2,2':6',2''-Terpyridine switches from tridentate to monodentate coordination in a gold(III) terpy complex upon reaction with sodium azide

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Supporting Information

Experimental Section

General procedures. Potassium tetrachloroaurate(III) was obtained from Strem. All other chemicals were purchased from commercial sources and used as received. 2,2':6',2"-Terpyridine was prepared according to a published procedure.[1] **Caution: Azides and azido complexes can violently decompose. Synthesis should only be performed on a very small scale (< 50 mg) and in particular heating of solid compounds avoided, as the gold(III) azido complex exploded upon scratching with a metal spatula.** NMR spectra were recorded at room temperature (298 K) on Bruker Avance 200, 400, and 500 spectrometers (^{1}H at 199.93 and 500.13 MHz, respectively; ^{13}C at 100.68 and 125.76 MHz). Solution chemical shifts δ in ppm represent a downfield shift relative to tetramethylsilane (TMS) and were referenced relative to the signal of the solvent.[2] Coupling constants J are given in Hertz. Peak multiplicities are marked as singlet (s), doublet (d), doublet of doublet (dd), doublet of doublet of doublet (ddd), doublet of triplet (dt), triplet (t), and multiplet (m), respectively. IR spectra of pure solid samples were recorded on a Nicolet 380 FT-IR spectrometer fitted with a smart iTR ATR accessory. The elemental composition of the compounds was determined with an Elementar Vario MICRO cube CHN analyser. Addition of V_2O_5 was usually required to obtain proper results in the case of the metal complexes.

Synthesis of [AuCl(terpy-κ^3-$N^{1,1',1''}$)]Cl$_2$·2H$_2$O. 2,2':6',2''-Terpyridine (116 mg, 0.50 mmol) was dissolved in acetonitrile (15 mL) under nitrogen to afford a clear colourless solution. Then, potassium tetrachloroaurate(III) (126 mg, 0.33 mmol) in water (15 mL) was added dropwise to the colourless solution. After stirring at room temperature for 1 h, the mixture was heated to reflux for 44 h. The resulting solution was cooled to room temperature and filtered. Then, the filtrate was evaporated to dryness to give an amber solid, which was washed with acetone (10 mL) and dried under vacuum for 1 d. Yield: 148 mg (0.28 mmol, 85%). **IR** (ATR): $\tilde{\nu}$ = 3374 (w), 1605 (s), 1467 (m), 1457 (s), 1349 (m), 1245 (m), 1036 (m), 769 (m), 753 (m) cm^{-1}; ^{1}**H NMR** (199.93 MHz, DMSO-d_6): δ = 8.77 (ddd, 2H, $^3J_{H6,H5/H6'',H5''}$ = 4.8 Hz, $^4J_{H6,H4/H6'',H4''}$ = 1.6 Hz, $^5J_{H6,H3/H6'',H3''}$ = 0.7 Hz, H6/H6''), 8.71 (d, 2H, $^3J_{H3,H4/H3'',H4''}$ = 8.0 Hz, H3/H3''), 8.49 (d, 2H, $^3J_{H3'/H5',H4'}$ = 7.9 Hz, H3'/H5'), 8.20–8.08 (m, 3H, H4/H4'/H4''), 7.59 (ddd, 2H, $^3J_{H5,H4/H5'',H4''}$ = 7.5 Hz, $^3J_{H5,H6/H5'',H6''}$ = 4.9 Hz, $^4J_{H5,H3/H5'',H3''}$ = 1.1 Hz, H5/H5''); ^{13}**C NMR** (100.68 MHz, DMSO-d_6): δ = 153.87 (C2'/C6'), 153.82 (C2/C2''), 148.48 (C6/C6''), 138.94 (C4/C4''), 138.83 (C4'), 124.94 (C5/C5''), 121.45 (C3/C3'', C3'/C5') ppm; **Elemental analysis** calcd. (%) for $C_{15}H_{11}AuCl_3N_3\cdot(H_2O)_2$: C 31.46, H 2.64, N 7.34; found (%): C 31.11, H 2.64, N 7.30.

Crystal structure determination. A crystal suitable for single-crystal X-ray diffraction was selected, coated in perfluoropolyether oil, and mounted on a MiTeGen sample holder. Diffraction data of **[Au(N$_3$)$_3$(terpy-κ^1-N^1)]** was collected on a Bruker X8-APEX II 4-circle diffractometer with a CCD area detector using multi-layer mirror monochromated Mo$_{K\alpha}$ radiation. The crystal was cooled using an Oxford Cryostreams low-temperature device. Data was collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structure was solved using the intrinsic phasing method (ShelXT)[3] and Fourier expansion techniques. All non-hydrogen atoms were refined in anisotropic approximation with hydrogen atoms "riding" in idealized positions, by full-matrix least squares against F^2 of all data, using the ShelXL software.[4] Crystal data and experimental details are listed in Table S1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1918121. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

DFT calculations. Density functional theory calculations were carried out on the Linux cluster of the Leibniz-Rechenzentrum (LRZ) in Munich with ORCA version 4.0.0.2[5] using the BP86 functional, a ZORA-def2-TZVP basis set on the light atoms and SARC-ZORA-TZVP on gold[6] together with `AutoAux`, the `tightscf`, `grid4`, and `DIISMaxEq 15` options, and the CPCM solvation model with water or acetone as the solvent for geometry optimizations and subsequent calculation of vibrational frequencies to characterize the structures obtained as minima by inspection for absence of imaginary modes. Graphics were created with gOpenmol.

References

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Table S1. Single-crystal X-ray diffraction data and structure refinement of **[Au(N₃)(terpy-κ¹-*N¹*)]**.

| CCDC	1918121
Formula	$C_{15}H_{11}AuN_{12}$
M_r (g·mol^{-1})	556.32
ρ_x (g·cm^{-3})	2.171
$F(000)$	2112
T (K)	100(2)
Radiation, λ (Å)	Mo$_{K\alpha}$ 0.71073
μ (mm^{-1})	8.674
Crystal size (mm)	$0.32 \times 0.33 \times 0.60$
Crystal colour, habit	orange-red block
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	16.174(7)
b (Å)	10.772(5)
c (Å)	19.565(8)
α (°)	90
β (°)	92.84(2)
γ (°)	90
V (Å^3)	3405(2)
Z	8
θ range (°)	2.084–26.022
Reflections collected	19200
Unique reflections	3350
Parameters / restraints	253 / 0
GooF on F^2	1.190
R_1 indices [$I>2\sigma(I)$]	0.0252
wR^2 (all data)	0.0607
Maximum/minimum residual electron density (e·Å^{-3})	1.317 / −1.380
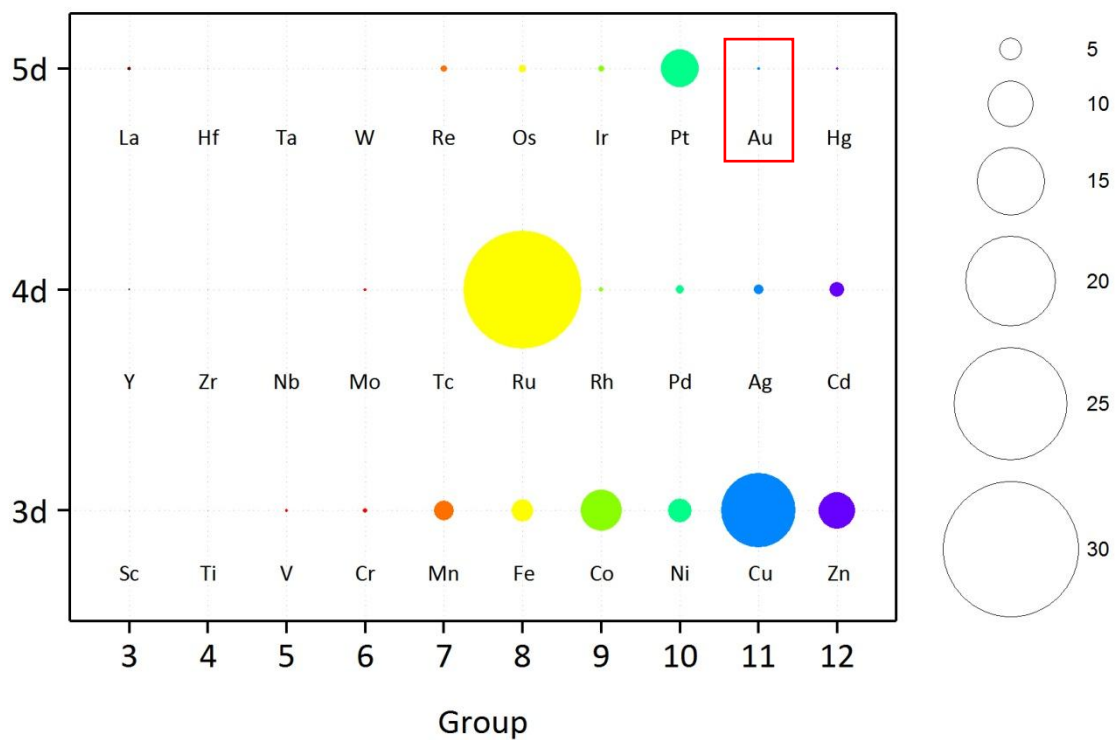
Figure S1. Bubble plot showing the relative abundancy (in %) of transition metal terpyridine complexes characterized by X-ray structure analysis across the periodic table. Data was obtained from the Cambridge Structural Database (CSD). The red box highlights the gold complexes in the focus of this study.

Spectroscopic data for [AuCl(terpy-κ^3-$N^{1,1',1''}$)]Cl$_2$·2H$_2$O
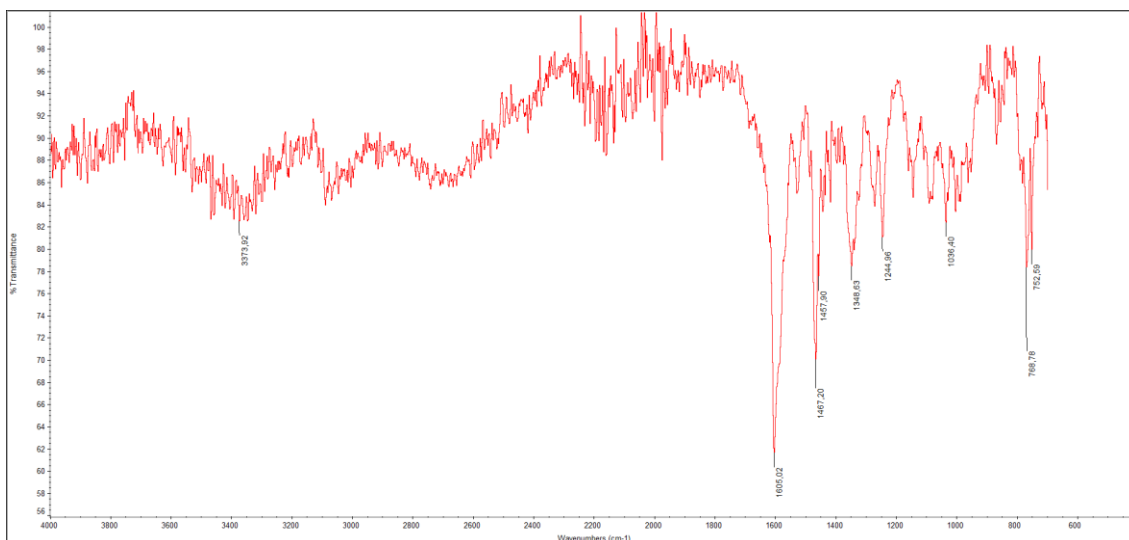
Figure S2. ATR IR spectrum of [AuCl(terpy-κ^3-$N^{1,1',1''}$)]C1$_2$·2H$_2$O
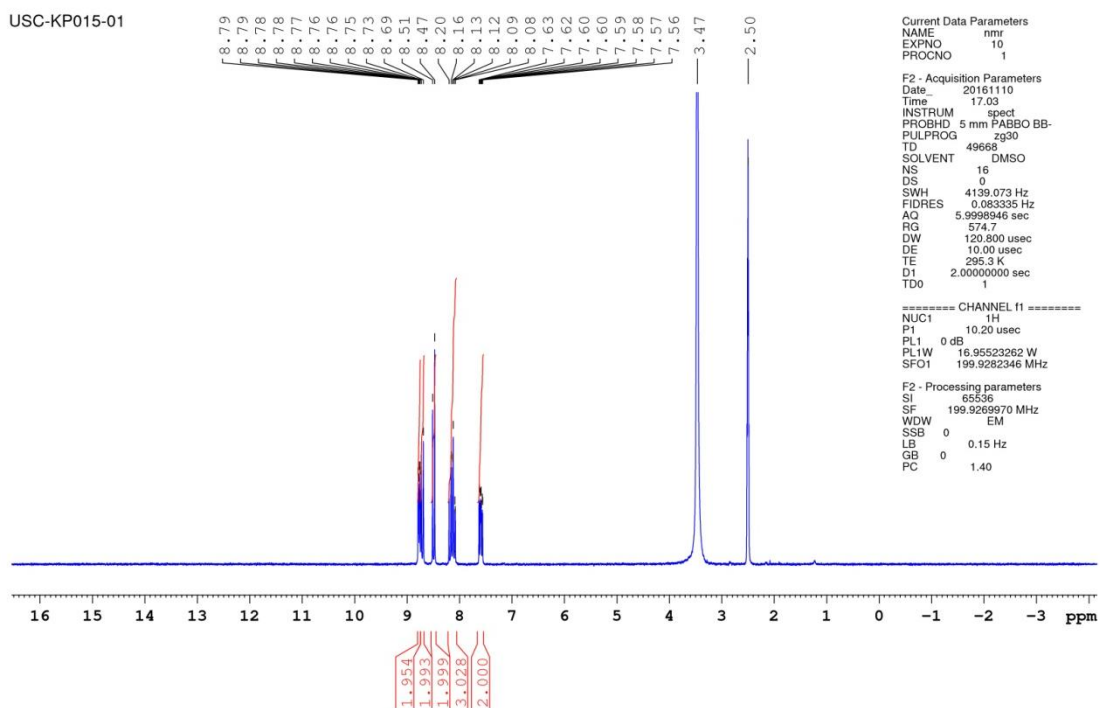
Figure S3. 199.93 MHz ^{1}H NMR spectrum of [AuCl(terpy-κ^3-$N^{1,1',1''}$)]C1$_2$·2H$_2$O in DMSO-d_6 (full range).

USC-KP015-01
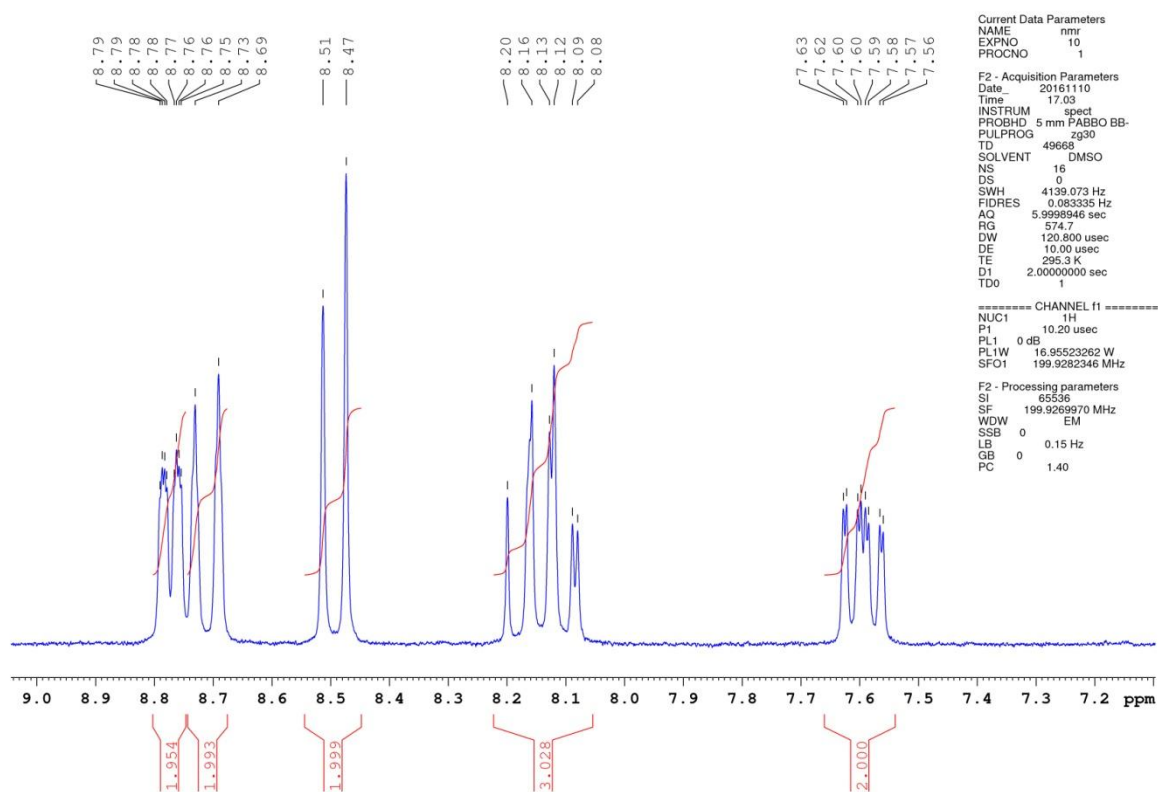
Figure S4. 199.93 MHz ^{1}H NMR spectrum of [AuCl(terpy-κ^3-$N^{1,1',1''}$)]Cl$_2$·2H$_2$O in DMSO-d_6 (aromatic region only).

USC-KP015-01
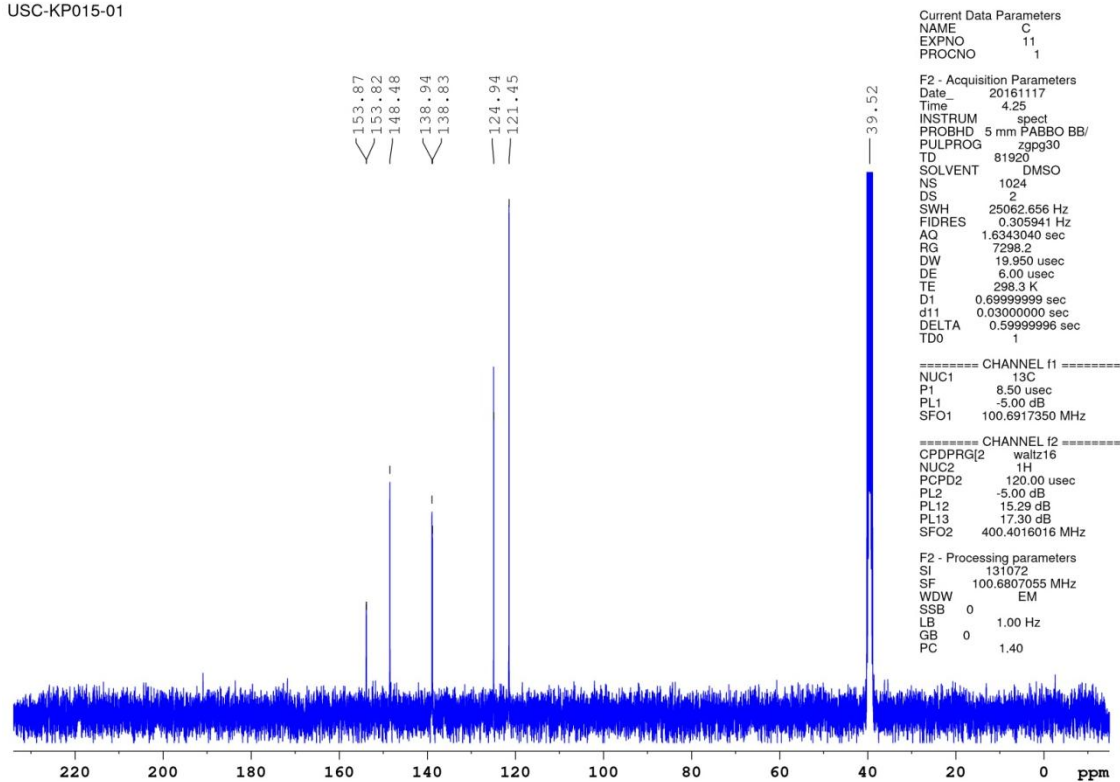
Figure S5. 100.68 MHz ^{13}C NMR spectrum of [AuCl(terpy-κ^3-$N^{1,1',1''}$)]Cl$_2$·2H$_2$O in DMSO-d_6 (full range).
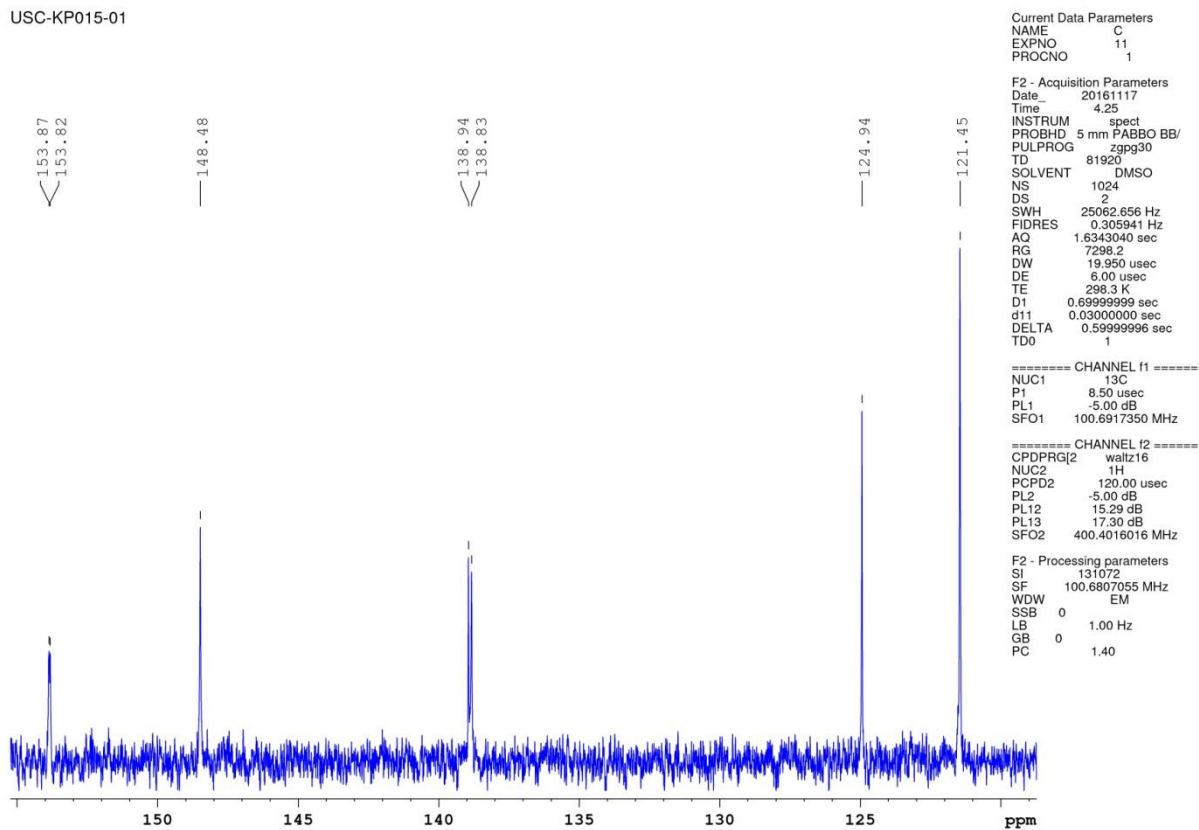
Figure S6. 100.68 MHz ^{13}C NMR spectrum of [AuCl(terpy-κ^3-$N^{1,1',1''}$)]Cl$_2$·2H$_2$O in DMSO-d_6 (aromatic region only).

Spectroscopic data for [Au(N$_3$)$_3$(terpy-κ^1-N^1)]
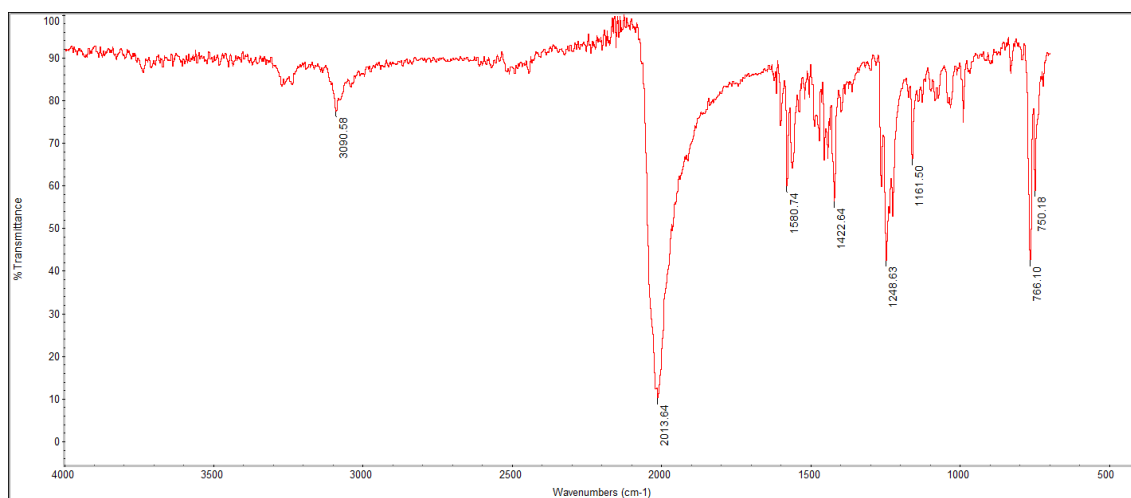
Figure S7. ATR IR spectrum of [Au(N$_3$)$_3$(terpy-κ^1-N^1)]
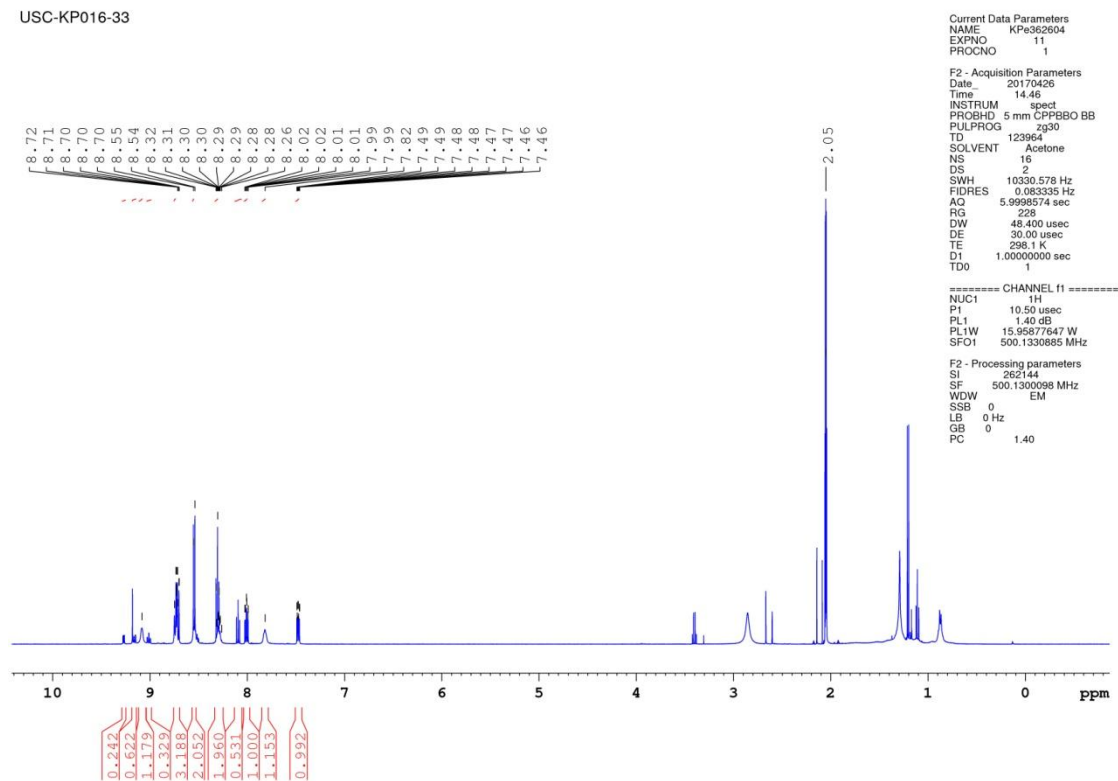
Figure S8. 500.13 MHz ^{1}H NMR spectrum of [Au(N$_3$)$_3$(terpy-κ^1-N^1)] in acetone-d_6 (full range).
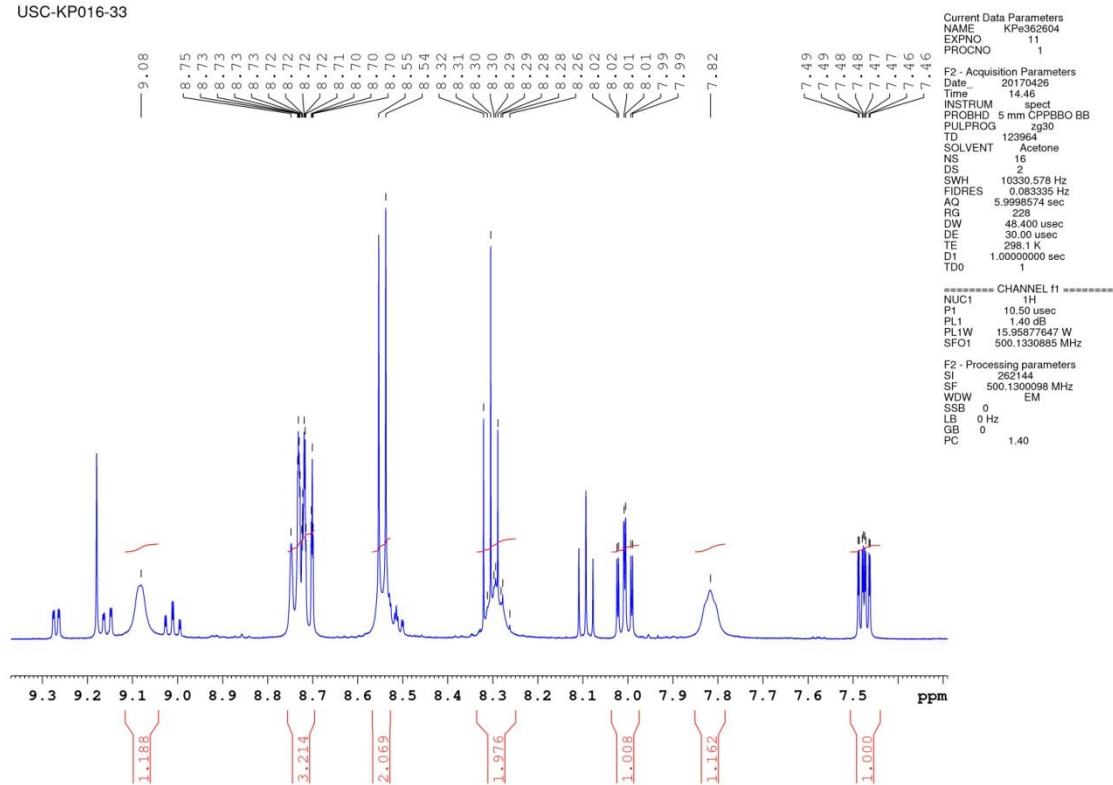
Figure S9. 500.13 MHz ¹H NMR spectrum of [Au(N₃)₃(terpy-κ¹-*N*¹)] in acetone-*d*₆ (aromatic region, major species).
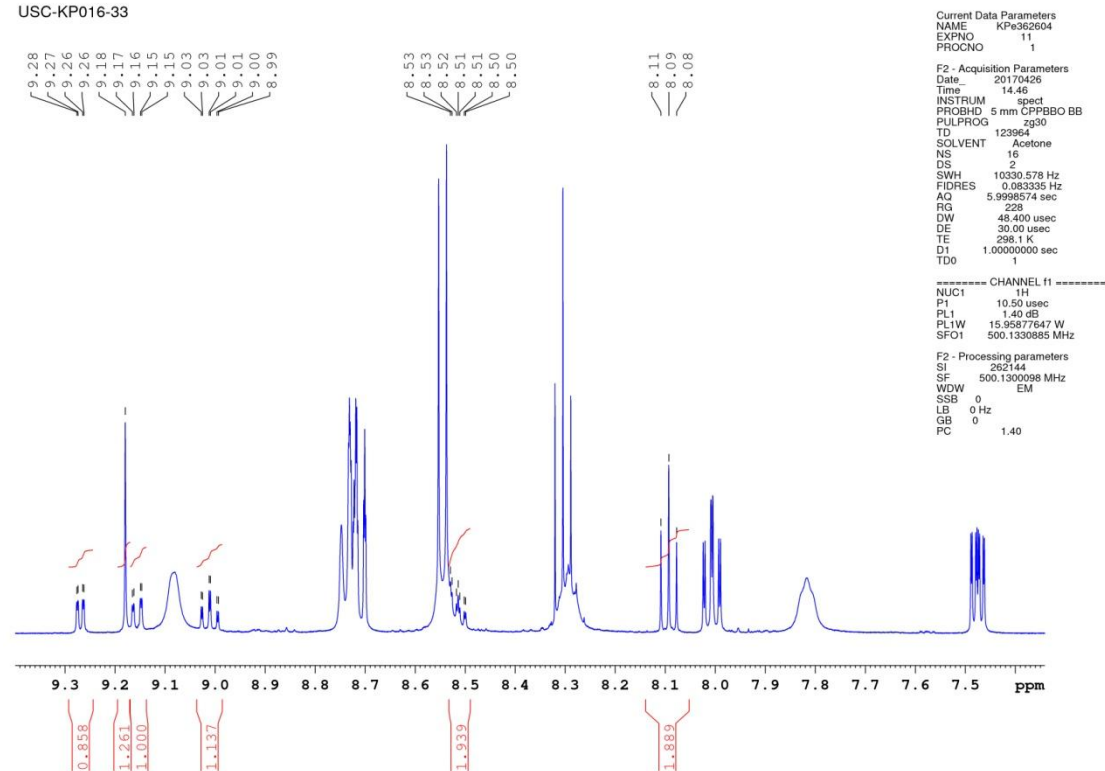
Figure S10. 500.13 MHz ¹H NMR spectrum of [Au(N₃)₃(terpy-κ¹-*N*¹)] in acetone-*d*₆ (aromatic region, minor species).

Current Data Parameters
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EXPNO   10
PROCNO   1

F2 - Acquisition Parameters
Date_   20170426
Time   14.42
INSTRUM   spect
PROBHD 5 mm CPPBBO BB
PULPROG   zgpg30
TD   125604
SOLVENT   Acetone
NS   512
DS   0
SWH   35211.270 Hz
FIDRES   0.280336 Hz
AQ   1.7835768 sec
RG   1150
DW   14.200 usec
DE   25.00 usec
TE   298.1 K
D1   2.00000000 sec
D11   0.03000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   13C
P1   9.60 usec
PL1   1.20 dB
PL1W   60.59365082 W
SFO1   125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG[2   waltz16
NUC2   1H
PCPD2   90.00 usec
PL2   1.40 dB
PL12   20.06 dB
PL13   22.00 dB
PL2W   15.95877647 W
PL12W   0.21726994 W
PL13W   0.13899513 W
SFO2   500.1320005 MHz

F2 - Processing parameters
SI   262144
SF   125.7576765 MHz
WDW   EM
SSB   0
LB   0.50 Hz
GB   0
PC   1.00

Figure S11. 125.76 MHz ^{13}C NMR spectrum of [Au(N$_3$)$_3$(terpy-κ^1-N^1)] in acetone-d_6 (full range).

Current Data Parameters
NAME   KPe362604
EXPNO   10
PROCNO   1

F2 - Acquisition Parameters
Date_   20170426
Time   14.42
INSTRUM   spect
PROBHD 5 mm CPPBBO BB
PULPROG   zgpg30
TD   125604
SOLVENT   Acetone
NS   512
DS   0
SWH   35211.270 Hz
FIDRES   0.280336 Hz
AQ   1.7835768 sec
RG   1150
DW   14.200 usec
DE   25.00 usec
TE   298.1 K
D1   2.00000000 sec
D11   0.03000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   13C
P1   9.60 usec
PL1   1.20 dB
PL1W   60.59365082 W
SFO1   125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG[2   waltz16
NUC2   1H
PCPD2   90.00 usec
PL2   1.40 dB
PL12   20.06 dB
PL13   22.00 dB
PL2W   15.95877647 W
PL12W   0.21726994 W
PL13W   0.13899513 W
SFO2   500.1320005 MHz

F2 - Processing parameters
SI   262144
SF   125.7576765 MHz
WDW   EM
SSB   0
LB   0.50 Hz
GB   0
PC   1.00

Figure S12. 125.76 MHz ^{13}C NMR spectrum of [Au(N$_3$)$_3$(terpy-κ^1-N^1)] in acetone-d_6

(aromatic region, major species).

S11
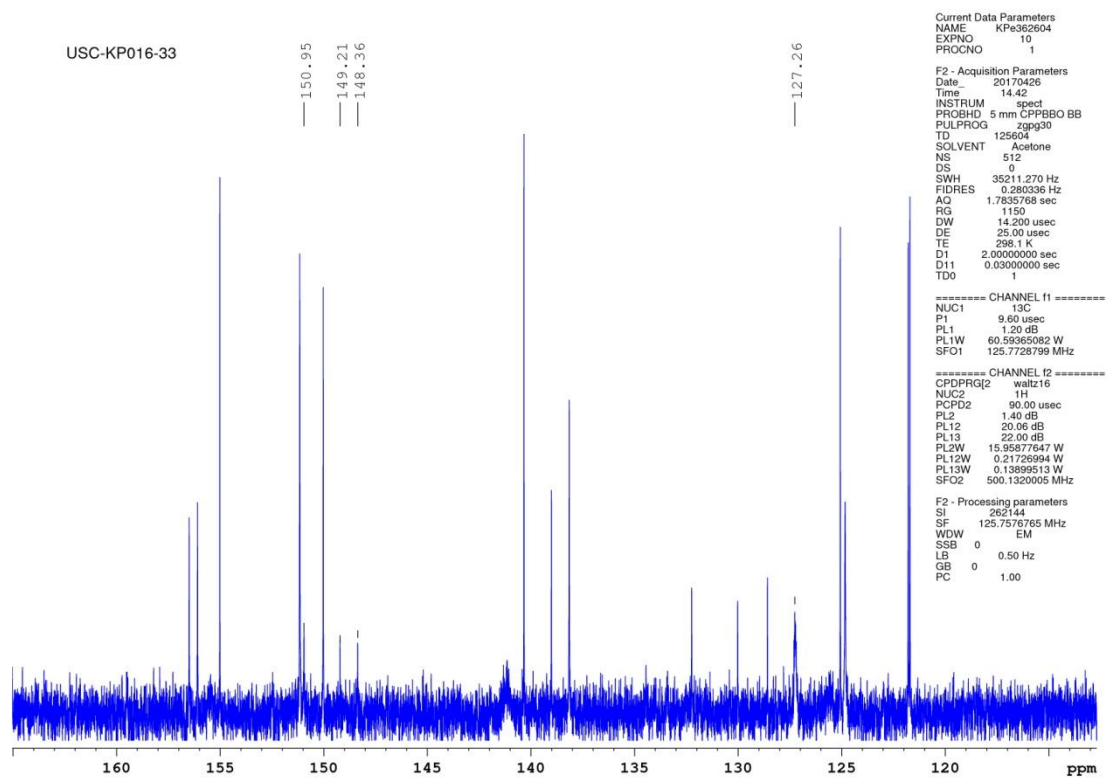
Figure S13. 125.76 MHz ^{13}C NMR spectrum of [Au(N$_3$)$_3$(terpy-κ^1-N^1)] in acetone-d_6 (aromatic region, minor species).