## Tracking Gold Acetylides in Gold(I)-Catalyzed Cycloisomerization Reactions of Enynes

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General Methods. THF distilled over sodium-benzophenone was ketvl. Dichloromethane, was distilled over calcium hydride. n-Butyllithium was purchased as 2.5 M solution in hexane. Other reagents were commercially available and used without further purification. Thin layer chromatography (TLC) was performed on Merck 60 F<sub>254</sub> silica gel. Merck Gerudan SI 60 Å silica gel (0.035-0.070 mm) was used for column chromatography. NMR spectra (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, DEPT, COSY, HMQC, HMBC, NOE) were recorded at room temperature on a Bruker AVANCE spectrometer (400 MHz). Chemical shifts are given in ppm, referenced to the residual proton resonance of the solvents ( $\delta = 7.26$  for CHCl<sub>3</sub>), to the residual carbon resonance of the solvent ( $\delta = 77.16$  for CDCl<sub>3</sub>), or to the phosphorus resonance of H<sub>3</sub>PO<sub>4</sub> ( $\delta = 0.0$  ppm). Coupling constants (*J*) are given in Hertz (Hz). The terms m, s, d, t and q refer to multiplet, singlet, doublet, triplet and quartet; br means that the signal is broad. When possible, <sup>1</sup>H and <sup>13</sup>C signals were assigned on the basis of DEPT and 2D-NMR (COSY, HMBC) experiments. Low resolution mass spectra (MS) and high resolution mass spectra (HRMS) were measured by the Service de Spectrométrie de Masse de l'Université Pierre et Marie Curie, Paris VI. Triphenylphosphinegold chloride was purchased from Strem, [bis(trifluoromethanesulfonyl)imidate](triphenylphosphine)gold (2:1 toluene adduct) and (Acetonitrile)[(2-biphenyl)di-tert-butylphosphine]gold(I) hexafluoroantimonate were purchased from Aldrich. Both were used as received. Infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer. Absorbance frequencies are given in cm<sup>-1</sup> at the peak maximum and at the medium C=C triple bond band. Due to the gold quadrupole, <sup>13</sup>C NMR signals of carbon atoms of triple bonds attached to gold and in propargylic positions are very broad and are not observed.

**Procedure for the synthesis of gold acetylides.** In a dry Schlenk apparatus under argon was dissolved 0.9 mmol of enyne or allenyne in 12 mL of THF. The solution was cooled down to 0 °C then 0.9 mmol of *n*-BuLi (2.25 M in hexanes, 380  $\mu$ L) was added. A brown color could appear. The mixture was stirred at 0 °C for 10 min, then 0.3 mmol of AuClPPh<sub>3</sub> was added. The reaction was warmed up to room temperature and allowed to stir for 3 hours, after what the reaction was quenched with 6 mL of a saturated aqueous solution of NH<sub>4</sub>Cl. The organic layer was removed under vacuum, then 12 mL of CH<sub>2</sub>Cl<sub>2</sub> were added. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic extracts were dried over MgSO<sub>4</sub>. After removal of the solvent, a gum was obtained that can be purified in several manners: direct precipitation in CHCl<sub>3</sub>/hexane followed by filtration on a fritted glass and washing with hexane; slow precipitation in a 5:95 CHCl<sub>3</sub>/hexane mixture at -25 °C when the direct precipitation was not effective; flash chromatography on neutral alumina in a 1:1 pentane/CH<sub>2</sub>Cl<sub>2</sub> mixture if the afore mentioned precipitation techniques were not able to furnish the acetylide with the desired purity. Any attempt to purify the acetylide on silica gel led to decomposition (PPh<sub>3</sub> observed).



White solid, 83 % upon precipitation in CHCl<sub>3</sub>/hexane. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 7.55 - 7.42$  (m, 15H), 5.93 – 5.82 (m, 1H), 5.11 (d, J = 17.1 Hz, 1H), 5.05 (d, J = 10.0 Hz, 1H), 3.36 (s, 4H), 3.34 (s, 6H), 2.40 (s, 2H), 2.27 (d, J = 7.5 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 134.9$  (3C), 134.5 (d, J = 13.7 Hz, 6C), 131.6, 131.2 (d, J = 21.9 Hz, 3C), 129.2 (d, J = 11.2 Hz, 6C), 117.6, 75.0 (2C), 59.4 (2C), 41.9, 36.6, 23.8. <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta = 42.9$ . IR (neat) 649, 710, 750, 917, 997, 1101, 1435, 1479, 2341, 2360. HRMS calculated for  $[C_{29}H_{32}O_2AuNaP]^+$ : 663.1698, found: 663.1703.



Pale yellow solid, 37 % upon precipitation in CHCl<sub>3</sub>/hexane at -25 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta = 7.56 - 7.40$  (m, 15H), 5.75 (dq, J = 10.0, 7.4 Hz, 1H), 5.20 (d, J = 17.0 Hz, 1H), 5.09 (d, J = 10.1 Hz, 1H), 4.26 - 4.15 (m, 4H), 2.99 (d, J = 1.8 Hz, 2H), 2.93 (d, J = 7.4 Hz, 2H), 1.25 (t, J = 7.1 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta = 170.6$  (2C), 134.5 (d, J = 13.8 Hz, 6C), 132.9, 131.6 (3C), 129.2 (d, J = 11.2 Hz, 6C), 119.2, 61.5 (2C), 57.6, 36.7, 24.3, 14.3 (2C). <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta = 42.8$ . IR (neat) 692, 710, 742, 754, 921, 998, 1018, 1101, 1187, 1210, 1435, 1731, 2360. HRMS calculated for [C<sub>31</sub>H<sub>32</sub>O<sub>4</sub>AuNaP]<sup>+</sup>: 719.1596, found: 719.1604.

**Preparation of the digold complexes.** The gold acetylide (14  $\mu$ mol) was dissolved in 0.2 mL of CDCl<sub>3</sub>. A solution of Ph<sub>3</sub>PAuNTf<sub>2</sub> (2:1 toluene adduct, 14  $\mu$ mol in 0.2 mL of CDCl<sub>3</sub>) was added to the former solution. The mixture was stirred for 5 min. The formation of the digold complex was checked by <sup>31</sup>P NMR. A minor residual peak was always observed in <sup>31</sup>P NMR which was attributed to (Ph<sub>3</sub>P)<sub>2</sub>AuNTf<sub>2</sub> in analogy with the previous observations made by Fürstner and co-workers in their study of *gem*-diaurated species.<sup>1</sup> Any attempt to precipitate or crystallize the digold complex failed.



<sup>&</sup>lt;sup>1</sup> Seidel, G.; Lehmann, C. W.; Fürstner, A. Angew. Chem. Int. Ed. 2010, 49, 8466.

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 7.57–7.39 (m, 30H), 7.28–7.15 (m, toluene), 5.82-5.72 (m, 1H), 5.14– 5.03 (m, 2H), 3.32 (q, *J* = 9.2 Hz, 4H), 3.24 (s, 6H), 2.96 (s, 2H), 2.35 (toluene), 2.27 (d, *J* = 7.6 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 134.0 (d, *J* = 13.7 Hz, 12C), 133.1 (6C), 132.8 (d, *J* = 5.6 Hz, 6C), 129.9 (d, *J* = 11.8 Hz, 12C), 129.2 (toluene), 128.4 (toluene), 128.1, 119.1, 74.0 (2C), 59.5 (2C), 42.6, 36.7, 25.4. <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  = 36.4 (2P).



<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta = 7.44 - 7.37$  (m, 30H), 5.68 - 5.63 (m, 1H), 5.19 (dd, J = 16.9, 1.7 Hz, 1H), 5.10 (dd, J = 10.1, 1.7 Hz, 1H), 4.18 - 4.07 (m, 4H), 3.47 (s, 2H), 2.90 (d, J = 7.4 Hz, 2H), 2.35 (toluene), 1.21 (t, J = 7.1 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta = 169.2$  (2C), 134.0 (d, J = 13.7 Hz, 12C), 133.1 (6C), 132.8 (d, J = 5.6 Hz, 6C), 131.2, 129.8 (d, J = 11.9 Hz, 12C), 129.2 (toluene), 128.4 (toluene), 127.9 (not attributed), 125.4 (toluene), 120.8, 62.4 (2C), 57.0, 36.9, 31.7, 25.4, 21.6 (toluene), 14.2 (2C). <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta = 36.1$  (2P).

An oven-dried round-bottom flask was introduced in a glove box and was loaded with  $Ph_3PAuCl$  (7.3 mg, 14.7 µmol) and AgBF<sub>4</sub> (2.9 mg, 14.7 µmol). The solids were dissolved in 0.2 mL of distilled and degassed CDCl<sub>3</sub> and the solution was stirred for 5-10 min. The supernatant was then added via a syringe through a UptidiscTM PTFE (13 mm/0.45 µm) syringe filter to a solution of **1-Au** (10 mg, 14 µmol) dissolved in 0.2 mL of CDCl<sub>3</sub>. The mixture was stirred for 5 min. The formation of the digold complex was checked by <sup>31</sup>P NMR. A minor residual peak was always observed in <sup>31</sup>P NMR which was attributed to (Ph<sub>3</sub>P)<sub>2</sub>AuBF<sub>4</sub> in analogy with our previous observations in the generation of **1-Au<sub>2</sub>NTf<sub>2</sub>**.



<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 7.67 – 7.41 (m, 30H), 5.84 – 5.74 (m, 1H), 5.15 – 5.04 (m, 2H), 3.34 – 3.28 (m, 4H), 3.25 (s, 6H), 2.80 (s, 2H) , 2.25 (d, *J* = 7.6 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  =

134.2 (d, J = 13.7 Hz, 12C), 133.6, 132.6 (6C), 129.8 (d, J = 11.7 Hz, 12C), 118.7, 74.3 (2C), 59.5 (2C), 42.4, 36.7, 25.5. <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta = 37.1$  (2P).

**Preparation of the trigold complex.** In round-bottom flask was introduced  $[(Ph_3PAu)_3O]BF_4$  (54 mg, 0.037 mmol, 0.5 equiv)<sup>2</sup> and CDCl<sub>3</sub> (3 mL). Enyne 1 (13 mg, 0.074 mmol, 1 equiv) was then dissolved in the solution, and the mixture took instantaneously a pale yellow color. Formation of the trigold complex was checked by <sup>1</sup>H and <sup>31</sup>P NMR and complete disappearance of the free enyne and gold complex was observed after 30 min.



<sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  = 7.57 – 7.37 (m, 45H), 5.82 (dq, *J* = 10.1, 7.5 Hz, 2H), 5.15 – 5.02 (m, 4H), 3.33 (q, *J* = 9.2 Hz, 8H), 3.28 (s, 12H), 2.70 (br s, 4H), 2.27 (d, *J* = 7.5 Hz, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 134.2 (d, *J* = 13.7 Hz, 18C), 133.9 (9C), 132.44 (9C), 129.7 (d, *J* = 11.7 Hz, 18C), 128.8 (2C), 118.5 (2C), 74.5 (4C), 59.5 (4C), 42.3 (2C), 36.64 (2C), 24.7 (2C). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  38.3 (3P). HRMS calculated for [C<sub>76</sub>H<sub>79</sub>Au<sub>3</sub>O<sub>4</sub>P<sub>3</sub>]<sup>+</sup>: 1739.4188, found: 1739.4181.

### Organic products.



To a solution of enyne (0.2 mmol) in  $CDCl_3$  (8 mL) was added 2 mol% (4 µmol) of the gold catalyst. The reaction was carried out either at room temperature or under reflux when the catalyst was not effective at room temperature, and monitored by thin layer chromatography. After completion, the solution was filtered over a short plug of silica (eluted with Et<sub>2</sub>O) and the solvents were removed under reduced pressure to afford a colorless oil.

<sup>&</sup>lt;sup>2</sup> Addition of only 0.33 equiv led to a mixture of free enyne and trigold complex.



Isolated after column chromatography (Pentane/Et<sub>2</sub>O 95:5). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 6.14 (dt, *J* = 2.0, 10.0 Hz, 1H), 5.77 (dt, *J* = 0.8, 8.8 Hz, 1H), 4.90 (dt, *J* = 0.8, 6.0 Hz, 2H), 4.21-4.10 (m, 4H), 2.85 (t, *J* = 1.4 Hz, 2H), 2.68-2.66 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 6H). Other spectral data identical to those reported.<sup>3</sup>



Isolated after column chromatography (Pentane/Et<sub>2</sub>O 95:5). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 6.47 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.57 (brs, 1H), 5.11 (d, *J* = 6.4 Hz, 1H), 5.08 (s, 1H), 4.20 (q, *J* = 7.2 Hz, 4H), 3.12 (brs, 2H), 3.09 (brs, 2H), 1.25 (t, *J* = 7.2 Hz, 6H). Other spectral data identical to those reported.<sup>4</sup>



Isolated after column chromatography (Pentane/Et<sub>2</sub>O 98:2). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 6.12 (dt, *J* = 2.0, 9.6 Hz, 1H), 5.69 (dt, *J* = 3.6, 9.6 Hz, 1H), 4.84 (s, 1H), 4.79 (s, 1H), 3.31 (s, 6H), 3.21 (s, 2H), 3.20 (s, 2H), 2.26 (t, *J* = 1.6 Hz, 2H), 2.04 (d, *J* = 1.6 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 141.3, 128.9, 127.7, 112.4, 75.9 (2C), 59.5 (2C), 38.8, 35.4, 29.8.



This product could not be separated from the *endo* one described above. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 6.50 (dd, *J* = 10.8, 17.2 Hz, 1H), 5.57 (s, 1H), 5.04 (d, *J* = 6.8 Hz, 1H), 5.00 (s, 1H), 3.35 (s, 6H), 2.31 (s, 2H), 2.29 (s, 2H).

<sup>&</sup>lt;sup>3</sup> Grigg, R.; Stevenson, P.; Worakun, T. Tetrahedron 1988, 44, 4967.

<sup>&</sup>lt;sup>4</sup> Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. J. Am. Chem. Soc. 1994, 116, 6049.

NMR Spectra of the Compounds Described Above













S11



















0



-30



-80

-130

-190





130

80

40













NMR Monitoring Corresponding to Scheme 5



























S39

Mass Spectrometry Analysis. All the ESI mass spectra were recorded using a Quattro II triple-quadrupole mass spectrometer (Micromass, Manchester, U.K.). The data were acquired using Masslvnx software (version 4.0). The ESI capillary voltage was maintained at 3.5 kV (positive mode), and the cone voltage ( $V_c$ ) was tuned between 20 to 60 V for complex ion desolvation. Nitrogen was used as the desolvation and nebulization gas. The source and desolvation temperatures were kept at 80 °C. The stock solution (1 µg/µL) was made in  $CDCl_3$  (except for AgSbF<sub>6</sub> prepared in acetonitrile) and the working standard was prepared by further diluting the stock solution with CDCl<sub>3</sub> (the special use of CH<sub>3</sub>CN is mentioned) to achieve a final concentration of 10  $\mu$ M for the catalyst (A, B, C or AgSbF<sub>6</sub>), 200  $\mu$ M for the substrate (1 or 1-D) and 10 µM for 1-Au. The sample solution was introduced into the ESI source of the mass spectrometer using an infusion pump at a flow rate of 300  $\mu$ L/h. The ESI mass spectra were recorded by scanning the first analyzer Q1. The collision-induced dissociation (CID) experiments were done by selecting the precursor ion of interest with Q1 and by scanning Q3. The collision voltage was set to 15-60 V. Argon was used as the collision target gas, and the collision cell pressure was maintained at  $7.10^{-4}$  mbar. All of the spectra were obtained as the average of 2 minutes. High-resolution mass spectrometry (HRMS) measurements were acquired with a recent ultra-high resolution mass spectrometer, the hybrid linear ion trap LTQ-Orbitrap (Thermo Fisher Scientific, Les Ulis, France). The analyses were performed using a syringe pump. Each direct introduction was carried out at a flow rate of 5 µL/min and solutions, previously analyzed, were diluted by a factor of 10 for HRMS measurements. The electrospray voltage was set to 3.7 kV, the capillary voltage and the tube lens offset was set to 40 V and 120 V, respectively. The sheath gas flow (nitrogen) was optimized at 12 (arbitrary units) and the drying gas temperature was set to 270 °C. The mass resolving power (full width at half maximum height) was set at  $10^5$  FWHM.



Fig S1. ESI mass spectra of 1 with A, 1-D with A, 1 with B leading to the formation of  $1-Au_2$  (*m*/*z* 1099) and 1 with C leading to the formation of  $1'-Au_2$  (*m*/*z* 1171), (V<sub>c</sub> = 40 V).

One can notice the presence of oxygen-containing species: m/z 935 ion  $[(Ph_3PAu)_2OH]^+$  is observed in weak abundance compared to the corresponding m/z 1007 ion  $[((biphenyl-2-yl)(t-Bu)_2PAu)_2OH]^+$ . The corresponding protonated mono-gold species are present at m/z 477  $[(Ph_3PAu)OH]H^+$  and m/z 513  $[((biphenyl-2-yl)(t-Bu)_2PAu)OH]H^+$ , respectively. The

enlargement of the ESI mass spectrum of 1 with C leading to 1'-Au<sub>2</sub> (m/z 1171) also shows [1 + ((biphenyl-2-yl)(t-Bu)<sub>2</sub>PAu)<sub>2</sub>OH]<sup>+</sup> at m/z 1189, (V<sub>c</sub> = 40 V).



**Fig S1bis**. HRMS of **1'-Au**<sub>2</sub> (C<sub>51</sub>H<sub>71</sub>O<sub>2</sub>P<sub>2</sub>Au<sub>2</sub><sup>+</sup>, theoretical value m/z 1171.42548, -3.3 ppm) and  $[1 + ((biphenyl-2-yl)(t-Bu)_2PAu)_2OH]^+$  (C<sub>51</sub>H<sub>73</sub>O<sub>3</sub>P<sub>2</sub>Au<sub>2</sub><sup>+</sup>, theoretical value m/z 1189.43605, -1.6 ppm).



Fig S2. Similar CID spectra of bimetallic ions:  $1-Au_2$  (m/z 1099) is formed in the ESI source starting from different mixtures (from up to down): 1 with A, 1 with B, 1-Au with A, and 1-Au with B ( $V_c = 60$  V and collision voltage 40 V).



**Fig S3**. CID spectra of bimetallic ions. (**1''-Au**<sub>2</sub> (m/z 1135) and **1-AuAg** (m/z 747) are formed in the ESI source using different mixtures: **1-Au** with C and **1-Au** with AgSbF<sub>6</sub> (V<sub>c</sub> = 60 V and collision voltage 50 V).



Fig S4. ESI mass spectrum of 1 with B (x = 1 equiv, see Scheme 5) prepared in CDCl<sub>3</sub> but analyzed in CH<sub>3</sub>CN (400  $\mu$ M) at low cone voltage (V<sub>c</sub> = 20 V). Low cone voltage (low internal energy) allows the study of labile species. Note that trimetallic ion 7 (m/z 1739) is eight times less abundant when analyzed in CDCl<sub>3</sub> instead of CH<sub>3</sub>CN, suggesting its decomposition in the ESI source during desolvation processes.



**Fig S4bis**. HRMS of **7** ( $C_{76}H_{79}O_4P_3Au_3^+$ , theoretical value *m*/*z* 1739.41823, -0.1 ppm).



Fig S5. CID spectra of the corresponding trimetallic ions 7 (m/z 1739, V<sub>c</sub> = 20 V and collision voltage 15 V) and [7 - PPh<sub>3</sub>] (m/z 1477, V<sub>c</sub> = 60 V and collision voltage 50 V).



**Fig S6**. ESI mass spectra of **1** with **B**, with or without 5% H<sub>2</sub>O, leading to the formation of **1**-Au<sub>2</sub> (m/z 1099) (V<sub>c</sub> = 40 V). For these experiments CH<sub>3</sub>CN is used as solvent instead of CDCl<sub>3</sub>. Note that m/z 944 corresponds to [(Ph<sub>3</sub>PAu)<sub>2</sub>CN]<sup>+</sup>.

**Computational Details:** All geometries of intermediates and transition states were optimized fully without symmetry constraints using the Gaussian 03 program.<sup>i</sup> The DFT computations were carried out using the B3LYP functional as implemented in Gaussian. The computations were done using the LACVP(d,p) basis set: the gold atom was described by a double- $\zeta$  basis set with the effective core potential of Hay and Wadt (LANL2DZ),<sup>ii</sup> and the 6-31G(d,p) basis set<sup>iii</sup> was used for the other elements. Frequency calculations were performed to confirm the nature of the stationary points and to obtain zero-point energies (ZPE).

		$\checkmark$					
		AuPH <sub>3</sub>					
		$\uparrow$ + /					
		Âu P H₃				`Au	
	E(RB+HF-LY	(P) = -1229.20	0066301		F(RB3I VP	$P = -4075343^{\circ}$	35752
С	-0.786719	1.715386	-0.778587	с	-1.15151	-1.078067	0.391231
C	-1.738497	2.72763	-1.216311	C	-2.484942	-1.65286	0.575523
С	-2.499279	3.487285	-0.102326	с	-3.519336	-1.259088	-0.506642
С	-3.707262	2.742502	0.495318	С	-4.16639	0.126927	-0.319661
С	-3.383386	1.520418	1.311638	С	-3.222511	1.296497	-0.393722
н	-2.444335	2.272159	-1.92371	н	-2.870694	-1.374739	1.566157
Н	-1.153933	3.44318	-1.812532	н	-2.386655	-2.746507	0.58617
н	-1.794704	3.767861	0.688648	н	-3.045162	-1.322759	-1.493042
н	-2.859852	4.422019	-0.543824	н	-4.319362	-2.009151	-0.495852
н	-4.231153	3.455846	1.147278	н	-4.929786	0.238095	-1.104539
Au	1.997895	0.40608	0.020095	Au	1.738352	0.075487	-0.039998
Р	4.255144	-0.042055	0.508832	С	-0.031621	-0.634536	0.223917
н	5.190528	0.314567	-0.479222	С	-3.138233	2.267158	0.516593
н	4.792512	0.60206	1.637983	н	-3.752493	2.262884	1.414545
н	4.621536	-1.377282	0.759004	н	-2.450867	3.099977	0.401764
С	0.076213	0.895548	-0.426834	н	-4.70432	0.153381	0.637088
С	-3.981075	0.331853	1.182737	н	-2.583209	1.339129	-1.275873
Au	-0.961356	-0.960943	-0.201433				
Р	-1.962353	-3.058602	0.009306				
Н	-2.391639	-3.433666	1.29538				
Н	-3.131106	-3.273591	-0.743093				
Н	-1.192406	-4.177334	-0.357555				
Н	-4.750451	0.156012	0.434111				

## Coordinates of the species involved

н	-3.759379	-0.487465	1.861152				
н	-4.415338	2.481364	-0.301229				
н	-2.638671	1.654575	2.097432				
	/				(H <sub>3</sub>	$PAu)_2OH^+$	
	ſ	`\``					1.000.00
	Ĺ	Âu			E(KB+HF-LY	(P) = -1032.92	168266
	E(RB3LYP	e) = -407.51094	45322				
С	-2.415994	0.524059	0.518657	Au	1.846818	-0.142252	0.000195
С	-2.603712	-0.960688	0.072663	Р	3.889544	0.875974	-0.005399
С	-1.749241	1.475924	-0.515964	Н	3.901313	2.241099	0.328783
С	-0.242981	1.74134	-0.520049	Н	4.839972	0.343303	0.882595
С	0.603469	2.041344	0.539296	н	4.581374	0.862484	-1.228423
С	-0.142525	-2.052074	-0.16144	0	-0.000071	-1.098574	0.07688
С	-1.319889	-1.655038	-0.082239	Au	-1.846764	-0.142164	0.000185
н	-3.41693	0.920276	0.724838	Р	-3.88948	0.876255	-0.0052
н	-1.872356	0.541848	1.469456	Н	-4.90253	0.196121	-0.70223
н	-3.183114	-0.982973	-0.861309	н	-3.947188	2.160714	-0.572639
н	-3.223678	-1.457302	0.830588	н	-4.477618	1.080387	1.25501
н	-2.020014	1.139784	-1.52295	н	-0.000011	-1.910061	-0.449214
н	-2.206495	2.470512	-0.407482				
н	0.142753	1.977809	-1.511992				
н	1.557577	2.520787	0.345819				
н	0.257156	2.036389	1.568748				
Au	0.774561	-0.200713	0.003275				
	А	$u(PH_3)_2^+$			Н	<sub>3</sub> PAuOH	
	E(RB3LYP	r = -821.58169	93988		E(RB+HF-LY	(P) = -554.451	632477
Au	0.000038	0.000105	-0.000065	Au	-0.236192	0.002746	0.000329
Р	-2.378296	-0.000223	0.000113	Р	2.053569	-0.002042	-0.000025
н	-2.98725	-1.076243	-0.66749	Н	2.715388	-0.844342	-0.918473
н	-2.987238	-0.040722	1.265842	Н	2.712419	1.212822	-0.277235
н	-2.987415	1.11608	-0.597611	Н	2.730696	-0.371258	1.181605
Р	2.378195	-0.000244	0.000095	0	-2.216616	-0.1205	-0.001154
Н	2.986339	-0.350182	1.217523	Н	-2.56995	0.780496	-0.002271
н	2.986691	1.228974	-0.304912				
Н	2.987403	-0.87919	-0.911331				
	(H	I <sub>3</sub> PAu) <sub>3</sub> O'				$H_2O$	
	E(RB+HF-LY	(P) = -1510.97	7907197		E(RB+HF-LY	(P) = -76.4197	365721
Au	-1.298225	-1.546824	-0.041471	0	0	0.119155	0
Р	-2.778206	-3.266819	0.198425	н	0.759322	-0.476617	0
н	-2.235082	-4.5643	0.19667	н	-0.759322	-0.476621	0
н	-3.530554	-3.287596	1.388548				
н	-3.790928	-3.388844	-0.770246				
0	0.032968	-0.018651	-0.265268				

$\begin{array}{cccccccccccccccccccccccccccccccccccc$								
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Au	-0.723162	1.862975	-0.037886				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Р	-1.577622	3.967297	0.189592				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	н	-2.978308	4.072158	0.267571				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	н	-1.285892	4.893685	-0.828298				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	н	-1.186314	4.68385	1.335687				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Au	2.035503	-0.324316	-0.032139				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Р	4.282853	-0.658331	0.185332				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	н	5.087986	0.49354	0.244254				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	н	4.920621	-1.386474	-0.835226				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	н	4.714168	-1.354	1.331134				
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		Ha	PAuOH <sub>2</sub> <sup>+</sup>			\$	$\searrow$	
E(RB+HF-LYP) = -554.840541868 $E(RB+HF-LYP) = -554.840541868$ $E(RB+HF-LYP) = -272.683213587$ $Au - 0.187345 - 0.000656 - 0.002242 C 1.716159 - 0.44382 - 0.118519 C 1.252233 - 0.870387 - 0.566026 C 0.170645 - 1.51615 - 0.332392 C 1.252233 - 0.870387 - 0.566026 C 0.170645 - 1.51615 - 0.332392 C - 1.463486 - 0.471126 - 0.422968 C - 1.463486 - 0.471126 - 0.422968 C - 1.463486 - 0.471126 - 0.422968 C - 2.370307 - 0.002479 - 0.056325 H 0.875147 - 0.79547 - 1.59504 H - 2.835133 - 0.779253 - 0.271571 H 2.119949 - 1.541386 - 0.610514 H - 2.831786 - 0.786571 - 0.270653 H 0.461216 - 1.394274 - 1.382388 H - 0.1672 - 2.594328 - 0.13319 H - 1.926273 - 1.581215 - 0.761493 C 2.2138271 - 1.508039 - 0.267147 C - 2.040343 - 1.349035 - 0.397315 H - 2.393987 - 1.060528 - 1.38462 H - 2.178721 - 2.388635 - 0.116385 H - 1.574321 - 1.1901 - 0.915703 H - 1.118721 - 0.806317 - 1.401329 H - 2.49133 - 2.456368 - 0.599475$ $H - 0.954874 - 0.204529 - 0 C - 1.772388 - 1.0992 - 0.352967 H - 0.654237 - 0.725148 0 C C - 1.178828 - 1.056402 - 0.611498 H - 0.300636 - 0.929423 0 C C - 3.15096 - 1.573663 - 0.480286 H - 0.300636 - 0.929423 0 C C - 3.615345 - 1.459157 - 0.371356$							$\sim$	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		E(RB+HF-LY	(P) = -554.840	0541868				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $							//	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $								
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						E(RB+HF-LY	(P) = -272.683	213587
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Au	-0.187345	0.000656	0.002242	С	1.716159	0.44382	0.118519
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Р	2.092837	-0.001486	-0.007521	С	1.252233	-0.870387	0.566026
$ \begin{array}{c ccccc} H & 2.677391 & 1.269971 & -0.11912 & C & -1.260616 & -0.987995 & -0.116751 \\ H & 2.683154 & -0.541269 & 1.146245 & C & -1.463486 & 0.471126 & -0.422968 \\ O & -2.370307 & -0.002479 & 0.063253 & H & 0.875147 & -0.79547 & 1.59504 \\ H & -2.835133 & 0.779253 & -0.271571 & H & 2.119949 & -1.541386 & 0.610514 \\ H & -2.831786 & -0.786571 & -0.270653 & H & 0.461216 & -1.394274 & -1.382388 \\ H & 0.1672 & -2.594328 & -0.13319 \\ H & -1.926273 & -1.581215 & -0.761493 \\ C & 2.138271 & 1.58039 & -0.267147 \\ C & -2.040343 & 1.349035 & 0.397315 \\ H & -2.393987 & 1.060528 & 1.38462 \\ H & -2.178721 & 2.388635 & 0.116385 \\ H & -1.118721 & 0.806317 & -1.401329 \\ H & 2.49133 & 2.456368 & -0.599475 \\ \end{array} $	н	2.676517	-0.731055	-1.055204	С	0.170645	-1.51615	-0.332392
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	н	2.677391	1.269971	-0.11912	С	-1.260616	-0.987995	-0.116751
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	н	2.683154	-0.541269	1.146245	С	-1.463486	0.471126	-0.422968
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0	-2.370307	-0.002479	0.063253	Н	0.875147	-0.79547	1.59504
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	н	-2.835133	0.779253	-0.271571	Н	2.119949	-1.541386	0.610514
$\begin{array}{c cccc} H & 0.1672 & -2.594328 & -0.13319 \\ H & -1.926273 & -1.581215 & -0.761493 \\ C & 2.138271 & 1.508039 & -0.267147 \\ C & -2.040343 & 1.349035 & 0.397315 \\ H & -2.393987 & 1.060528 & 1.38462 \\ H & -2.178721 & 2.388635 & 0.116385 \\ H & -1.574321 & -1.1901 & 0.915703 \\ H & -1.118721 & 0.806317 & -1.401329 \\ H & 2.49133 & 2.456368 & -0.599475 \\ \hline \\ H_3O^+ \\ E(RB+HF-LYP) = -76.7037352582 \\ \hline \\ H & 0.954874 & -0.204529 & 0 \\ H & 0.954874 & -0.204529 & 0 \\ H & -0.654237 & -0.725148 & 0 \\ H & -0.654237 & -0.725148 & 0 \\ H & -0.300636 & 0.929423 & 0 \\ \hline \\ H & -0.300636 & 0.929423 & 0 \\ \hline \\ C & 3.615345 & 1.459157 & 0.371356 \\ \hline \end{array}$	н	-2.831786	-0.786571	-0.270653	Н	0.461216	-1.394274	-1.382388
$\begin{array}{c ccccc} H & -1.926273 & -1.581215 & -0.761493 \\ C & 2.138271 & 1.508039 & -0.267147 \\ C & -2.040343 & 1.349035 & 0.397315 \\ H & -2.393987 & 1.060528 & 1.38462 \\ H & -2.178721 & 2.388635 & 0.116385 \\ H & -1.574321 & -1.1901 & 0.915703 \\ H & -1.118721 & 0.806317 & -1.401329 \\ H & 2.49133 & 2.456368 & -0.599475 \\ \hline \\ H & 2.49133 & 2.456368 & -0.599475 \\ \hline \\ H & 2.49133 & 2.456368 & -0.599475 \\ \hline \\ H & 0.954874 & -0.204529 & 0 \\ H & -0.654237 & -0.725148 & 0 \\ H & -0.654237 & -0.725148 & 0 \\ H & -0.300636 & 0.929423 & 0 \\ \hline \\ H & -0.500000000000000000000000000000000000$					Н	0.1672	-2.594328	-0.13319
$ \begin{array}{c cccc} C & 2.138271 & 1.508039 & -0.267147 \\ C & -2.040343 & 1.349035 & 0.397315 \\ H & -2.393987 & 1.060528 & 1.38462 \\ H & -2.178721 & 2.388635 & 0.116385 \\ H & -1.574321 & -1.1901 & 0.915703 \\ H & -1.118721 & 0.806317 & -1.401329 \\ H & 2.49133 & 2.456368 & -0.599475 \\ \hline \\ H & 2.49133 & 2.456368 & -0.599475 \\ \hline \\ H & -1.197 & H_3O^+ \\ \hline \\ E(RB+HF-LYP) = -76.7037352582 \\ \hline \\ H & 0.954874 & -0.204529 & 0 \\ H & 0.954874 & -0.204529 & 0 \\ H & -0.654237 & -0.725148 & 0 \\ H & -0.654237 & -0.725148 & 0 \\ H & -0.300636 & 0.929423 & 0 \\ \hline \\ H & -0.300636 & 0.929423 & 0 \\ \hline \\ \end{array} $					Н	-1.926273	-1.581215	-0.761493
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					С	2.138271	1.508039	-0.267147
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					С	-2.040343	1.349035	0.397315
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					н	-2.393987	1.060528	1.38462
$\begin{array}{c c c c c c c c c c c c c c c c c c c $					Н	-2.178721	2.388635	0.116385
$\begin{array}{c c c c c c c c c c c c c c c c c c c $					Н	-1.574321	-1.1901	0.915703
$\begin{array}{c c c c c c c c c c c c c c c c c c c $					Н	-1.118721	0.806317	-1.401329
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					Н	2.49133	2.456368	-0.599475
$E(RB+HF-LYP) = -76.7037352582$ $H_{3}PAu$ $E(RB+HF-LYP) = -750.731790440$ $E(RB+HF-LYP) = -750.73179040$			$H_3O^+$				$\gg$	
$E(RB+HF-LYP) = -76.7037352582$ $H_{3}P Au$ $E(RB+HF-LYP) = -750.731790440$ $C = 1.772388 -1.09992 -0.352967$ $H = 0.954874 -0.204529 = 0$ $C = 3.15096 -1.573663 -0.480286$ $H = -0.654237 -0.725148 = 0$ $C = 4.118882 -1.056402 = 0.611498$ $H = -0.300636 = 0.929423 = 0$ $C = 4.654954 = 0.371311 = 0.389862$ $C = 3.615345 = 1.459157 = 0.371356$								
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		E(RB+HF-L)	(P) = -76.703	/352582				
H3F Au         E(RB+HF-LYP) = -750.731790440         O       0.000032       0       C       1.772388       -1.09992       -0.352967         H       0.954874       -0.204529       0       C       3.15096       -1.573663       -0.480286         H       -0.654237       -0.725148       0       C       4.118882       -1.056402       0.611498         H       -0.300636       0.929423       0       C       4.654954       0.371311       0.389862         C       3.615345       1.459157       0.371356							Λ	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $						ПЗГ	Au	
O         0         0.000032         0         C         1.772388         -1.09992         -0.352967           H         0.954874         -0.204529         0         C         3.15096         -1.573663         -0.480286           H         -0.654237         -0.725148         0         C         4.118882         -1.056402         0.611498           H         -0.300636         0.929423         0         C         4.654954         0.371311         0.389862           C         3.615345         1.459157         0.371356						E(RB+HF-LY	(P) = -750.731	790440
H       0.954874       -0.204529       0       C       3.15096       -1.573663       -0.480286         H       -0.654237       -0.725148       0       C       4.118882       -1.056402       0.611498         H       -0.300636       0.929423       0       C       4.654954       0.371311       0.389862         C       3.615345       1.459157       0.371356	0	0	0.000032	0	С	1.772388	-1.09992	-0.352967
H-0.654237-0.7251480C4.118882-1.0564020.611498H-0.3006360.9294230C4.6549540.3713110.389862C3.6153451.4591570.371356	н	0.954874	-0.204529	0	С	3.15096	-1.573663	-0.480286
H -0.300636 0.929423 0 C 4.654954 0.371311 0.389862 C 3.615345 1.459157 0.371356	н	-0.654237	-0.725148	0	с	4.118882	-1.056402	0.611498
C 3.615345 1.459157 0.371356	н	-0.300636	0.929423	0	С	4.654954	0.371311	0.389862
					с	3.615345	1.459157	0.371356
Н 3.548115 -1.306231 -1.470194					н	3.548115	-1.306231	-1.470194
Н 3.146276 -2.671935 -0.447493					н	3.146276	-2.671935	-0.447493

				Н	3.62051	-1.121564	1.585988
				Н	4.979897	-1.735049	0.65454
				н	5.36998	0.580052	1.200501
				Au	-1.261074	-0.13593	-0.033037
				Р	-3.493983	0.570437	0.204528
				н	-4.263119	0.030166	1.256377
				н	-3.749465	1.940116	0.424665
				н	-4.389539	0.347016	-0.862214
				С	0.614354	-0.732603	-0.230343
				С	3.518961	2.404949	-0.563665
				н	4.192887	2.435239	-1.417305
				н	2.759607	3.179875	-0.516008
				н	5.232498	0.405265	-0.543478
				н	2.911884	1.462009	1.203868
		$\sim$			(H	I <sub>3</sub> PAu) <sub>2</sub> O	
		Ì					
					E(RB+HF-LY	(P) = -1032.48	3326477
		// +					
		Au P H <sub>3</sub>					
		VD) = 751.100	126020				
	_3 570837	1/31.103	-0 508742	A	-1 67/509	-0 161130	0.000256
	-2 081691	1.420211	-0.04185	D	-3 690881	0.01873/	-0.000230
C	-4 528456	0 725524	-0.04185		-2 60272	0.918734	-0.000333
	-4.528450	0.735524	0.40700		-3.09373	0 5 9 9 1 7 6	-0.134324
	-4.405590	-0.770313	0.343343		-4.044072	0.388170	1 12078
	-4.107244	-1.387777	-0.487003		-4.319893	1 106251	1.13978
	1 452652	0.342383	-0.02431	<u> </u>	1 674512	0 161140	-0.000003
	-1.452055	0.113423	-0.027301	D AU	2 600972	-0.101143	-0.000243
P A	3.493399	0.407014	0.038781	Г Ц	3.090872	0.918734	0.000518
Au	1.215547	-0.159550	0.004145		4.045524	0.569069	0.99054
	-3.843775	2.483058	-0.602747		3.093579	2.322123	0.152787
	-3.637423	0.996272	-1.510963	П	4.520741	0.822446	-1.139025
	-2.01223	1.807221	0.959228				
	-1.50/3/4	2.059101	-0.728235				
	-4.394555	1.104054	1.407804				
	-5.555/98	0.994441	0.1/6914				
	-4.5/289/	-1.210128	1.525389				
	-4.13231	-2.00401	-0.352112				
н	-4.031015	-1.230115	-1.505194				
Н 	-0.86/55	-2.016642	-0.012962				
Н	3./9/247	1.//4085	0.158171				
H 	4.242045	-0.15787	1.085381				
Н	4.233908	0.033953	-1.095884				
		H <sub>3</sub> PAu					
	E(RB+HF-L)	(P) = -478354	5305184				
Au	-0.441492	0.000001	-0.000005				
L							

Р	1.846349	-0.000007	-0.000017
н	2.394333	1.288083	-0.091861
н	2.393585	-0.564269	1.161659
н	2.39473	-0.723773	-1.069137

(<sup>i</sup>) Gaussian 03, Revision D.02, Frisch, M. J. et al; Gaussian, Inc., Wallingford CT, 2004.

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