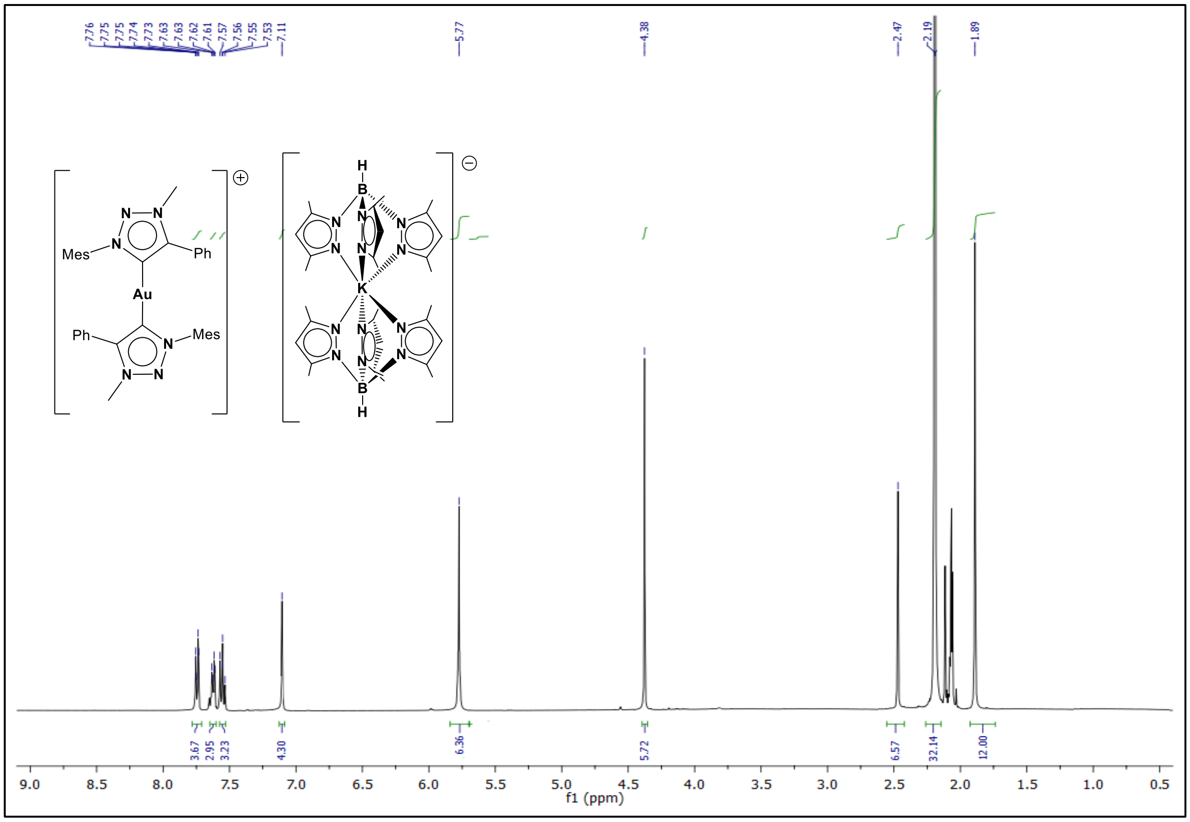
^{13}C-NMR (100 MHz) spectra for complex **2** in $(CD_3)_2CO$



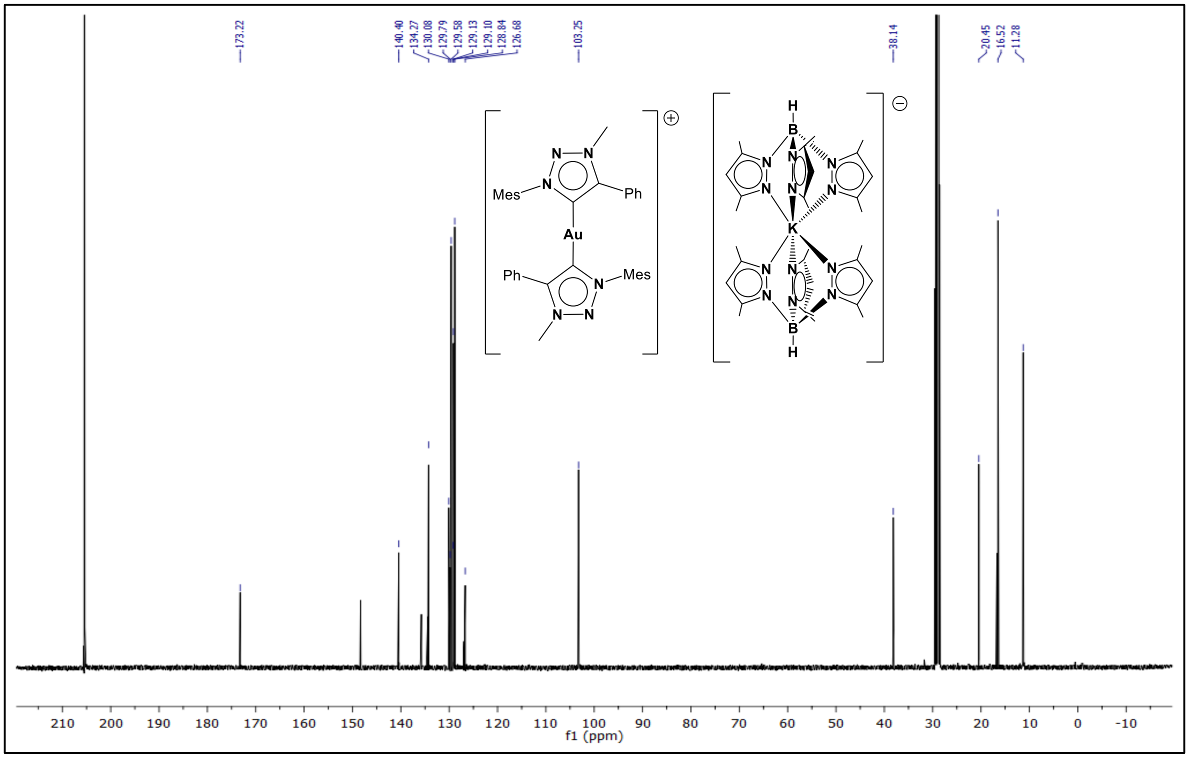
^{1}H-NMR (400 MHz) spectra for complex **2a** in $CDCl_3$



^{13}C-NMR (100 MHz) spectra for complex **2a** in $CDCl_3$



^{1}H-NMR (400 MHz) spectra for complex **3** in $(CD_3)_2CO$



^{13}C-NMR (100 MHz) spectra for complex **3** in $(CD_3)_2CO$