SUPPORTING INFORMATION

Trapping Atmospheric CO_2 with Gold

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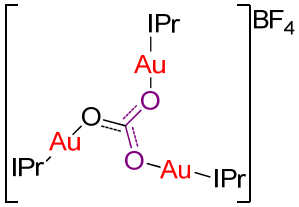
General information

- All reactions were carried under air and technical grade solvent were used, unless otherwise stated.
- Dry solvents were used in the isolation of **3** and the kinetics experiments. Solvents were dried following standard procedures.
- ^{1}H, and $^{13}C\{^{1}H\}$ Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker-400 MHz or 300 MHz spectrometer at ambient temperature in $CDCl_3$. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks.
- Elemental analyses were performed at London Metropolitan University 166-220 Holloway Road, London, N7 8DB.
- **1**,[1] **2**,[2] **6**,[3] [Au(OH)(SIPr)],[1] and $[Au(NTf_2)(IPr^{Cl})]$[1] were prepared according to reported procedures.
- Infrared spectra (ν) were recorded on a Shimadzu Fourier transform IR Affinity-1 Infrared specrophotometer using a MIRacleTM single reflection horizontal ATR (diamond).
- Crystals of **3** were grown by slow diffusion of pentane into a saturated dichloromethane solution. CCDC 1006986 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

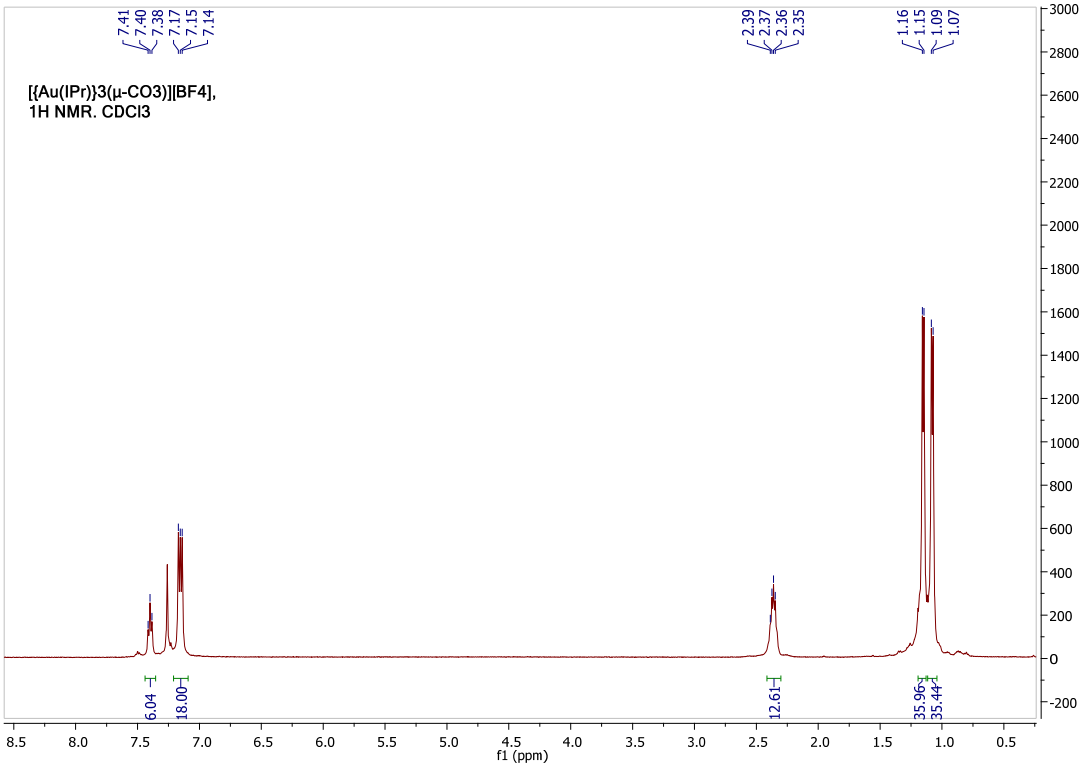
Reaction of [Au(OH)(IPr)] (1) and $[\{Au(IPr)\}_2(\mu\text{-OH})][BF_4]$ (2) with CO_2: Formation of $[\{Au(IPr)\}_3(\mu\text{-}CO_3)][BF_4]$ (3): In a vial, under air, [Au(OH)(IPr)] (**1**) (5.0 mg, 8.3 μmol) and $[\{Au(IPr)\}_2(\mu\text{-OH})][BF_4]$ (**2**) (10.6 mg, 8.3 μmol) were dissolved in 0.7 mL of $CDCl_3$. CO_2 was bubbled through the solution for 5 min and the solution was analysed by ^{1}H NMR spectroscopy. Full conversion to **3** was obtained. **Isolation of $[\{Au(IPr)\}_3(\mu^3\text{-}CO_3)][BF_4]$ (3)** In a Schlenk flask containing activated 4 Å molecular sieves, under argon, [Au(OH)(IPr)] (**1**) (50.0 mg, 0.083

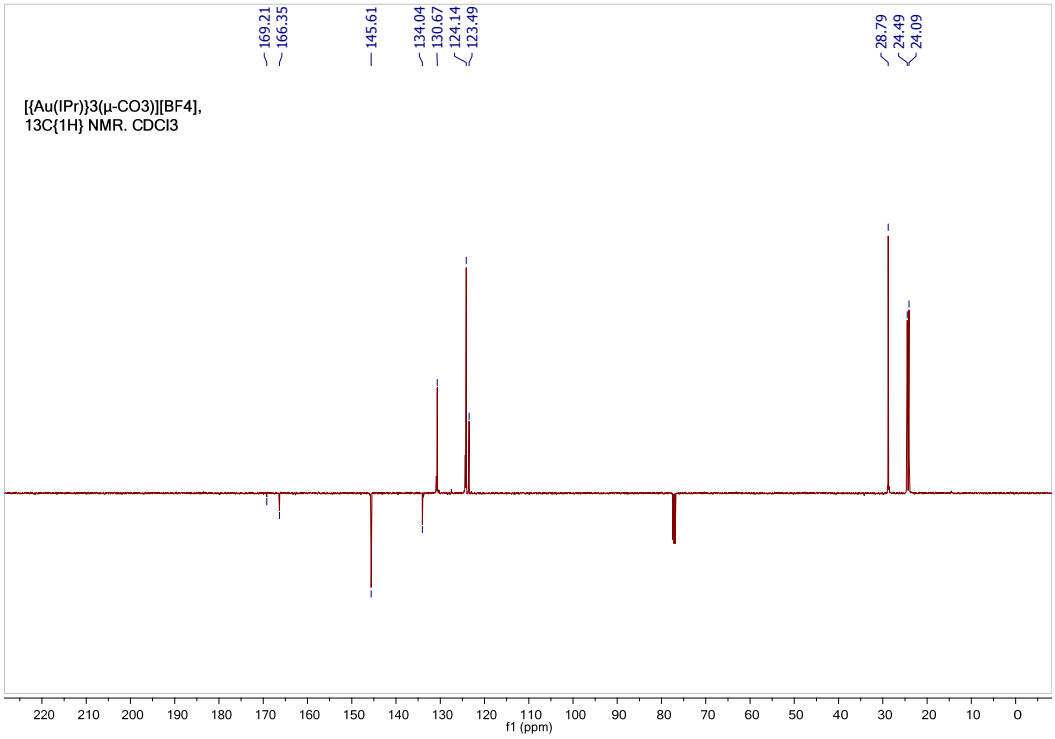
[1] S. R. Patrick, A. Gómez-Suárez, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2013**, *33*, 421-424.
[2] R. S. Ramón, S. Gaillard, A. Poater, L. Cavallo, A. M. Z. Slawin, S. P. Nolan, *Chem. Eur. J.* **2011**, *17*, 1238-1246
[3] S. Gaillard, A. M. Z. Slawin, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 2742-2744.

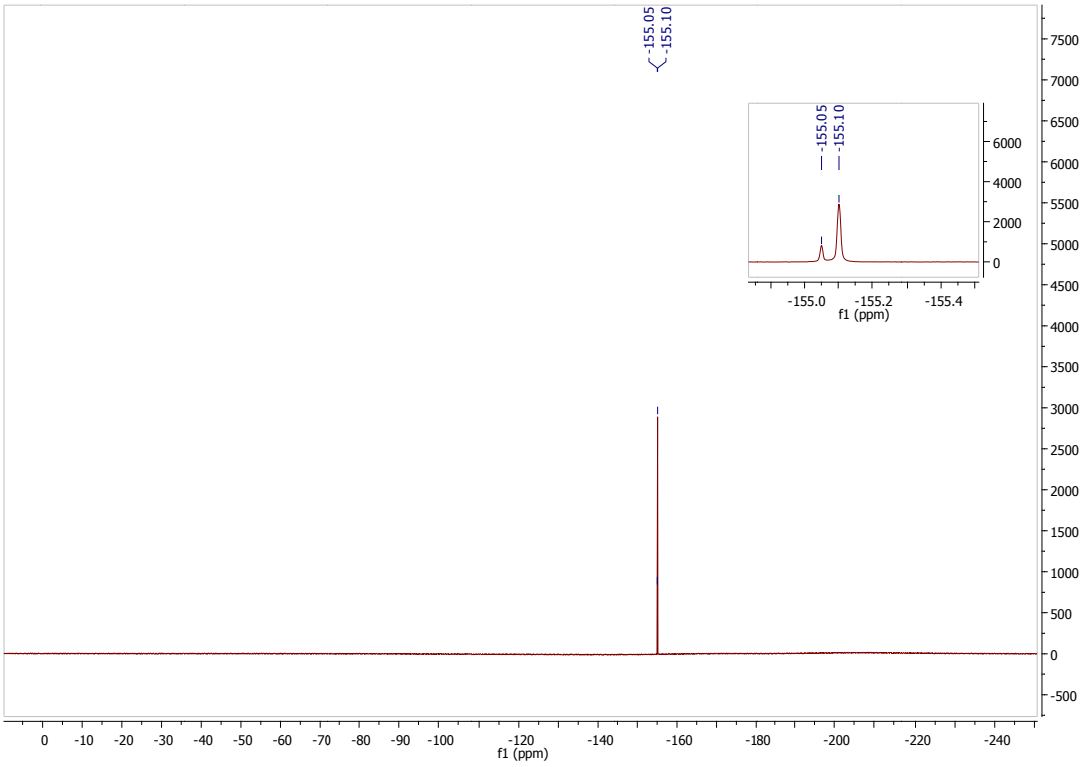
mmol) and [{Au(IPr)}$_2$(μ-OH)][BF_4] (**2**) (106.0 mg, 0.083 mmol) were dissolved in 4.0 mL of dry dichloromethane. The argon atmosphere was then replaced with CO_2 by three vacuum-CO_2 cycles. The solution was then stirred for 15 min. After this time, the solution was transferred *via* cannula to another Schlenk flask and concentrated under vacuum. The subsequent addition of hexane (3.0 mL) afforded a white solid that was washed with further portions of hexane (2 x 1.0 mL) and dried under vacuum. Yield 120 mg (76 %).



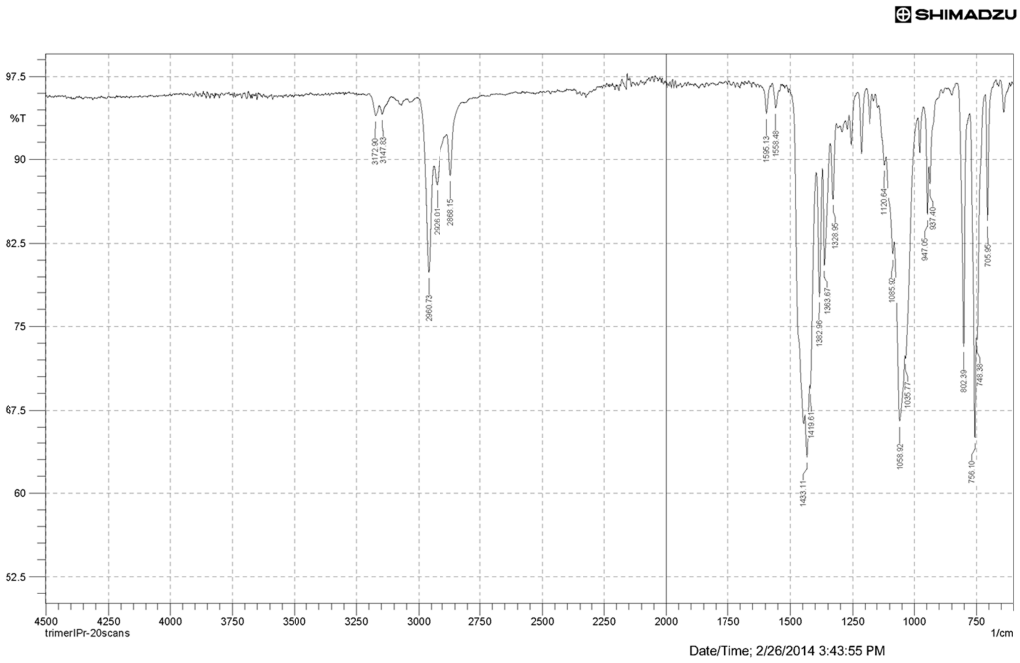
Anal. Calcd. for $C_{82}H_{109}Au_3BF_4N_6O_3$: C 51.71; H 5.77; N 4.41. Found: C 51.84; H 5.67; N 4.53. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.8 Hz, 6 H, C*H* $_{p\text{-Ar}}$), 7.16 (d, *J* = 7.8 Hz, 12 H, C*H*$_{m\text{-Ar}}$), 7.14 (s, 6 H, CH^{4,5}), 2.36 (sept, *J* = 6.8 Hz, 12 H, C*H*(CH_3)$_2$), 1.15 (d, *J* = 6.8 Hz, 36 H, CH(C*H*$_3$)$_2$), 1.08 (d, *J* = 6.8 Hz, 36 H, CH(C*H*$_3$)$_2$). **^{13}C{^{1}H}-DEPTQ NMR** (126 MHz, $CDCl_3$) δ 169.2 (CO_3), 166.4 (C_{carb}), 145.6 ($C_{o\text{-Ar}}$), 134.0 ($C_{N\text{-Ar}}$), 130.7 ($CH_{p\text{-Ar}}$), 124.1 ($CH_{m\text{-Ar}}$), 123.5 (CH_{imid}), 28.8 (*C*H^{i}Pr), 24.5 (CH_3), 24.1 (CH_3). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ -155.05, -155.10. **ATR-IR** (cm^{-1}): *υ* 1433.1 (CO_3) (s).


[{Au(IPr)}3(μ-CO3)][BF4],
1H NMR. CDCl3
7.41
7.40
7.38
7.17
7.15
7.14
2.39
2.37
2.36
2.35
1.16
1.15
1.09
1.07
6.04
18.00
12.61
35.96
35.44
f1 (ppm)


[{Au(IPr)}3(μ-CO3)][BF4],
13C{1H} NMR. CDCl3
169.21
166.35
145.61
134.04
130.67
124.14
123.49
28.79
24.49
24.09
f1 (ppm)

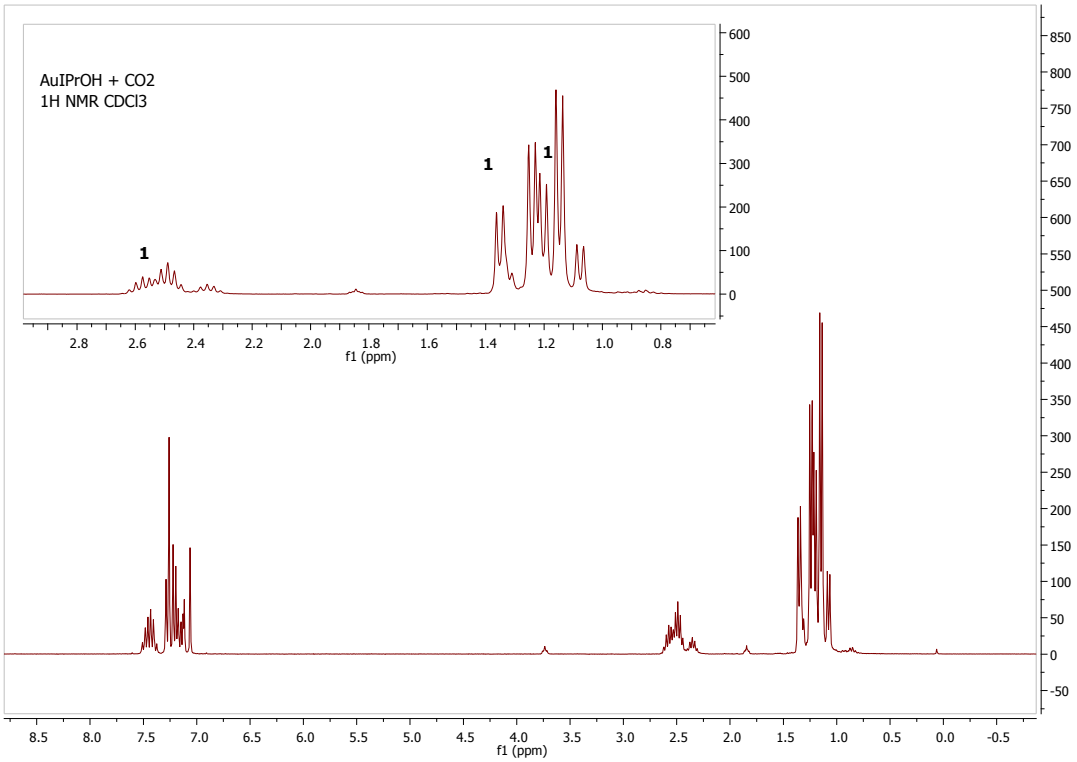


ATR-IR spectrum of [{Au(IPr)}$_3$(μ-CO_3)][BF_4](3)



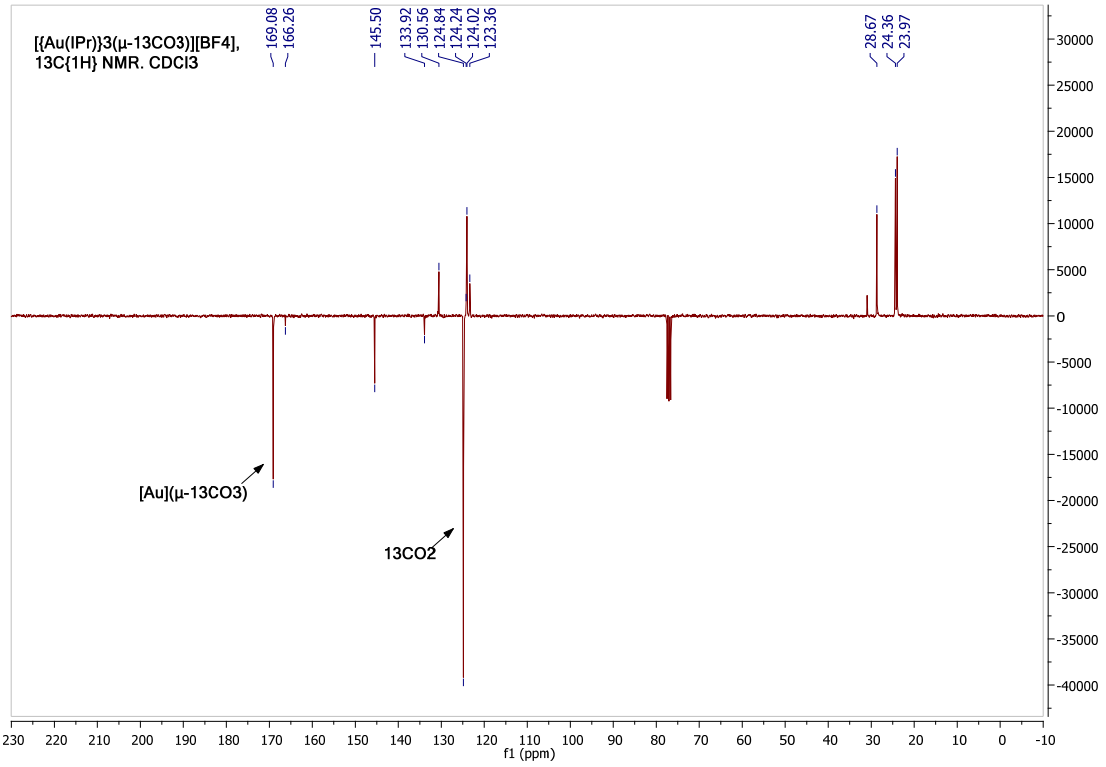
Reaction of [Au(OH)(IPr)] (1) with CO_2

10 mg of [Au(OH)IPr] were place in a J-Young NMR tube, and dissolved in 0.5 mL of $CDCl_3$. The solution was exposed to CO_2 atmosphere by freezing-thaw cycles. A mixture of complexes was obtained. One of the species in the mixture was identified as starting material.



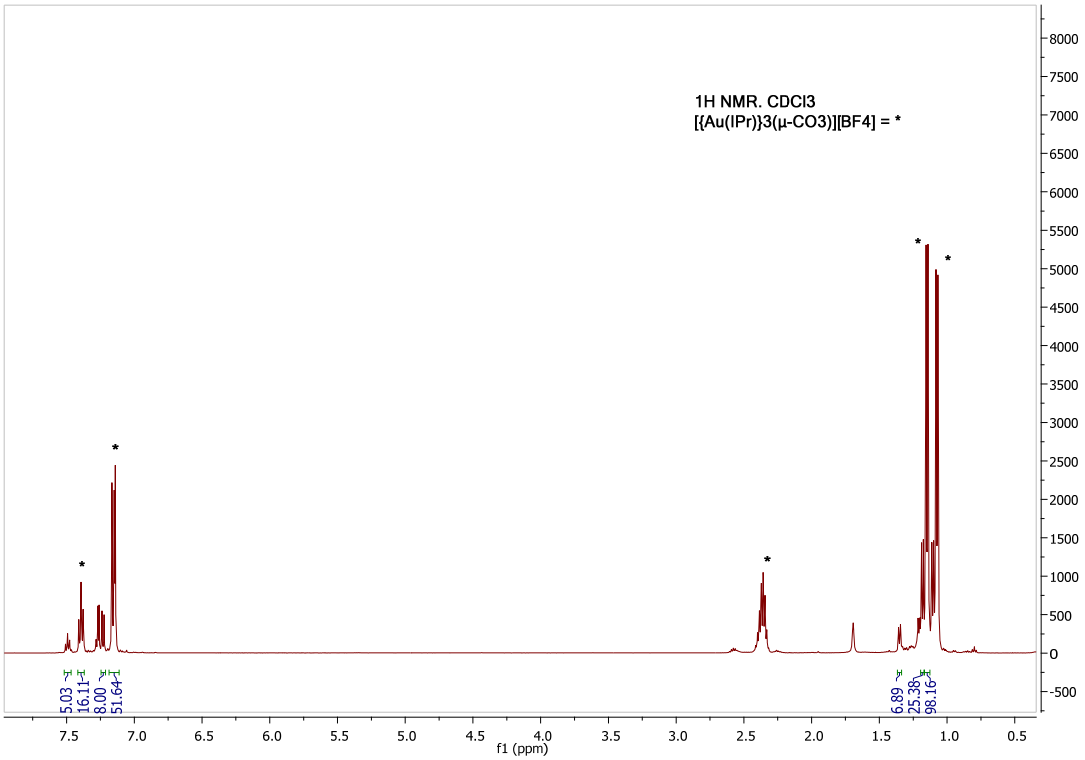
Reaction of [Au(OH)(IPr)] (1) and [{Au(IPr)}$_2$(μ-OH)][BF_4] (2) with $^{13}CO_2$

The incorporation of CO_2 in the molecule was confirmed by placing **1** and **2** in $CDCl_3$ a J-Young NMR tube and exposing the solution to $^{13}CO_2$. The intensity of the signal at 169.2 ppm in the $^{13}C\{^1H\}$-DEPTQ NMR spectrum, assigned to the μ^3-CO_3 increased significantly, confirming the origin of the carbonate moiety.



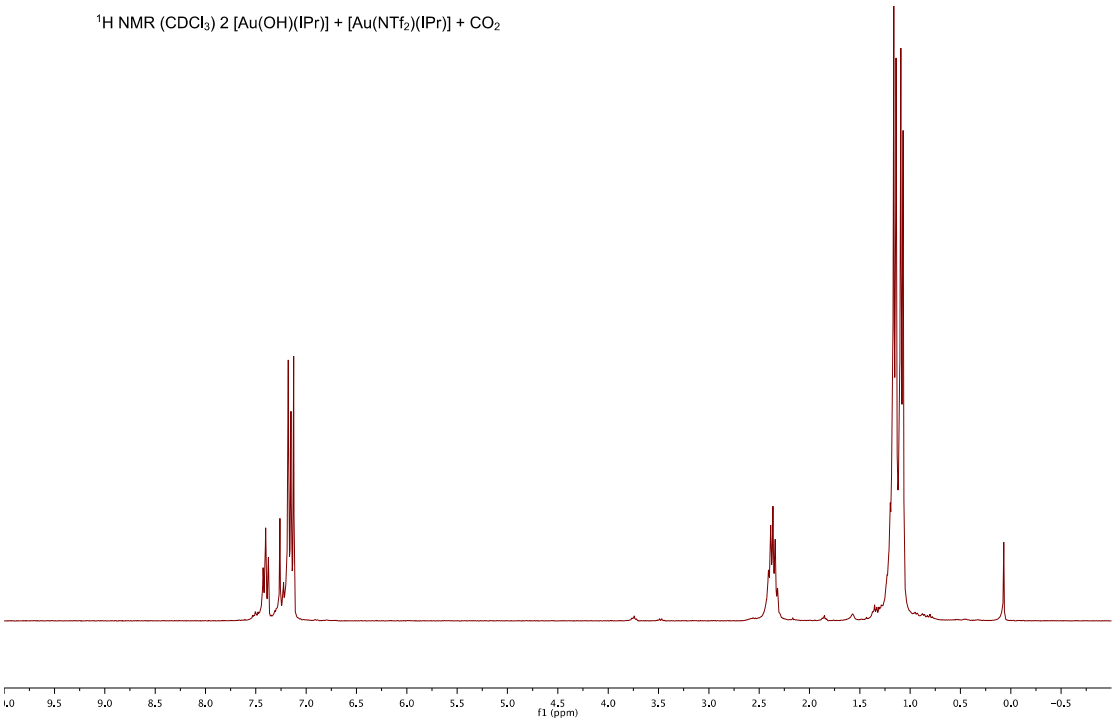
Reaction of [Au(OH)(IPr)] (1) and [{Au(IPr)}$_2$(μ-OH)][BF_4] (2) with air:

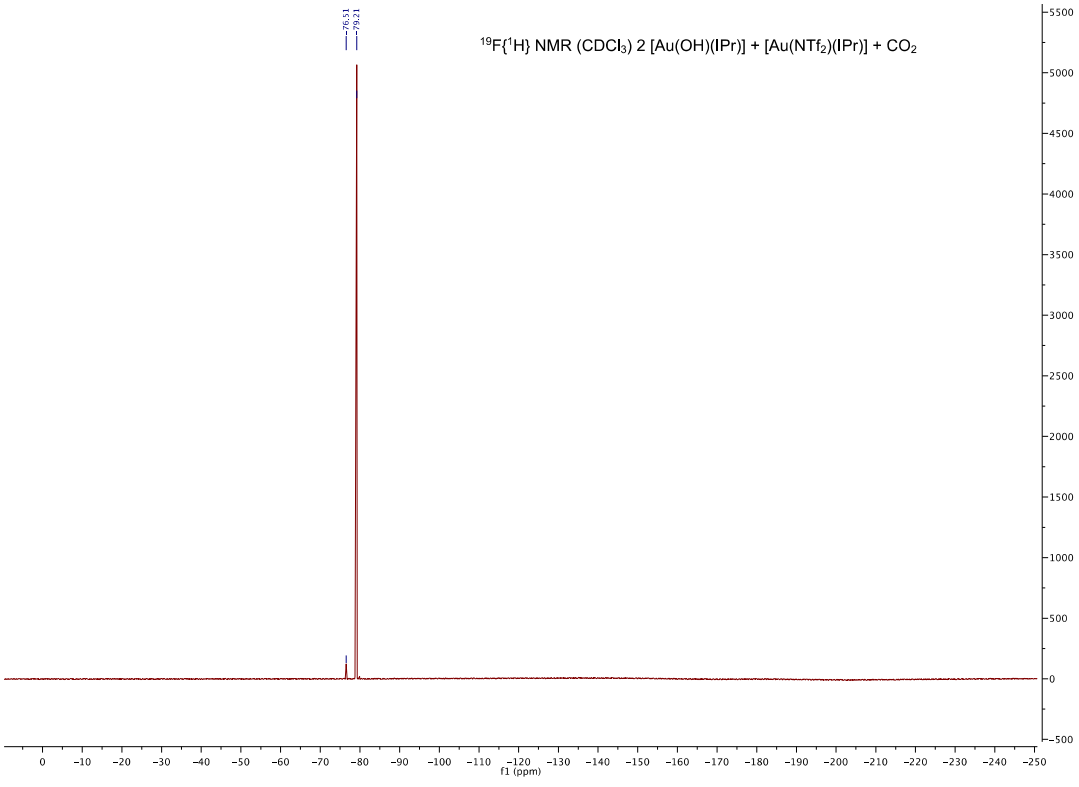
In a vial, under air [Au(OH)(IPr)] (**1**) (10.0 mg, 16.6 μmol) and [{Au(IPr)}$_2$(μ-OH)][BF_4] (**2**) (21.2 mg, 16.6 μmol) were dissolved in 5.0 mL of $CDCl_3$. Air was bubbled through the solution for 20 min and the solution was analyzed by ^{1}H NMR spectroscopy. The formation of **3** was observed in ca. 75 % conversion. The same reaction conducted in toluene, in a vial open to the air, also afforded **3**. In this case the reaction is slower and 7 h were required to obtain **3** in 75 % conversion.



Reaction of [Au(OH)(IPr)] and [Au(NTf$_2$)(IPr)] with CO$_2$:

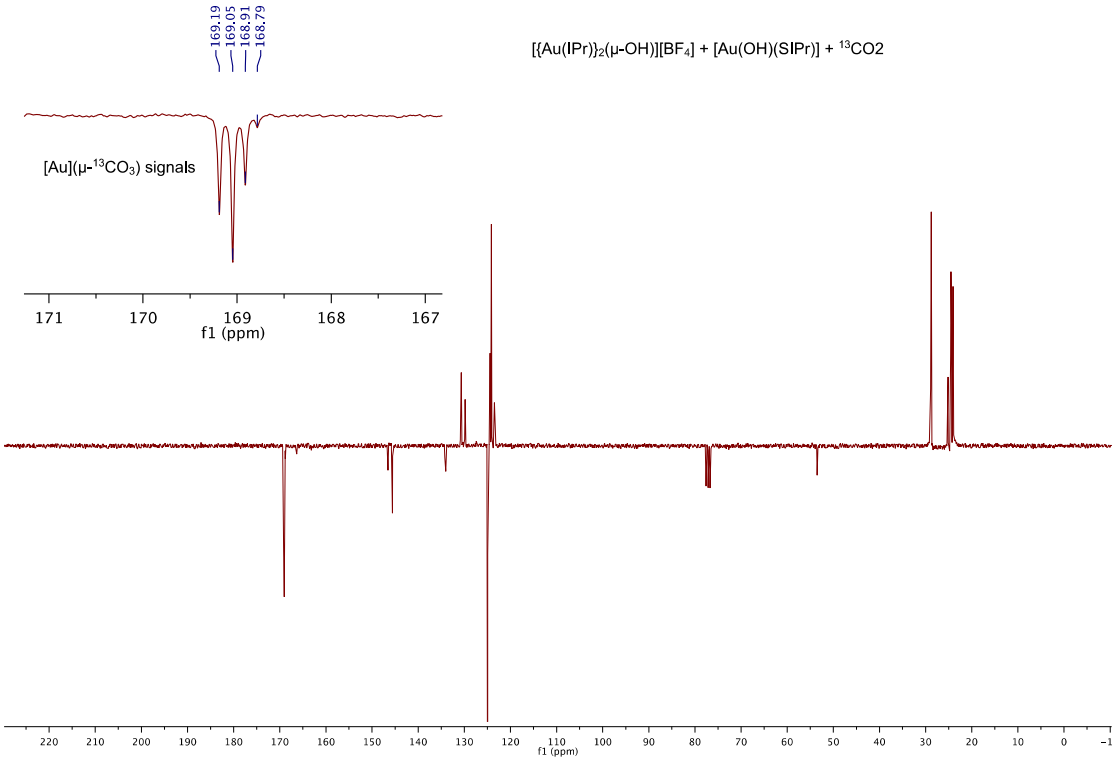
$CDCl_3$ (0.7 mL) was added to a vial containing [Au(OH)(IPr)] (10 mg, 16.6 µmol, 2 equiv.) and [Au(NTf$_2$)(IPr)] (7.2 mg, 8.3 µmol, 1 equiv.). CO_2 was bubbled through the solution for 5 min and the solution was analyzed by ^{1}H NMR spectroscopy. Full conversion to **3** was obtained.



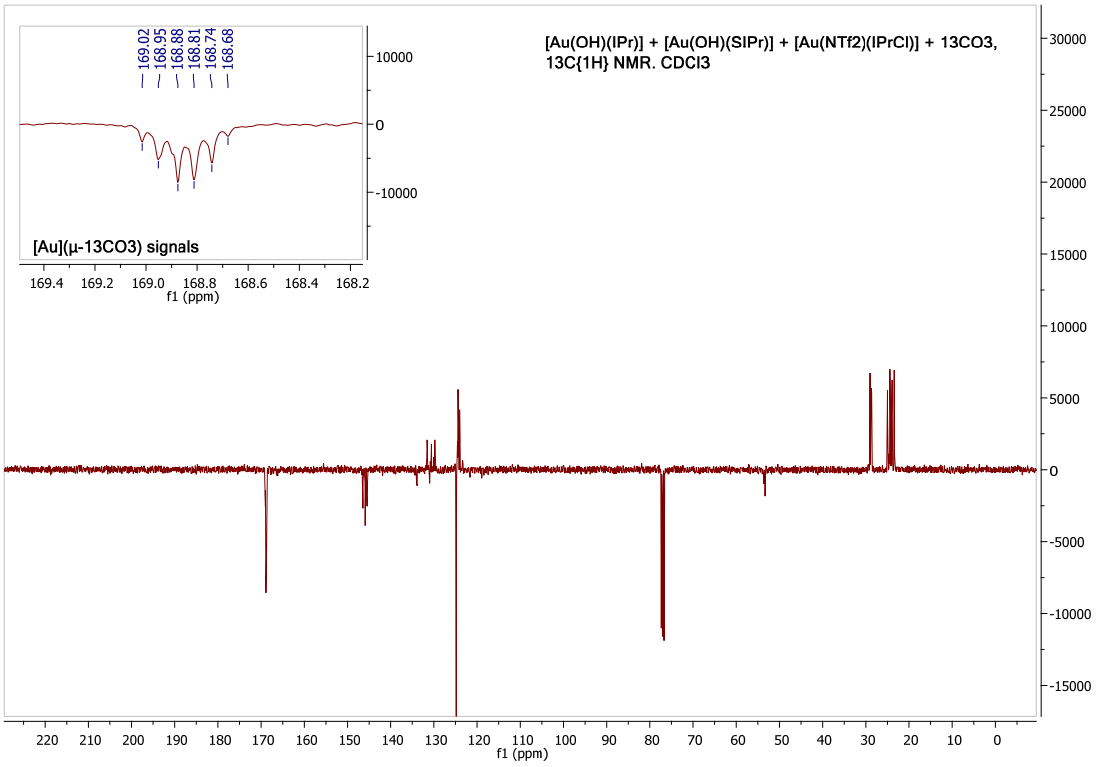


Reaction of [Au(OH)(SIPr)] and [{Au(IPr)}$_2$(μ-OH)][BF_4] with $^{13}CO_2$:

[Au(OH)(SIPr)] (5.0 mg, 8.29 μmol) and [{Au(IPr)}$_2$(μ-OH)][BF_4] (10.6 mg, 8.3 μmol) were dissolved in $CDCl_3$ (0.6 mL) at -30 ºC and placed in a J-Young NMR tube. The mixture was frozen, placed under vacuum, and exposed to $^{13}CO_2$. $^{13}C\{^{1}H\}$-DEPTQ NMR analyses indicated the formation of a series of [{Au(NHC)}$_3$(μ-CO_3)][BF_4] complexes.

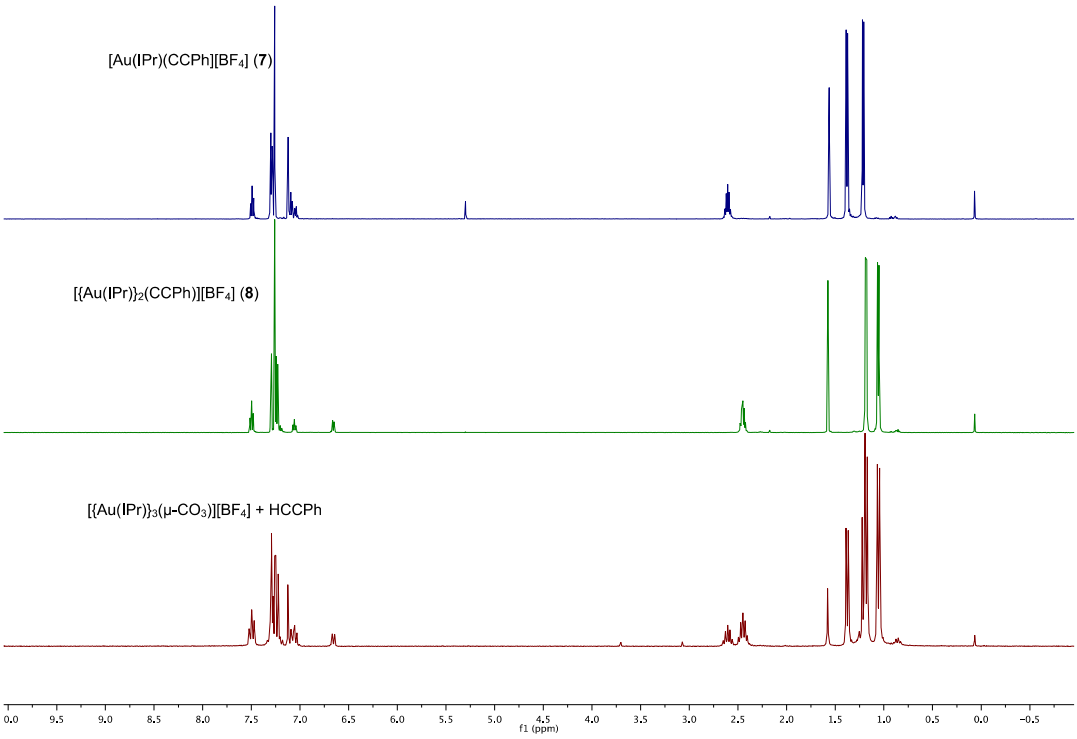


Reaction of [Au(OH)(IPr)], [Au(OH)(SIPr)] and [Au(NTf$_2$)(IPr^{Cl})] with $^{13}CO_2$: [Au(OH)(IPr)] (5.0 mg, 8.3 μmol), [Au(OH)(SIPr)] (5.0 mg, 8.3 μmol) and [Au(NTf$_2$)(IPr^{Cl})] (7.8 mg, 8.3 μmol) were dissolved in $CDCl_3$ at -30 ºC and placed in a J-Young NMR tube. The mixture was frozen, placed under vacuum, and exposed to $^{13}CO_2$. $^{13}C\{^1H\}$-DEPTQ NMR analyses indicated the formation of a series of [{Au(NHC)}$_3$(μ-CO_3)][BF_4] complexes.



Reaction of [{Au(IPr)}$_3$(μ^3-CO_3)][BF_4] with phenylacetylene.

To a NMR tube, under Ar, containing [{Au(IPr)}$_3$(μ^3-CO_3)][BF_4] (10 mg, 5.2 μmol) a 0.5 mL solution of phenylacetylene (1.1 mg, 10.4 μmol, 2 equiv.) in $CDCl_3$ was added. The mixture was stirred for 16 h at room temperature. After this time a ^{1}H NMR was acquired revealing complete conversion to monoaurated acetylide **7** and diaurated σ,π-acetylide **8**.



Catalytic experiments :

[{Au(IPr)}$_2$(μ-OH)][BF$_4$] under air:[{Au(IPr)}$_2$(μ-OH)][BF$_4$] (3.2 mg, 2.5 μmol, 0.5 mol%) was added to a solution of alkyne (89 mg, 0.5 mmol) and phenol (52 mg, 0.55 mmol, 1.1 equiv.) in toluene (1 mL). The reaction mixture was stirred at 80 °C for 1 h. After this time an aliquot was analized by GC.

[{Au(IPr)}$_2$(μ-OH)][BF$_4$] under CO$_2$:[{Au(IPr)}$_2$(μ-OH)][BF$_4$] (3.2 mg, 2.5 μmol, 0.5 mol%) was added to a solution of alkyne (89 mg, 0.5 mmol) and phenol (52 mg, 0.55 mmol, 1.1 equiv.) in toluene (1 mL) and CO_2 was bubbled through the solution for 5 min. The reaction mixture was stirred at 80 °C. After this time an aliquot was analized by GC.

1 + ***2*** *under air*: **1** (1 mg, 1.65 μmol, 0.33 mol%) + **2** (2.1 mg, 1.65 μmol, 0.33 mol%) was added to a solution of alkyne (89 mg, 0.5 mmol) and phenol (52 mg, 0.55 mmol, 1.1 equiv.) in toluene (1 mL). The reaction mixture was stirred at 80 °C for 1 h. After this time an aliquot was analized by GC.

1 *+* ***2*** *under* CO_2: **1** (1 mg, 1.65 µmol, 0.33 mol%) + **2** (2.1 mg, 1.65 µmol, 0.33 mol%) was added to a solution of alkyne (89 mg, 0.5 mmol) and phenol (52 mg, 0.55 mmol, 1.1 equiv.) in toluene (1 mL) and CO_2 was bubbled through the solution for 5 min. The reaction mixture was stirred at 80 °C for 1 h. After this time an aliquot was analized by GC.

3 *under air*: **3** (3.1 mg, 1.62 µmol, 0.33 mol%) was added to a solution of alkyne (89 mg, 0.5 mmol) and phenol (52 mg, 0.55 mmol, 1.1 equiv.) in toluene (1 mL). The reaction mixture was stirred at 80 °C for 1 h. After this time an aliquot was analized by GC.

3 *under* CO_2: **3** (3.1 mg, 1.62 µmol, 0.33 mol%) was added to a solution of alkyne (89 mg, 0.5 mmol) and phenol (52 mg, 0.55 mmol, 1.1 equiv.) in toluene (1 mL) and CO_2 was bubbled through the solution for 5 min. The reaction mixture was stirred at 80 °C for 1 h. After this time an aliquot was analized by GC.

- **DFT Calculations.**

Geometries were fully optimized at the PBE0/ECP1 level of theory, i.e. using the PBE hybrid functional,[4] a fine integration grid (75 radial shells with 302 angular points per shell), the Stuttgart-Dresden effective core potential (together with its [6s5p3d] valence basis) on Au,[5] and 6-31G*(*) basis on the ligands (6-31G* on the iPr and Ph groups, 6-31G** elsewhere).[6] Minima where characterized by the harmonic vibrational frequencies computed at that level, which were also used to evaluate standard thermodynamic corrections at ambient temperature and pressure. Refined energies were obtained through single-point calculations at the PBE0-D3/ECP2 level, i.e. including Grimme's three-body dispersion correction,[7] the same SDD core potential and valence basis as above on Au, 6-31G* basis on the $C_6H_3(i\text{Pr})_2$ groups, and 6-311+G** basis elsewhere, in conjunction with the polarizable continuum model (PCM) by Tomasi and coworkers employing the parameters of dichloromethane (and the default settings in Gaussian09),[8]. These and similar levels have performed well in the computation of structures and reaction profiles of 5d and late transition metal complexes.[9] Enthalpies ΔH and free energies ΔG were obtained by adding the PBE0/ECP1 thermodynamic corrections to the PBE0-D3/ECP2 single point energies. Atomic charges were obtained from natural population analysis[10] of the PBE0/ECP2/PCM wavefunctions. All computations employed the Gaussian suite of programs.[11]

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([9]) See e.g.: (a) Bühl, M.; Reimann, C.; Pantazis, D. A.; Bredow, T.; Neese, F. *J. Chem. Theory Comput*. **2008**, *4*, 1449-1459. (b) Quintal, M. M.; Karton, A.; Iron, M. A.; Boese, A. D.; Martin, J. M. L. J. *Phys. Chem. A* **2006**, *110*, 709-716.

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Optimized Geometries:

Cartesian coordinates of all compounds, PBE0/ECP1 optimized (xyz format in Å)

3
CO_2
C 0.000000 0.000000 0.000000
O 0.000000 0.000000 1.165689
O 0.000000 0.000000 -1.165689

3
H_20
O 0.000000 0.000000 0.110812
H 0.000000 0.783976 -0.443248
H 0.000000 -0.783976 -0.443248

136
[$IPr_2Au_2CO_3$]

Au	2.192019	-0.124214	-0.301590
Au	-2.647754	-0.378590	-0.948180
C	4.104195	0.128586	0.104812
N	5.122851	-0.720638	-0.185394
C	6.341653	-0.181324	0.179012
H	7.267483	-0.712154	0.024940
C	6.084216	1.035996	0.714231
H	6.737964	1.789503	1.123596
N	4.712849	1.208377	0.661392
C	4.958438	-2.011938	-0.793779
C	4.799463	-3.127251	0.043464
C	4.659145	-4.373681	-0.568731
H	4.524909	-5.258691	0.047881
C	4.677575	-4.497061	-1.952148
H	4.562160	-5.475808	-2.410156
C	4.830973	-3.373098	-2.752695
H	4.829628	-3.479597	-3.833616
C	4.970051	-2.100977	-2.194284
C	4.743531	-3.013721	1.555355
H	4.950990	-1.972623	1.827801
C	3.340489	-3.347644	2.072796
H	2.589303	-2.694150	1.616420
H	3.295095	-3.222036	3.161523
H	3.070776	-4.385076	1.842131
C	5.807453	-3.882533	2.231847
H	6.814488	-3.630470	1.881115
H	5.642862	-4.947800	2.033664
H	5.779041	-3.741524	3.318568
C	5.142986	-0.891102	-3.092137
H	5.066233	0.006383	-2.467758
C	6.536411	-0.894262	-3.731637
H	6.671609	-0.003971	-4.356811
H	6.672334	-1.775116	-4.370525
H	7.331845	-0.904883	-2.976738
C	4.041124	-0.797018	-4.151207
H	4.161012	0.132207	-4.721544
H	3.042725	-0.802663	-3.700643
H	4.102135	-1.625248	-4.867787
C	4.029281	2.380662	1.126837

Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc., Pittsburgh PA, 2003; (b) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.

C	3.798379	3.427907	0.221833
C	3.147341	4.563734	0.708778
H	2.950369	5.392062	0.033365
C	2.744550	4.647563	2.035129
H	2.238847	5.540677	2.392896
C	2.983156	3.591344	2.905671
H	2.655763	3.663175	3.939517
C	3.631014	2.433384	2.471937
C	4.212407	3.359722	-1.235762
H	4.710471	2.398942	-1.405161
C	2.991184	3.404797	-2.159490
H	2.299667	2.584398	-1.941118
H	3.304990	3.314180	-3.205638
H	2.446065	4.350426	-2.054027
C	5.215848	4.464405	-1.581416
H	6.104972	4.415497	-0.942435
H	4.773350	5.460285	-1.461559
H	5.539388	4.369677	-2.624172
C	3.843788	1.275807	3.428957
H	4.460528	0.525078	2.922411
C	2.506579	0.610029	3.770486
H	2.666683	-0.255341	4.424906
H	1.998632	0.268326	2.861927
H	1.841566	1.308762	4.292818
C	4.593179	1.703701	4.693456
H	4.784299	0.833826	5.332100
H	4.014294	2.422945	5.284164
H	5.556095	2.167791	4.452783
C	-4.062012	0.036878	0.359109
N	-4.656693	-0.809477	1.238726
C	-5.570863	-0.142401	2.032835
H	-6.143410	-0.650074	2.792592
C	-5.550013	1.154568	1.642194
H	-6.100860	2.014092	1.989311
N	-4.623625	1.245349	0.620224
C	-4.357936	-2.209838	1.344368
C	-3.321424	-2.610848	2.201588
C	-3.056697	-3.979082	2.288578
H	-2.255384	-4.324233	2.936319
C	-3.790449	-4.900964	1.553805
H	-3.563935	-5.960897	1.633196
C	-4.807113	-4.471626	0.710438
H	-5.366488	-5.200108	0.129671
C	-5.114141	-3.115673	0.584302
C	-2.490906	-1.627989	3.005091
H	-2.879932	-0.620468	2.820199
C	-1.025789	-1.638666	2.555127
H	-0.919598	-1.372557	1.497597
H	-0.572222	-2.626092	2.705918
H	-0.449711	-0.915120	3.144874
C	-2.614035	-1.896566	4.508366
H	-3.658315	-1.868769	4.840201
H	-2.055277	-1.142642	5.074728
H	-2.205533	-2.878459	4.774266
C	-6.199647	-2.670355	-0.377122
H	-6.339523	-1.590035	-0.258037
C	-7.542348	-3.340825	-0.074248
H	-7.863572	-3.152289	0.956341
H	-7.491703	-4.426577	-0.215030
H	-8.316885	-2.958270	-0.748811
C	-5.767446	-2.916601	-1.826605
H	-4.825084	-2.403740	-2.047292
H	-6.532987	-2.549893	-2.520786
H	-5.622940	-3.986208	-2.019427
C	-4.292442	2.461007	-0.068341
C	-5.046452	2.814756	-1.198095
C	-4.712083	4.005319	-1.845464
H	-5.268236	4.305735	-2.729359
C	-3.671792	4.802710	-1.386039
H	-3.424585	5.723722	-1.907369
C	-2.940709	4.422041	-0.268535
H	-2.120909	5.047149	0.075114
C	-3.231188	3.240815	0.417559
C	-6.156435	1.938769	-1.747578
H	-6.323865	1.116303	-1.042978

C	-5.735664	1.316398	-3.083304
H	-4.811382	0.739057	-2.973082
H	-5.562290	2.089188	-3.841520
H	-6.520180	0.647717	-3.457240
C	-7.477069	2.702130	-1.879518
H	-8.270902	2.028000	-2.220994
H	-7.401786	3.515969	-2.609781
H	-7.787555	3.138527	-0.923500
C	-2.404216	2.844485	1.625748
H	-2.801008	1.900364	2.015765
C	-2.523281	3.885974	2.743250
H	-3.566752	4.045713	3.038577
H	-2.112703	4.854131	2.433250
H	-1.964447	3.557947	3.627325
C	-0.940221	2.599262	1.245367
H	-0.841261	1.809227	0.493115
H	-0.368250	2.293772	2.129764
H	-0.471716	3.509146	0.850986
C	0.015138	-0.673102	-1.974890
O	0.956851	-0.830568	-2.758488
O	-1.235495	-0.808071	-2.343849
O	0.198015	-0.350075	-0.693584

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$[Au_3IPr_3CO_3]^+$

Au	0.50724	19.02742	8.51958
Au	-4.60258	19.15113	9.19822
Au	-1.65131	19.75648	12.99603
O	-1.47332	19.08045	8.97838
O	-0.95536	19.56967	11.07163
O	-3.08237	19.19966	10.52363
N	-7.40833	19.95442	8.13725
N	-6.34563	18.48819	6.85645
N	3.14031	17.86068	7.69439
N	-2.80638	20.76757	15.60224
N	3.22873	19.99837	7.81546
N	-2.27789	18.68287	15.63410
C	-8.55025	21.67696	11.12261
H	-9.08234	21.49170	11.85859
C	-5.36094	15.92736	15.19123
H	-5.45594	15.23807	14.52853
H	-6.21833	16.32203	15.36647
H	-5.01057	15.54887	16.00050
C	-3.52308	17.12524	4.97347
H	-2.80349	17.42585	4.46689
C	2.14953	23.96357	8.46542
H	1.90549	24.84850	8.61198
C	-2.94626	22.15161	15.21354
C	0.40768	22.50543	15.58312
H	0.84996	23.35791	15.58312
H	0.10966	22.30029	14.69421
H	1.01881	21.82674	15.87943
C	-3.17775	20.29438	16.81614
H	-3.55887	20.78876	17.50433
C	-2.95833	16.56148	14.69102
C	4.76234	15.78538	10.67974
H	5.18532	16.27456	11.38705
H	5.37835	15.68149	9.95013
H	4.49650	14.92024	10.99835
C	-3.70458	15.77970	5.11047
H	-3.11383	15.18070	4.71540
C	-0.77051	22.55739	16.50390
H	-0.95807	21.63351	16.77472
C	-2.66624	20.01081	5.67760
H	-2.04284	19.45182	5.20924
H	-2.49945	19.95261	6.62386
H	-2.56127	20.91999	5.39085
C	-4.78446	17.48981	13.24773
H	-4.77693	16.75136	12.63600
H	-4.13846	18.14375	12.97054
H	-5.65847	17.88624	13.26047
C	-4.01163	22.51935	14.41383
C	-2.52372	15.29273	14.16532
H	-3.14383	14.68044	13.83715
C	-0.21118	15.83311	14.60818

H	0.68527	15.59344	14.56039
C	-4.57834	22.89118	8.30293
H	-3.96001	22.86128	7.56694
H	-4.32197	22.24096	8.96245
H	-4.56690	23.76760	8.69481
C	-3.19585	24.83290	14.64960
H	-3.27898	25.73795	14.45206
C	-4.93750	21.41691	12.29190
H	-5.19370	22.25360	11.90001
H	-5.54784	20.73133	12.01153
H	-4.04793	21.18968	12.00834
C	-4.13843	23.87646	14.13027
H	-4.84083	24.16987	13.59820
C	2.45444	16.11442	4.23430
H	3.38578	15.99763	4.43821
H	2.36466	16.71141	3.48876
H	2.06644	15.26494	4.01128
C	4.64485	21.42619	11.05570
H	4.62346	22.36140	11.26917
H	5.29912	21.26889	10.37069
H	4.87366	20.92314	11.83948
C	-2.16186	24.36997	15.45568
H	-1.56854	24.98718	15.81571
C	-1.19994	15.00062	14.15257
H	-0.94232	14.17642	13.80848
C	1.18069	21.14487	5.06906
H	0.58541	21.89591	5.02445
H	0.83756	20.50014	5.69034
H	1.25338	20.74383	4.19925
C	-6.55031	23.74368	6.96477
H	-6.58789	24.53129	7.50959
H	-7.43023	23.52978	6.64617
H	-5.96994	23.90090	6.21604
C	1.10158	17.48407	16.89897
H	0.43450	17.19404	17.52663
H	1.62237	18.18934	17.29086
H	1.67490	16.74706	16.67595
C	3.13689	22.58474	4.48282
H	2.92665	22.26096	3.60664
H	4.08891	22.64452	4.58477
H	2.74611	23.45399	4.60707
C	-7.58590	14.55673	6.61430
H	-7.02221	13.78532	6.52191
H	-7.86189	14.85952	5.74769
H	-8.36067	14.32492	7.13364
C	-6.45060	21.91765	14.20674
H	-6.57608	21.75120	15.14344
H	-7.07212	21.38665	13.70333
H	-6.60448	22.84717	14.02513
C	-4.47904	19.93997	3.96030
H	-4.71315	20.87099	3.94118
H	-5.22785	19.41705	3.66718
H	-3.73392	19.78736	3.37406
C	-0.56591	23.35728	17.78152
H	0.19526	23.01424	18.25624
H	-1.34640	23.28328	18.33590
H	-0.41605	24.27925	17.56168
C	-6.22646	15.30278	8.66614
H	-6.94116	15.14085	9.28424
H	-5.67038	16.01091	8.99749
H	-5.70217	14.50430	8.56737
C	1.72371	16.71051	5.46413
H	2.06690	17.62051	5.58839
C	2.27129	20.97534	11.59733
H	2.55598	20.37699	12.29190
H	1.42325	20.68576	11.25324
H	2.18512	21.86182	11.95418
C	-8.28484	20.69916	10.18590
C	3.23700	20.97766	10.54274
H	3.32539	20.05407	10.23051
C	0.45343	17.97359	15.70101
H	0.01090	18.81299	15.94315
C	-0.61538	17.05949	15.14982
C	-4.75361	15.33199	5.83053
H	-4.88607	14.41439	5.89425

C	-1.94786	17.40279	15.17212
C	2.57264	21.61942	5.53422
H	3.15944	20.83216	5.55015
C	-1.97891	23.03927	15.73605
C	-4.10170	19.53874	5.38129
H	-4.70572	20.00630	5.99620
C	2.56540	16.81071	11.29147
H	2.10370	15.99893	11.51768
H	1.93071	17.46821	10.99517
H	3.02944	17.13991	12.06569
C	-8.21715	18.66469	11.60689
H	-7.26570	18.76598	11.52406
H	-8.43724	17.73009	11.62920
H	-8.51334	19.08294	12.41934
C	-4.96953	21.53411	13.79255
H	-4.77321	20.65013	14.16850
C	-4.42554	16.97939	14.68465
H	-4.50541	17.74621	15.29000
C	1.55435	18.33060	14.65279
H	2.12731	19.01171	15.00963
H	1.13944	18.65009	13.84671
H	2.07440	17.54700	14.45525
C	2.38891	18.95733	7.97158
C	-6.19625	19.18520	7.97476
C	4.45974	19.57535	7.37259
H	5.17412	20.12111	7.13364
C	-2.88877	18.96989	16.84162
H	-3.06734	18.37349	17.53300
C	-1.86165	19.21164	10.17953
C	2.65721	16.52129	7.80271
C	4.44489	18.22636	7.35029
H	5.15491	17.66019	7.14638
C	-8.04730	19.77673	7.02531
H	-8.79894	20.27195	6.78635
C	-5.40457	17.55744	6.27658
C	-10.41179	19.36040	10.54593
H	-10.65817	19.96922	11.24687
H	-10.74011	18.48177	10.75621
H	-10.79266	19.65444	9.71755
C	-7.48361	20.95703	9.10263
C	-7.54654	18.84512	6.27658
H	-7.92180	18.48983	5.50236
C	-2.27541	19.75937	14.86944
C	2.86475	21.37661	8.03211
C	1.56840	14.63169	6.87238
H	1.11855	14.20968	6.17781
C	2.46931	14.53167	9.10263
H	2.60858	14.04687	9.88322
C	2.46470	23.16646	9.51364
H	2.42877	23.52315	10.37069
C	-6.88574	22.26249	8.97519
C	2.89788	15.83813	8.99749
C	2.84619	21.80883	9.35115
C	3.54365	16.54079	10.20502
H	3.85909	17.41245	9.88641
C	2.53731	22.17658	6.92335
C	-6.79521	15.69467	7.33754
H	-7.40586	16.44821	7.47773
C	1.82765	13.96250	8.02574
H	1.55895	13.07424	8.08946
C	1.98610	15.96876	6.73856
C	-5.64307	16.17285	6.47730
C	2.18545	23.48547	7.21329
H	1.96467	24.05512	6.51235
C	-8.90091	19.31755	10.42167
H	-8.69445	18.77285	9.63471
C	-7.17942	23.21157	9.88960
H	-6.81450	24.06166	9.80039
C	-8.00336	22.94551	10.94100
H	-8.20285	23.61909	11.54954
C	0.22452	16.83374	5.19650
H	0.08285	17.37265	4.41272
H	-0.20306	17.24833	5.94841
H	-0.14833	15.96121	5.05631
C	-6.00570	22.57305	7.78997

H	-5.96187	21.78020	7.21647
C	-4.34185	18.04131	5.53741

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$[Au_2(IPr)_2OH]^+$

Au	-1.892291	-0.553365	-0.226866
O	-0.003214	-1.324530	-0.514737
H	0.001585	-2.283710	-0.451134
Au	1.872326	-0.540554	-0.168838
C	-3.728056	0.132917	0.000421
N	-4.822255	-0.591689	0.334501
C	-5.943650	0.212418	0.387838
H	-6.915450	-0.182787	0.637630
C	-5.537642	1.468143	0.079118
H	-6.081243	2.396596	0.005115
N	-4.177649	1.400175	-0.155061
C	-4.820646	-2.008377	0.582566
C	-5.050012	-2.874375	-0.498754
C	-5.036956	-4.244969	-0.231848
H	-5.208455	-4.946395	-1.043836
C	-4.810883	-4.724241	1.052347
H	-4.807725	-5.794807	1.237692
C	-4.595728	-3.839579	2.101631
H	-4.425427	-4.226387	3.102690
C	-4.596475	-2.458668	1.893215
C	-5.298775	-2.381106	-1.912166
H	-5.305432	-1.285111	-1.897972
C	-4.172298	-2.816655	-2.854876
H	-3.201088	-2.445375	-2.508490
H	-4.348438	-2.426362	-3.863726
H	-4.111615	-3.908683	-2.926081
C	-6.664682	-2.839822	-2.432243
H	-7.476789	-2.509715	-1.775551
H	-6.720311	-3.931523	-2.507116
H	-6.847039	-2.430485	-3.431984
C	-4.360408	-1.516937	3.059425
H	-4.414871	-0.487856	2.686159
C	-5.445165	-1.674942	4.129682
H	-5.289294	-0.953207	4.939158
H	-5.428383	-2.677244	4.572056
H	-6.445774	-1.511186	3.715255
C	-2.962814	-1.711907	3.655579
H	-2.795166	-0.998709	4.470716
H	-2.184400	-1.558368	2.899706
H	-2.841632	-2.720830	4.066148
C	-3.361157	2.527955	-0.513733
C	-2.798944	3.297206	0.517320
C	-2.020134	4.393334	0.141993
H	-1.565403	5.010213	0.911714
C	-1.818986	4.705984	-1.196628
H	-1.216893	5.569580	-1.466469
C	-2.392095	3.925391	-2.192284
H	-2.231012	4.181827	-3.235791
C	-3.179174	2.816083	-1.875509
C	-2.992972	2.967879	1.985649
H	-3.720288	2.151337	2.060807
C	-1.683206	2.471976	2.607568
H	-1.306695	1.586682	2.082733
H	-1.837042	2.208916	3.660776
H	-0.904655	3.242089	2.560425
C	-3.563658	4.155515	2.766066
H	-4.505948	4.506990	2.332270
H	-2.867900	5.001792	2.781901
H	-3.754134	3.867949	3.805914
C	-3.789634	1.979607	-2.983927
H	-4.397083	1.191169	-2.524995
C	-2.702232	1.289854	-3.814270
H	-3.157316	0.656197	-4.584044
H	-2.062897	0.660718	-3.184733
H	-2.062623	2.021796	-4.320988
C	-4.718684	2.814277	-3.870917
H	-5.190012	2.178887	-4.628735
H	-4.170700	3.603878	-4.397394
H	-5.511745	3.292148	-3.285736
C	3.713713	0.122483	0.088893

N	4.842213	-0.605528	-0.091887
C	5.964238	0.161516	0.149459
H	6.960011	-0.242357	0.058013
C	5.524696	1.397358	0.489119
H	6.056747	2.296534	0.756320
N	4.143765	1.354857	0.447559
C	4.871355	-1.991941	-0.473759
C	4.894264	-2.309434	-1.841112
C	4.920354	-3.664051	-2.179621
H	4.938582	-3.950655	-3.227653
C	4.927053	-4.649265	-1.200169
H	4.950194	-5.696945	-1.487090
C	4.911399	-4.300251	0.144517
H	4.921797	-5.080149	0.901194
C	4.884575	-2.961778	0.541576
C	4.893360	-1.255509	-2.932607
H	4.880233	-0.267936	-2.457032
C	3.636490	-1.357878	-3.802327
H	2.727487	-1.262045	-3.197916
H	3.592265	-2.317529	-4.329795
H	3.632203	-0.563364	-4.557243
C	6.164370	-1.336803	-3.784132
H	7.066591	-1.236410	-3.171103
H	6.171210	-0.537961	-4.533874
H	6.228770	-2.291957	-4.317134
C	4.865597	-2.608873	2.017140
H	4.870721	-1.516602	2.109592
C	6.113042	-3.134457	2.734202
H	7.031386	-2.752664	2.275218
H	6.158946	-4.228894	2.709469
H	6.104446	-2.827578	3.785927
C	3.585353	-3.115834	2.688270
H	2.695145	-2.705693	2.198221
H	3.564819	-2.818693	3.742978
H	3.520355	-4.209204	2.648988
C	3.306779	2.481145	0.760150
C	2.952333	2.694640	2.101926
C	2.189395	3.828996	2.387316
H	1.901442	4.031195	3.415309
C	1.802665	4.704842	1.380553
H	1.222925	5.590428	1.627579
C	2.162551	4.459039	0.061757
H	1.852511	5.150656	-0.716820
C	2.926731	3.341826	-0.281675
C	3.345830	1.744980	3.217944
H	4.019784	0.986980	2.802906
C	2.115234	1.010740	3.760966
H	1.603361	0.457053	2.965908
H	1.397094	1.712798	4.200704
H	2.409478	0.299421	4.541314
C	4.103448	2.462382	4.339058
H	4.430793	1.740621	5.095301
H	3.473682	3.203248	4.844050
H	4.989426	2.981470	3.958015
C	3.308765	3.102101	-1.730139
H	3.937479	2.205515	-1.775706
C	4.130317	4.265333	-2.294376
H	5.031764	4.447201	-1.699269
H	3.551096	5.195314	-2.314280
H	4.439578	4.047316	-3.322503
C	2.067834	2.830942	-2.586813
H	1.509657	1.965186	-2.213434
H	2.359326	2.630634	-3.624215
H	1.388359	3.690988	-2.589522

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[Au(IPr)OH]

Au	-0.016872	-0.086223	1.570527
O	-0.139290	-0.229258	3.546027
H	0.752795	-0.231507	3.908361
C	0.005910	0.025679	-0.401276
N	-1.063767	0.060215	-1.240956
C	-0.662377	0.118777	-2.563121
H	-1.373303	0.152613	-3.373229
C	0.691205	0.121489	-2.557644

H	1.408752	0.157863	-3.361748
N	1.082236	0.064145	-1.231833
C	-2.434859	0.041420	-0.816684
C	-3.069459	-1.198773	-0.646193
C	-4.407609	-1.185695	-0.248145
H	-4.926946	-2.128715	-0.099999
C	-5.079402	0.009793	-0.028256
H	-6.119745	-0.002886	0.285548
C	-4.422426	1.221402	-0.199947
H	-4.952964	2.151420	-0.013645
C	-3.084690	1.266001	-0.596540
C	-2.354330	-2.520269	-0.852374
H	-1.332182	-2.306079	-1.183872
C	-3.025711	-3.358854	-1.944079
H	-3.068592	-2.819666	-2.897154
H	-4.051338	-3.629564	-1.667816
H	-2.470030	-4.290041	-2.103471
C	-2.252738	-3.297474	0.464070
H	-1.744609	-2.705934	1.233128
H	-1.689139	-4.225897	0.313571
H	-3.245118	-3.567146	0.844312
C	-2.382098	2.602046	-0.743465
H	-1.363790	2.414481	-1.101853
C	-2.263878	3.305273	0.612697
H	-1.741010	2.673584	1.338628
H	-3.251724	3.545793	1.023094
H	-1.707860	4.244416	0.506825
C	-3.074755	3.495127	-1.776769
H	-3.132766	3.006928	-2.756130
H	-2.524291	4.435315	-1.896200
H	-4.096069	3.747688	-1.469419
C	2.450182	0.046432	-0.799461
C	3.090019	-1.193062	-0.643627
C	4.425897	-1.179788	-0.237672
H	4.949299	-2.122438	-0.101591
C	5.091403	0.015683	0.001663
H	6.130820	0.003405	0.318757
C	4.430227	1.226704	-0.158536
H	4.956689	2.156736	0.039325
C	3.094300	1.270752	-0.561834
C	2.381484	-2.514371	-0.873591
H	1.365437	-2.299443	-1.222604
C	2.256309	-3.300801	0.435184
H	1.725636	-2.716461	1.194548
H	3.242217	-3.565753	0.835393
H	1.702152	-4.231855	0.267604
C	3.073831	-3.344297	-1.958678
H	3.135742	-2.796904	-2.905951
H	2.520115	-4.273144	-2.137110
H	4.093526	-3.619289	-1.665275
C	2.388764	2.605915	-0.702638
H	1.371305	2.417690	-1.062620
C	3.081190	3.504412	-1.731511
H	3.140994	3.020032	-2.712617
H	4.101812	3.757442	-1.422122
H	2.529059	4.443942	-1.848050
C	2.266813	3.303714	0.655813
H	1.738433	2.669601	1.375737
H	1.711996	4.243663	0.552080
H	3.253401	3.541829	1.070915

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[Au(IPr)CO_3H]

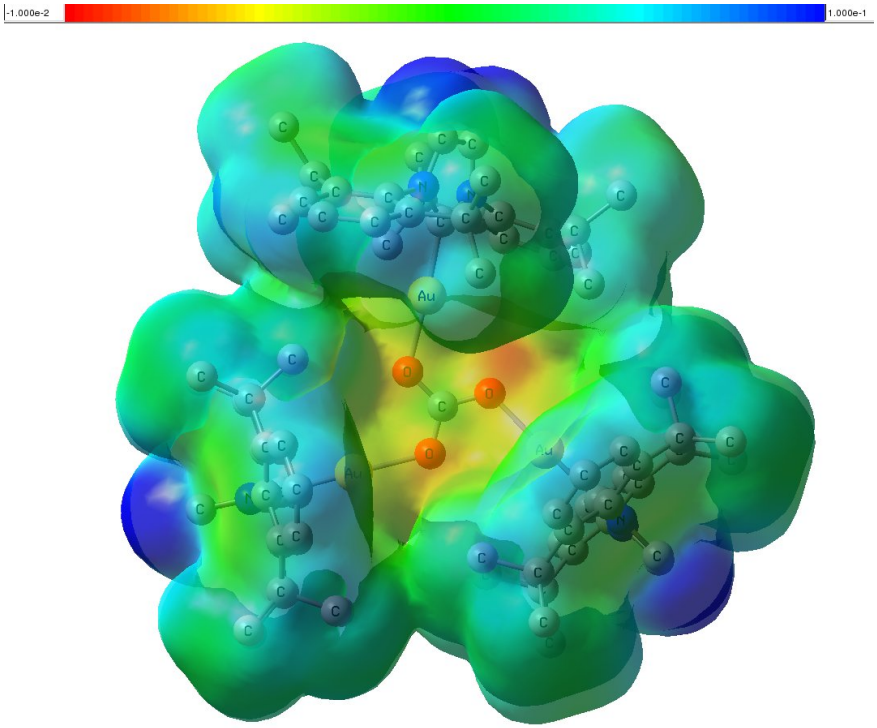
Au	0.000170	-0.624266	-1.091128
O	0.000745	-1.726189	-2.805798
C	-0.000254	0.503472	0.525872
N	1.073171	0.960937	1.216991
C	0.676902	1.691208	2.321137
H	1.391438	2.137321	2.994292
C	-0.678090	1.690990	2.321025
H	-1.392895	2.136867	2.994051
N	-1.073941	0.960619	1.216789
C	0.001601	-3.017849	-2.787638
O	0.002452	-3.765974	-3.745046
O	0.001442	-3.543976	-1.509652

H	0.002116	-4.499019	-1.650246
C	-2.442196	0.717038	0.852779
C	-3.071467	-0.436611	1.345853
C	-3.088626	1.647511	0.024220
C	-4.404372	-0.641213	0.983434
C	-4.420604	1.392302	-0.306905
C	-5.073220	0.261524	0.167066
H	-4.922772	-1.526239	1.342303
H	-4.950624	2.086747	-0.953087
H	-6.109175	0.079923	-0.106069
C	2.441563	0.717787	0.853215
C	3.087872	1.648480	0.024804
C	3.071092	-0.435689	1.346363
C	4.419977	1.393663	-0.306106
C	4.404123	-0.639889	0.984179
C	5.072843	0.263063	0.167945
H	4.949918	2.088295	-0.952153
H	4.922710	-1.524781	1.343105
H	6.108906	0.081788	-0.105001
C	-2.364223	-1.445150	2.231132
H	-1.338210	-1.096753	2.394726
C	-2.274836	-2.815639	1.552002
H	-3.271360	-3.233245	1.365876
H	-1.746012	-2.757033	0.594841
H	-1.735542	-3.519388	2.197158
C	-3.038938	-1.547511	3.602560
H	-4.065085	-1.923075	3.515801
H	-2.486494	-2.240473	4.247313
H	-3.081608	-0.574423	4.104749
C	-2.390333	2.873920	-0.532378
H	-1.384616	2.921566	-0.099547
C	-3.116172	4.165071	-0.143383
H	-2.562928	5.036398	-0.511744
H	-4.122169	4.207239	-0.576165
H	-3.216392	4.258921	0.943706
C	-2.228417	2.763166	-2.051983
H	-1.678812	1.856158	-2.325328
H	-3.202998	2.730487	-2.553036
H	-1.680577	3.629491	-2.440969
C	2.364021	-1.444427	2.231547
H	1.337842	-1.096402	2.394886
C	3.038490	-1.546422	3.603124
H	2.486227	-2.239609	4.247792
H	4.064826	-1.921523	3.516585
H	3.080616	-0.573294	4.105282
C	2.275285	-2.814999	1.552520
H	1.746719	-2.756663	0.595201
H	3.271990	-3.232330	1.366759
H	1.736012	-3.518850	2.197589
C	2.389346	2.874726	-0.531864
H	1.383566	2.922144	-0.099156
C	2.227622	2.763923	-2.051479
H	3.202255	2.731533	-2.552454
H	1.678277	1.856777	-2.324879
H	1.679573	3.630101	-2.440504
C	3.114835	4.166046	-0.142808
H	4.120881	4.208443	-0.575458
H	2.561439	5.037243	-0.511251
H	3.214897	4.259941	0.944291

Optimization of $[(IPrAu)_3CO_3]^+$ (**3**) at the PBE0/ECP1 level afforded a minimum with essentially planar CO_3 moiety (sum of the OCO bond angles 360.0º) and the three Au atoms and the C atoms from the NHCs bonded to them all within ±0.06 Å of this plane. Two of the NHCs are essentially perpendicular to this plane (with $C_{central}$-

$O^{\cdots}C_{NHC}$-N dihedral angles of ca. 87º and one is slightly twisted (dihedral angle ca. 58º). Gold atoms show the expected linear coordination (C-Au-O angles ca. 177º - 179º) and a κ^1, "side-on" coordination mode to the carbonate O atoms (C-O-Au angles ca. 119º - 120º).

Figure S1 Electrostatic Potential of 3



The central carbon atom of the CO_3 moiety has the highest positive charge of any atom (+1.0*e* from natural population analysis at the PBE0/ECP2/PCM level). As apparent from the electrostatic potential plotted in **Figure S1**, the charge on this atom is rather offset by the negative charges on the O atoms around it (-0.8*e*), and the most positive areas are at the CH=CH bridges of the NHCs. Because the CO_3 moiety is sterically shielded by the bulky IPr groups it is rather difficult to predict its reactivity, e.g. with nucleophiles, on these grounds.

- **Kinetic Experiments**

A purpose-built, high-pressure, continuously stirred tank reactor (CSTR), fitted with spectroscopic windows (CaF_2), was purged with N_2 and charged with a solution of **1** (150 mg, 0.25 mmol) and **2** (317 mg, 0.25 mmol) in dry, degassed dichloromethane (40 mL) under a continuous stream of N_2. After cooling to the desired reaction temperature, CO_2 (BOC, CO_2 vapour withdrawal cylinder) was added to the CSTR via a needle valve to a total reactor pressure of 1.2 bar. During the gas addition, single beam infrared spectra were recorded continuously using a Nicolet Nexus spectrometer (4 cm^{-1} resolution, 8 - 64 scans depending on reaction temperature). Single beam spectra were ratioed against backgrounds of dichloromethane under identical gas compositions. Kinetic information was then calculated from the integrated absorbance of the Au-OH stretching region as a function of time. The limits of integration were taken as 3626 – 3482 cm^{-1} with a linear baseline defined by the same limits. Kinetic traces were fitted to single exponentials of the general form Area = A + B exp(-k_{obs}t) and the activation parameters were derived from the corresponding Eyring-Polanyi plot.

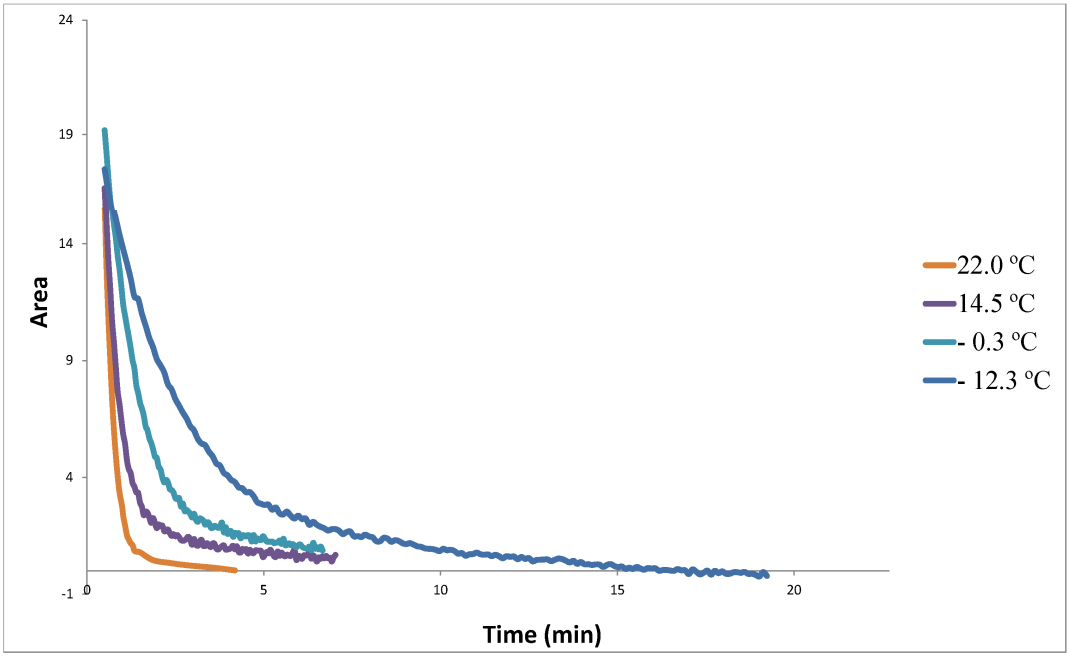


Fig S2. Integrated absorbance of the Au-OH stretching vs time (min)

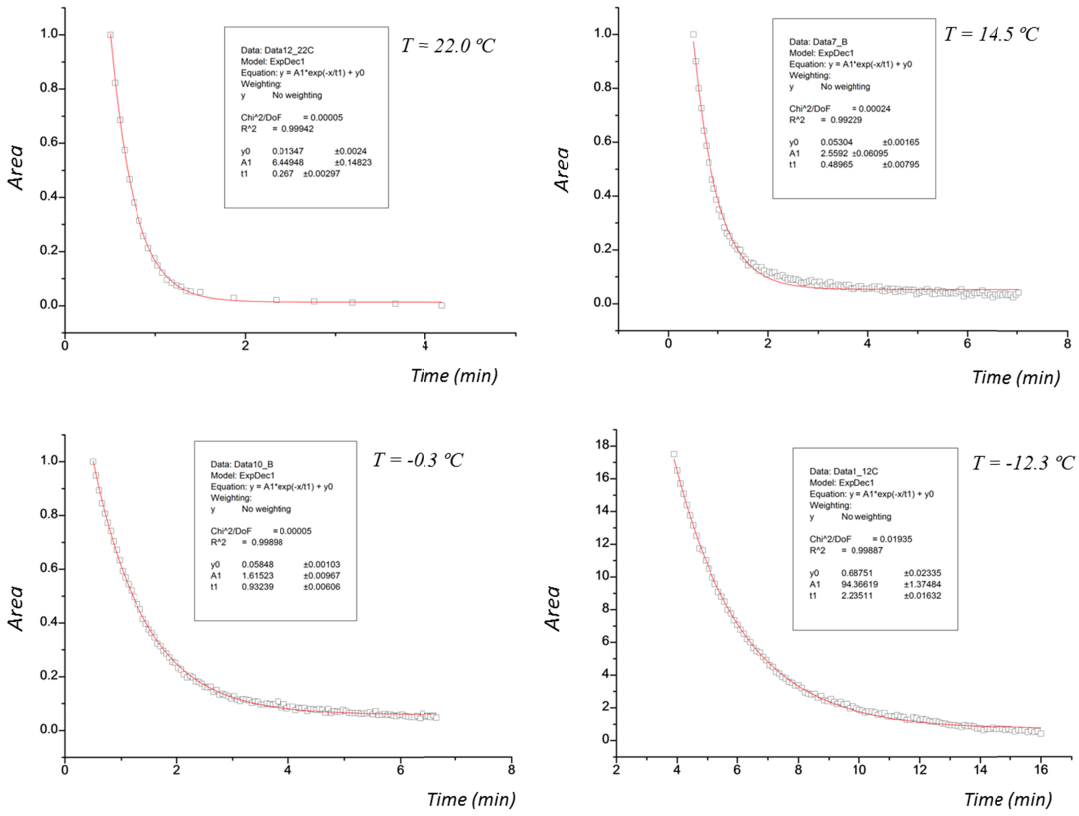


Fig S3. Plot of [**1**+**2**] *vs* time at four different temperatures. Data fitted to single exponentials.

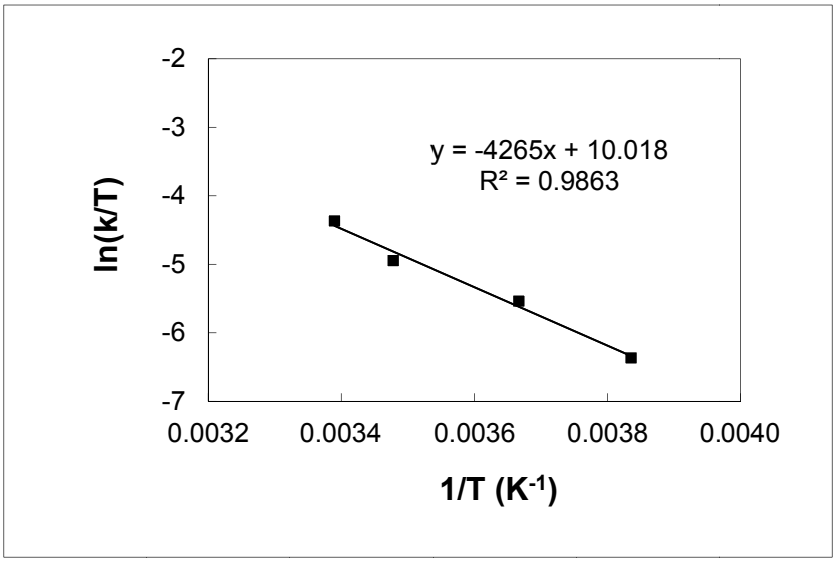


Fig. S4 Eyring-Polanyi plot for the obtained kinetic data

- **Crystallographic information of complex 3**

EXPERIMENTAL DETAILS

Data Collection

A colorless prism crystal of $C_{164.5}H_{217}Au_6B_2ClF_8N_{12}O_6$ having approximate dimensions of 0.240 x 0.090 x 0.090 mm was mounted in a loop. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-Kα radiation.

The crystal-to-detector distance was 45.01 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive triclinic cell with dimensions:

a = 18.436(2) Å α = 99.0625(14)°
b = 18.589(2) Å β = 91.888(2)°
c = 30.244(3) Å γ = 117.078(3)°
V = 9048.7(17) Å^3

For Z = 2 and F.W. = 3849.46, the calculated density is 1.413 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P-1 (#2)

The data were collected at a temperature of -100 ± 1°C to a maximum 2θ value of 51.2°. A total of 1440 oscillation images were collected. A sweep of data was done using ω scans from -100.0 to 80.0° in 0.50° step, at χ=45.0° and ϕ = 0.0°. The exposure rate was 40.0 [sec./°]. The detector swing angle was -10.41°. A second sweep was performed using ω scans from -100.0 to 80.0° in 0.50° step, at χ=45.0° and ϕ = 90.0°. The exposure rate was 40.0 [sec./°]. The detector swing angle was -10.41°. Another sweep was performed using ω scans from -100.0 to 80.0° in 0.50° step, at χ=45.0° and ϕ = 180.0°. The exposure rate was 40.0 [sec./°]. The detector swing angle was -10.41°. Another sweep was performed using ω scans from -100.0 to 80.0° in 0.50° step, at χ=45.0° and ϕ = 120.0°. The exposure rate was 40.0 [sec./°]. The detector swing angle was -10.41°. The crystal-to-detector distance was 45.01 mm. Readout was performed in the 0.086 mm pixel mode.

Data Reduction

Of the 144400 reflections were collected, where 33347 were unique (R_{int} = 0.1068); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku). [12]

The linear absorption coefficient, μ, for Mo-Kα radiation is 49.362 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.469 to 0.641. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[13] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[14] on F^2 was based on 33347 observed reflections and 1854 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.1043$$

$$wR2 = [\Sigma (w (Fo^2 - Fc^2)^2) / \Sigma \, w(Fo^2)^2]^{1/2} = 0.3191$$

The goodness of fit[15] was 1.05. Unit weights were used. Plots of Σ w (|Fo| - |Fc|)^2 versus |Fo|, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 6.25 and -2.43 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4 [16]. Anomalous dispersion effects were

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[12] CrystalClear: Data Collection and Processing Software, Rigaku Corporation (1998-2014). Tokyo 196-8666, Japan.

[13] SIR2004: Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. and Spagna R. (2005). J. Appl. Cryst. 38, 381-388.

[14] Least Squares function minimized: (SHELXL2013)

$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

[15] Goodness of fit is defined as:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations

N_v = number of variables

[16] International Tables for Crystallography, Vol.C (1992). Ed. A.J.C. Wilson, Kluwer Academic Publishers, Dordrecht, Netherlands, Table 6.1.1.4, pp. 572.

included in Fcalc;[17] the values for Δf' and Δf'' were those of Creagh and McAuley.[18] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[19] All calculations were performed using the CrystalStructure[20] crystallographic software package except for refinement, which was performed using SHELXL-2013.[21]

A. Crystal Data

Empirical Formula	$C_{164.5}H_{217}Au_6B_2ClF_8N_{12}O_6$
Formula Weight	3849.46
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.240 X 0.090 X 0.090 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 18.436(2) Å b = 18.589(2) Å c = 30.244(3) Å α = 99.0625(14) ° β = 91.888(2) ° γ = 117.078(3) ° V = 9048.7(17) Å^3
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.413 g/cm^3
F_{000}	3818.00

[17] Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).
[18] Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
[19] Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).
[20] CrystalStructure 4.1: Crystal Structure Analysis Package, Rigaku Corporation (2000-2014). Tokyo 196-8666, Japan.
[21] SHELX2013: Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

μ(MoKα)	49.362 cm^{-1}

B. Intensity Measurements

Diffractometer	XtaLAB P200
Radiation monochromated	MoKα (λ = 0.71075 Å) multi-layer mirror
Voltage, Current	45kV, 66mA
Temperature	-100.0°C
Detector Aperture	83.8 x 70.0 mm
Data Images	1440 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	-100.0 - 80.0°
Exposure Rate	40.0 sec./°
Detector Swing Angle	-10.41°
ω oscillation Range (χ=45.0, ϕ=90.0)	-100.0 - 80.0°
Exposure Rate	40.0 sec./°
Detector Swing Angle	-10.41°
ω oscillation Range (χ=45.0, ϕ=180.0)	-100.0 - 80.0°
Exposure Rate	40.0 sec./°
Detector Swing Angle	-10.41°
ω oscillation Range (χ=45.0, ϕ=120.0)	-100.0 - 80.0°
Exposure Rate	40.0 sec./°
Detector Swing Angle	-10.41°
Detector Position	45.01 mm

Pixel Size	0.086 mm
$2\theta_{max}$	51.2^{o}
No. of Reflections Measured	Total: 144400 Unique: 33347 (R_{int} = 0.1068)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.469 - 0.641)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR2004)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\ w\ (Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\ \sigma^2(Fo^2) + (0.1678 \cdot P)^2 + 85.7639 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	51.2^{o}
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	33347
No. Variables	1854
Reflection/Parameter Ratio	17.99
Residuals: R1 ($I>2.00\sigma(I)$)	0.1043
Residuals: R (All reflections)	0.1382
Residuals: wR2 (All reflections)	0.3191
Goodness of Fit Indicator	1.046
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	6.25 $e^-/Å^3$

Minimum peak in Final Diff. Map	-2.43 $e^-/Å^3$

B. Intensity Measurements

Diffractometer	XtaLAB P200
Radiation monochromated	MoKα (λ = 0.71075 Å) multi-layer mirror
Voltage, Current	45kV, 66mA
Temperature	-100.0°C
Detector Aperture	83.8 x 70.0 mm
Data Images	1440 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	-100.0 - 80.0°
Exposure Rate	40.0 sec./°
Detector Swing Angle	-10.41°
ω oscillation Range (χ=45.0, ϕ=90.0)	-100.0 - 80.0°
Exposure Rate	40.0 sec./°
Detector Swing Angle	-10.41°
ω oscillation Range (χ=45.0, ϕ=180.0)	-100.0 - 80.0°
Exposure Rate	40.0 sec./°
Detector Swing Angle	-10.41°
ω oscillation Range (χ=45.0, ϕ=120.0)	-100.0 - 80.0°
Exposure Rate	40.0 sec./°
Detector Swing Angle	-10.41°
Detector Position	45.01 mm
Pixel Size	0.086 mm

$2\theta_{max}$	51.2°
No. of Reflections Measured	Total: 144400 Unique: 33347 (R_{int} = 0.1068)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.469 - 0.641)