Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION – XYZ STRUCTURES

Bond analysis

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  56
[(N^C^N)Au(III)CO]+ OPT C2v -  Figure 1
  N          0.000000    0.000000    1.258783
  C          1.215366    0.000000    1.893205
  C          1.215727    0.000000    3.293623
  C          0.000000    0.000000    3.980650
  C         -1.215727    0.000000    3.293623
  C         -1.215366    0.000000    1.893205
  C          2.367224    0.000000    0.994432
  C          3.702240    0.000000    1.436796
  C          4.749633    0.000000    0.520720
  C          4.519776    0.000000   -0.869845
  C          3.173766    0.000000   -1.306186
  C          2.114445    0.000000   -0.401346
  Au         0.000000    0.000000   -0.769057
  C          0.000000    0.000000   -2.709855
  O          0.000000    0.000000   -3.848038
  C         -2.367224    0.000000    0.994432
  C         -2.114445    0.000000   -0.401346
  C         -3.173766    0.000000   -1.306186
  C         -4.519776    0.000000   -0.869845
  C         -4.749633    0.000000    0.520720
  C         -3.702240    0.000000    1.436796
  H          5.767466    0.000000    0.899580
  H          2.973756    0.000000   -2.372228
  H          3.928708    0.000000    2.499773
  H          2.155938    0.000000    3.832889
  H         -2.973756    0.000000   -2.372228
  H          0.000000    0.000000    5.067326
  H         -2.155938    0.000000    3.832889
  H         -3.928708    0.000000    2.499773
  H         -5.767466    0.000000    0.899580
  C         -5.712656    0.000000   -1.850487
  C          5.712656    0.000000   -1.850487
  C          5.263488    0.000000   -3.331713
  C          6.579473    1.270142   -1.600374
  C          6.579473   -1.270142   -1.600374
  H          6.147692    0.000000   -3.979070
  H          4.675162   -0.891633   -3.581832
  H          4.675162    0.891633   -3.581832
  H          7.435315   -1.273551   -2.286680
  H          6.971592   -1.301946   -0.577711
  H          5.999701   -2.185510   -1.771844
  H          7.435315    1.273551   -2.286680
  H          5.999701    2.185510   -1.771844
  H          6.971592    1.301946   -0.577711
  C         -5.263488    0.000000   -3.331713
  H         -6.147692    0.000000   -3.979070
```

H	-4.675162	0.891633	-3.581832
H	-4.675162	-0.891633	-3.581832
C	-6.579473	1.270142	-1.600374
C	-6.579473	-1.270142	-1.600374
H	-6.971592	-1.301946	-0.577711
H	-7.435315	-1.273551	-2.286680
H	-5.999701	-2.185510	-1.771844
H	-6.971592	1.301946	-0.577711
H	-5.999701	2.185510	-1.771844
H	-7.435315	1.273551	-2.286680

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[(Idipp)Au(I)CO]$^+$ OPT C2V – Figure S1

N	0.000000	1.089867	-2.880028
C	0.000000	0.682223	-4.207877
C	0.000000	-0.682223	-4.207877
N	0.000000	-1.089867	-2.880028
C	0.000000	2.488528	-2.442045
C	0.000000	-2.488528	-2.442045
C	0.000000	0.000000	-2.057975
Au	0.000000	0.000000	-0.003257
C	0.000000	0.000000	1.964365
O	0.000000	0.000000	3.100542
H	0.000000	-1.391384	-5.021525
H	0.000000	1.391384	-5.021525
C	1.244824	-3.131590	-2.255589
C	1.209428	-4.475593	-1.849129
C	0.000000	-5.139728	-1.647083
C	-1.209428	-4.475593	-1.849129
C	-1.244824	-3.131590	-2.255589
C	2.594396	-2.443528	-2.491837
H	2.143486	-5.009586	-1.694147
H	0.000000	-6.181065	-1.335224
H	-2.143486	-5.009586	-1.694147
C	-2.594396	-2.443528	-2.491837
C	-1.244824	3.131590	-2.255589
C	-1.209428	4.475593	-1.849129
C	0.000000	5.139728	-1.647083
C	1.209428	4.475593	-1.849129
C	1.244824	3.131590	-2.255589
C	-2.594396	2.443528	-2.491837
H	-2.143486	5.009586	-1.694147
H	0.000000	6.181065	-1.335224
H	2.143486	5.009586	-1.694147
C	2.594396	2.443528	-2.491837
H	-2.407478	-1.395759	-2.749207
C	-3.351351	-3.077141	-3.689066
C	-3.477524	-2.445014	-1.218513
C	3.351351	-3.077141	-3.689066
H	2.407478	-1.395759	-2.749207
C	3.477524	-2.445014	-1.218513
C	-3.477524	2.445014	-1.218513
C	-3.351351	3.077141	-3.689066
H	-2.407478	1.395759	-2.749207
H	2.407478	1.395759	-2.749207
C	3.351351	3.077141	-3.689066

C	3.477524	2.445014	-1.218513
H	-4.407759	-1.894722	-1.405485
H	-3.749348	-3.463652	-0.918074
H	-2.963265	-1.971619	-0.373197
H	-4.286364	-2.533953	-3.873936
H	-2.751540	-3.047783	-4.606586
H	-3.605564	-4.124955	-3.489121
H	-4.407759	1.894722	-1.405485
H	-2.963265	1.971619	-0.373197
H	-3.749348	3.463652	-0.918074
H	-4.286364	2.533953	-3.873936
H	-3.605564	4.124955	-3.489121
H	-2.751540	3.047783	-4.606586
H	4.407759	1.894722	-1.405485
H	3.749348	3.463652	-0.918074
H	2.963265	1.971619	-0.373197
H	4.286364	2.533953	-3.873936
H	2.751540	3.047783	-4.606586
H	3.605564	4.124955	-3.489121
H	4.286364	-2.533953	-3.873936
H	3.605564	-4.124955	-3.489121
H	2.751540	-3.047783	-4.606586
H	4.407759	-1.894722	-1.405485
H	2.963265	-1.971619	-0.373197
H	3.749348	-3.463652	-0.918074

Mechanistic analysis

Reactant complex (Anion=triflate)

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Au(III)- Figure S4

C	-0.127786	6.074807	-1.785037
C	1.183144	5.641858	-1.449857
C	2.300545	6.260644	-2.034147
C	2.121689	7.296201	-2.948452
C	0.830566	7.722263	-3.275091
C	-0.290130	7.117743	-2.690575
C	1.291180	4.564570	-0.470839
C	2.455928	3.992158	0.054932
C	2.348332	2.972240	0.999571
C	1.099476	2.516474	1.425295
C	-0.056189	3.096941	0.892843
N	0.094827	4.086341	-0.029653
C	-1.449395	2.772163	1.199726
C	-2.447283	3.552415	0.551728
C	-3.789771	3.258992	0.783481
C	-4.147906	2.219371	1.654273
C	-3.165635	1.463226	2.300299

C	-1.817646	1.736820	2.073249
Au	-1.567656	5.006710	-0.688609
C	-3.150418	5.905065	-1.365253
O	-4.070393	6.242002	-1.946736
H	2.989195	7.779417	-3.399589
H	-1.283727	7.499338	-2.921036
H	3.310279	5.938823	-1.771890
H	3.429877	4.352499	-0.270643
H	-4.572819	3.854368	0.313444
H	3.253327	2.527072	1.415784
H	1.016593	1.724667	2.167409
H	-1.053570	1.139748	2.574950
H	-3.450357	0.659461	2.980462
H	-5.203854	2.005361	1.830239
H	0.691060	8.543615	-3.980436
O	-4.428736	6.202749	1.117958
H	-4.191248	7.136540	1.326258
H	-3.869333	5.704189	1.740329
O	-1.075308	6.909254	1.204764
S	-1.857732	8.098895	0.811698
O	-2.322242	8.081435	-0.594602
O	-2.872892	8.524235	1.780307
C	-0.586708	9.481122	0.819265
F	0.422720	9.199478	-0.039037
F	-1.144836	10.650706	0.444847
F	-0.060382	9.632912	2.053029

Au(I)- Figure S4

C	1.219749	0.477324	8.792624
N	2.207835	0.579280	9.751927
C	2.982371	-0.536284	9.755883
N	2.480722	-1.330362	8.774926
C	1.391569	-0.728935	8.176755
C	2.286215	1.628278	10.765669
Au	4.451309	-0.997472	11.070440
C	5.887175	-1.425154	12.325365
O	6.793701	-1.635167	12.984021
C	2.891342	-2.716110	8.564583
O	4.000946	-2.283645	13.863725
H	0.474111	1.248747	8.647051
H	0.821120	-1.213773	7.394726
H	3.327004	-1.568713	13.899226
H	3.524270	-2.918797	13.279991
H	1.738853	2.507801	10.409016
H	1.846804	1.248444	11.698762
H	3.336911	1.894529	10.932187
H	2.538287	-3.047227	7.581611
H	3.985591	-2.778553	8.600596
H	2.460000	-3.337547	9.361907
O	1.671123	-0.871274	12.821415
S	1.134882	-2.026317	12.065871
O	0.319874	-1.685179	10.901469
O	2.129755	-3.101981	11.841333

C	-0.074055	-2.806009	13.272315
F	-0.643283	-3.906019	12.732519
F	0.558328	-3.171390	14.411262
F	-1.055197	-1.934461	13.593665

Transition State (Anion=Triflate)

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Au(I)- Figure S4

N	1.638528	-0.089811	9.033149
C	2.770690	-0.849256	9.002118
N	3.312361	-0.619223	7.770346
C	2.532142	0.266956	7.045730
C	1.475758	0.597766	7.842560
Au	3.462058	-2.084581	10.475874
C	4.059161	-3.352943	11.945992
O	4.518225	-4.437019	12.022294
C	4.551832	-1.219340	7.282936
C	0.692231	-0.033289	10.151472
O	3.728671	-2.730544	13.426754
O	1.478568	-3.353779	14.131544
S	0.604216	-2.127119	13.901229
C	0.203001	-1.608846	15.665439
F	-0.562312	-0.497845	15.646471
O	1.390132	-1.011358	13.355064
O	-0.668383	-2.441729	13.288262
F	-0.465608	-2.584441	16.306928
F	1.336290	-1.338604	16.347660
H	0.634245	1.257268	7.664630
H	2.791967	0.586873	6.043275
H	3.481803	-1.790218	13.263671
H	2.655773	-3.123540	13.813728
H	0.412387	1.011654	10.335375
H	-0.206162	-0.619649	9.916530
H	1.162285	-0.444040	11.052704
H	5.287386	-0.436124	7.054571
H	4.946699	-1.872195	8.069716
H	4.354618	-1.813723	6.380566

Product complex (Anion=triflate)

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Au(III)- Figure S4

N	-0.131950	0.914535	0.033259
C	0.832162	1.772111	0.447205
C	0.455886	3.095008	0.717501
C	-0.879232	3.464930	0.540012
C	-1.834117	2.546741	0.096328

C	-1.434112	1.229732	-0.166967
C	2.167535	1.162680	0.544049
C	3.287409	1.870764	1.008222
C	4.527378	1.238088	1.094375
C	4.650726	-0.105313	0.726323
C	3.537218	-0.820469	0.263282
C	2.290843	-0.206076	0.156633
Au	0.454531	-0.993551	-0.449459
C	1.080921	-2.841441	-0.983006
O	1.740886	-3.624506	-0.359133
C	-2.253673	0.103585	-0.643625
C	-1.594072	-1.146440	-0.862909
C	-2.364401	-2.238640	-1.267124
C	-3.745126	-2.109200	-1.479040
C	-4.378201	-0.879781	-1.282097
C	-3.635157	0.222978	-0.858656
H	5.395931	1.790753	1.455493
H	3.644908	-1.873453	-0.003099
H	3.193815	2.915786	1.311489
H	1.194695	3.820601	1.053593
H	-1.911440	-3.222247	-1.401950
H	-1.181578	4.493054	0.746420
H	-2.870569	2.847965	-0.046113
H	-4.139250	1.176846	-0.688980
H	-5.452126	-0.780918	-1.446814
H	-4.323818	-2.980079	-1.792757
H	5.620277	-0.602147	0.801641
O	0.701910	-3.204585	-2.295061
H	0.578163	-4.768989	-2.737680
H	0.060272	-2.546408	-2.635027
O	0.433677	-5.704836	-3.113489
S	-1.064125	-6.150321	-2.898298
O	-1.145268	-7.570830	-3.102238
O	-1.644327	-5.491657	-1.747367
C	-1.867820	-5.340639	-4.396146
F	-1.373962	-5.838227	-5.538369
F	-3.194544	-5.548901	-4.356142
F	-1.638529	-4.003024	-4.369569

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Au(I)- Figure S4

C	1.367101	0.499209	7.934392
N	1.642605	-0.106855	9.148604
C	2.799454	-0.824780	9.084972
N	3.243639	-0.649739	7.806703
C	2.380456	0.160110	7.085605
C	0.781441	-0.039324	10.330141
Au	3.627544	-1.965639	10.564363
C	4.358239	-3.185880	12.026368
O	4.836872	-4.280326	11.992091
C	4.469971	-1.236610	7.277138
O	4.125098	-2.664314	13.427696
H	0.488312	1.113856	7.779605
H	2.560180	0.427856	6.051183

H	3.900438	-1.712075	13.317786
H	2.809997	-3.089862	13.787634
H	0.232469	0.909554	10.316343
H	0.073254	-0.877940	10.340055
H	1.399408	-0.094213	11.232519
H	5.163156	-0.445503	6.961292
H	4.930731	-1.830166	8.075137
H	4.238570	-1.888053	6.424002
O	1.844931	-0.838997	13.441348
S	0.950785	-1.953610	13.739588
O	-0.230120	-2.168430	12.937340
O	1.748467	-3.271294	13.930428
C	0.347185	-1.665025	15.496780
F	-0.415061	-2.691760	15.905879
F	1.395022	-1.532348	16.330409
F	-0.382833	-0.533810	15.525439

Distance C(CO)-O(H2O) 1.8 Å (Anion=triflate)

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Au(III)- Figure S5

C	-0.452644	5.932293	-2.169280
C	0.905108	5.655465	-1.847742
C	1.938248	6.283468	-2.558545
C	1.636428	7.177080	-3.585480
C	0.303063	7.446707	-3.905645
C	-0.735591	6.826054	-3.198225
C	1.149003	4.720874	-0.746691
C	2.373832	4.365289	-0.172762
C	2.385006	3.493742	0.916104
C	1.197385	2.978974	1.438763
C	-0.017828	3.342605	0.849747
N	0.022127	4.172345	-0.224413
C	-1.372475	2.959745	1.261254
C	-2.454435	3.555743	0.554253
C	-3.758844	3.227376	0.916167
C	-4.002637	2.326844	1.962915
C	-2.938241	1.746207	2.657453
C	-1.625138	2.060561	2.307656
Au	-1.744731	4.877470	-0.907004
C	-3.450906	5.701125	-1.463571
O	-4.314288	5.672534	-2.242844
H	2.442000	7.666892	-4.134053
H	-1.768896	7.059662	-3.459942
H	2.981535	6.077700	-2.311484
H	3.298899	4.789933	-0.557836
H	-4.606777	3.668755	0.388963
H	3.335821	3.224580	1.378583
H	1.207540	2.321408	2.305987
H	-0.797583	1.601826	2.852411
H	-3.131293	1.048672	3.473522
H	-5.030504	2.081188	2.237121

H	0.066817	8.149614	-4.706893
O	-3.739045	7.042086	-0.284437
H	-2.890120	7.644196	-0.351822
H	-3.494648	6.659139	0.614938
O	-2.123679	6.586857	1.813202
S	-1.049748	7.467067	1.292083
O	0.287347	6.894870	1.266731
O	-1.465369	8.174453	0.043811
C	-0.961014	8.855515	2.550841
F	-0.619227	8.367532	3.761386
F	-0.041163	9.769258	2.180149
F	-2.158547	9.471184	2.659288

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Au(I)- Figure S5

C	1.199890	0.471463	8.467923
N	1.909496	0.326199	9.646016
C	2.866139	-0.630521	9.516370
N	2.751143	-1.075903	8.233376
C	1.728387	-0.413694	7.574434
C	1.634941	1.080911	10.867336
Au	4.093773	-1.355044	10.958011
C	5.267714	-2.148077	12.389451
O	6.337905	-2.526806	12.643662
C	3.551389	-2.149157	7.654528
O	4.215772	-2.445193	13.836252
H	0.384161	1.177415	8.369310
H	1.463083	-0.631349	6.546868
H	3.593306	-1.653256	13.877537
H	3.518585	-3.097274	13.494063
H	1.925517	2.131158	10.729468
H	0.567994	1.001893	11.104275
H	2.194434	0.631152	11.693817
H	3.992130	-1.817211	6.705546
H	4.349367	-2.398380	8.363158
H	2.927756	-3.037093	7.485179
O	2.014636	-0.971533	13.417767
S	1.213793	-2.080376	12.826876
O	0.478681	-1.737875	11.616359
O	1.959047	-3.361890	12.792536
C	-0.112667	-2.377140	14.120889
F	-0.920940	-3.389234	13.745762
F	0.446774	-2.692672	15.309329
F	-0.864895	-1.266480	14.284744