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Supporting Information

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Reactions of Gold(III) Oxo Complexes with Cyclic Alkenes. Isolation of an Unprecedented Auraoxetane: a Plausible Intermediate in the Oxidation of Alkenes.

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General experimental details

Compounds **1a-1d** were synthesized according to ref. 9. Norbornene (nb) and 2,5-norbornadiene (nbd) were obtained from Aldrich Chimica. Solvents were purchased from Carlo Erba Reagents and distilled prior to use, while anhydrous MeCN (H_2O = 0.001 %; acidity = 0.002 %) was used as received. Elemental analyses were performed with a Perkin-Elmer Elemental Analyzer 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Infrared spectra were recorded with a Jasco FTIR-480 Plus spectrophotometer using Nujol mulls, ^{1}H and ^{13}C{^{1}H} NMR spectra with a Varian VXR 300 spectrometer operating at 300.0 and 75.4 MHz, respectively; chemical shifts are given in ppm relative to internal tetramethylsilane. Mass spectra were recorded with a VG 7070 instrument operating under FAB conditions, with 3-nitrobenzyl alcohol as supporting matrix. Organic products were analysed by capillary GC/MS with two different apparatus. Apparatus (A): "*Trace GC- PolarisQ*" mass spectrometer system. Typical electron energy was 70 eV with the ion source temperature maintained at 240°C. The individual component were separated using a *Rtx-5MS* capillary column (i.d. 0.25 mm, length 30 m, film thickness 0.25 μM), carrier gas Helium 1mL min^{-1} injector temperature 270°C, split injection 1:50, 1μL injection volume, transfer line 300°C. (B): "*ThermoQuest GC 8000 TOP–ThermoQuest Voyager*" mass spectrometer system. Typical electron energy was 70 eV with the ion source temperature maintained at 240°C. The individual component were separated using a *Alltech AT-1* capillary column (i.d. 0.25 mm, length 30 m, film thickness 0.25 μM), carrier gas Helium 1mL min^{-1} injector temperature 260°C. In both cases the fragmentation was obtained by Ion Trap in EI (electronic impact) with MS/MS. Separations in LC-MS were performed using a Agilent Technologies (Palo Alto, CA, USA) 1100 series LC/MSD equipped with a diode-array detector (DAD) and Rheodyne injector 20 μl loop. A chemstation HP A.08.03 was used for data analysis. The compounds described were monitored at 280, 320 and 520 nm. Chromatographic separation was achieved using a Luna® C18 (2) (250mm × 4.6 i.d., 3μm) (Phenomenex, USA). The mobile phase used in the separation consisted of eluent A water: 0.4 %

acetic acid and eluent B methanol. The flow rate was 0.5 mL/min. The injection volume was 20 µL, and the column temperature was set at 25 °C. The photodiode array detector was coupled to a mass spectrometer (quadrupole analyzer) directly to the sprayer needle where ions were generated by Electrospray ionisation ESI in both Positive and Negative ionisation modes. Nitrogen was used as nebulizing and drying gas and 60V fragmentor voltage were applied. The mass spectrometer was operated in positive ion mode. Full scan data acquisition was performed, scanning from 100-700 m/z using a cycle time of 2 s with step size of 0.1 ? . The following ESI conditions were applied: drying gas (nitrogen) heated at 350 °C at a flow rate of 9.5 L/min; nebulizer gas (nitrogen) at a pressure of 40 psi; capillary voltage in positive mode at 3400 V; fragmentor voltage at 60 V.

Reaction of $[Au_2(bipy^R)_2(\mu\text{-}O)_2][PF_6]_2$ (**1**-PF_6) [R = Me (**1a**); $CHMe_2$ (**1b**); CH_2CMe_3 (**1c**)] with 2,5-norbornadiene (nbd). To a solution of **1**-PF_6 (0.3 mmol) in acetonitrile (40 mL) were added nbd (0.65 mL, 6.0 mmol) and water (5 mL). The resulting yellow solution was stirred for 7 days at room temperature and then filtered through Celite. The solution was evaporated to dryness and the residue extracted with diethyl ether (3 x 15 mL), then with CH_2Cl_2 (3 x 15 mL). The combined dichloromethane extracts were filtered and concentrated to a small volume. Addition of diethyl ether gave a whitish precipitate of $[Au_2(bipy^R)_2(\mu\text{-}\eta^2,\eta^2\text{-nbd})][PF_6]_2$ (**2**-PF_6) (**2a**-PF_6, 15 %; **2b**-PF_6 10 %; **2c**-PF_6 41 %). The combined diethyl ether extracts were evaporated to dryness to give the organic fraction containing bipy^R and oxygenated organic products. Unreacted complex **1**-PF_6 was recovered from the residue insoluble in dichloromethane (**1a**-PF_6, 64 %; **1b**-PF_6, 71 %; **1c**-PF_6, 30 %).

Reaction of $[Au_2(bipy^R)_2(\mu\text{-}O)_2][PF_6]_2$ (**1**-PF_6) [R = $CHMe_2$ (**1b**); CH_2CMe_3 (**1c**); $C_6H_3Me_2$-2,6 (**1d**)] with norbornene (nb): typically, to a solution of **1**-PF_6 (0.3 mmol) in acetonitrile (40 – 50 mL) were added nb (6 ÷ 8 mmol) and water (2 - 5 mL). The resulting yellow solution was stirred for 10-12 days at room temperature. During this period the colour faded and some metallic gold was formed. After filtration through Celite, the solution was evaporated to dryness and the residue extracted with diethyl ether (3 x 5 mL), then with CH_2Cl_2 (3 x 10 mL). The combined dichloromethane extracts were filtered and concentrated to a small volume. Addition of diethyl ether gave a whitish precipitate of $[Au(bipy^R)(\eta^2\text{-nb})][PF_6]$ (**3**-PF_6) (**3c**-PF_6, 40 %; **3d**-PF_6, 19 %) or of a mixture of **3**-PF_6 and **4**-PF_6 (**3b**-PF_6/**4b**-PF_6 = 2/1), based on ^{1}H NMR criterion. The combined diethyl ether extracts were filtered and evaporated to dryness to give a pale yellow organic fraction containing bipy^R and oxygenated organic products. Unreacted complex **1**-PF_6 was recovered from the residue insoluble in dichloromethane (**1b**-PF_6, 40 %; **1c**-PF_6, 47%; **1d**-PF_6, 64%).

The reaction of **1a**-PF_6 with nb was runned under different nb/**1a** ratios and **1a** concentrations both in MeCN and MeCN-H_2O.

Reaction in MeCN

T = 10 – 15 °C; t = 12 days; [**1**-PF_6] = $4 \cdot 10^{-3}$ mol/L

nb/**1a** = 4: 1**a** conversion = 50 %; nb/**1a** = 8: 60 %; nb/**1a** = 16: 78 %; nb/**1a** = 32: 84 %

Average **3a**/**4a** = 6.5/1 (based on ^{1}H NMR)

T = 25 – 30 °C*; t = 14 days; [**1**-PF_6] = $7.5 \cdot 10^{-3}$ mol/L; nb/**1a** = 32: conv. = 85 %; **3a**/**4a** = 5.5/1

Same T, t and nb/**1**-PF_6 ratio; [**1**-PF_6] = $3.75 \cdot 10^{-3}$ mol/L: conv = 90 % ; **3a**/**4a** = 7/1

Reaction in MeCN-H_2O

T = 10 – 15 °C; t = 12 days; [**1**-PF_6] = $4 \cdot 10^{-3}$ mol/L; 2.5 % H_2O

nb/**1a** = 4: **1a** conversion = 54 %; nb/**1a** = 8: 65 %; nb/**1a** = 16: 80 %; nb/**1a** = 32: 85 %

Average **3a**/**4a** = 1.5/1

Same T and t; [**1**-PF_6] = $8 \cdot 10^{-3}$ mol/L; 10 % H_2O; nb/**1a** = 24: conv. = 89 %; **3a**/**4a** = 1/1.2

T = 25 – 30 °C*; t = 14 days; [**1**-PF_6] = $7.5 \cdot 10^{-3}$ mol/L; 6% H_2O; nb/**1a** = 32: conv. = 88 %; **3a**/**4a** = 1/1

Same T, t and nb/**1**-PF_6 ratio; [**1**-PF_6] = $3.75 \cdot 10^{-3}$ mol/L; 3% H_2O: conv. = 92 %; **3a**/**4a** = 1.5/1

*At this temperature, the overall (**3a** + **4a**) yield is *ca.* 10 % lower than that at 10 - 15 °C: more metallic gold and bipy^{Me} are formed by decomposition of **3a**.

Reaction of **1c**-PF_6 with nb in CD_3CN. **1c**-PF_6 (0.087 g, 0.074 mmol) and nb (0.070 g, 0.74 mmol) were dissolved in CD_3CN (2 mL) ([**1c**-PF_6] = $3.7 \cdot 10^{-2}$ mol/L) and the reaction mixture stirred at room temperature for 15 days. ^{1}H NMR spectra were recorded throughout this period at intervals of *ca.*12 hours starting from the first spectrum, which was recorded 1 hour after mixing the reactants. Detectable amounts of **3c**-PF_6, **4c**-PF_6, and an organic product [δ = 9.58 (d, *J* = 1.9 Hz)] appeared after about 40 hours. The reaction mixture was worked up as described above to give 0.040 g of a 2:1 mixture of **3c**-PF_6 and **4c**-PF_6, 0.013 g (15 %) of unreacted **1c**-PF_6 and an organic fraction containing free bipy^n and oxygenated organic products.

*Separation of **3a**-PF_6 and **4a**-PF_6*

a) To an acetone solution of a 2:1 mixture of **3a**-PF_6 and **4a**-PF_6 (0.120 g, *ca.* 0.2 mmol) was added an acetone solution of KOTf (0.113 g, 0.6 mmol). The resulting colourless solution was stirred for 3 hours at room temperature and then evaporated to dryness. The whitish residue was taken up with dichlorometane and the filtered solution concentrated to a small volume. Addition of diethyl ether gave a whitish solid resulting to be a *ca.* 2:1 mixture of **3a**-OTf and **4a**-OTf.

b) To an acetone solution of a 2:1 mixture of **3a**-PF_6 and **4a**-PF_6 (0.139 g, *ca.* 0.23 mmol) was added an acetone solution of Na[BPh_4] (0.229 g, 0.67 mmol). The resulting brown solution (colloidal gold is formed by decomposition of **3a**) was stirred for 1 hour at 0 °C and then evaporated to dryness. The brown residue was taken up with dichloromethane and filtered through Celite. Addition of a 1:3 mixture of diethyl ether/pentane to the concentrated solution gave **4a**-BPh_4 as a light brown solid (0.118 g).

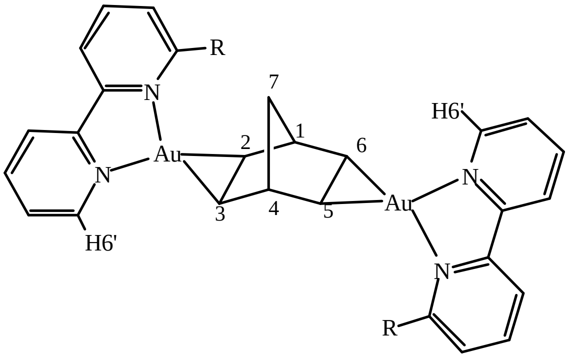
c) Upon addition of MeOH (15 mL) to a dichlomethane solution (15 mL) of a 1.5:1 mixture of **3a**-PF_6 and **4a**-PF_6 (0.200 g) cooled to -20 °C a white precipitate of **3a**-PF_6 was formed. It was collected by filtration under vacuum and washed with diethyl ether (0.065 g). The mother liquor was concentrated to a small volume and diethyl ether added to give a whitish precipitate of the mixture. Almost pure **4a**-PF_6 (0.015 g) was obtained after repeated recrystallization of the mixture.

Crystals of **3a**-PF_6 and **4a**-PF_6 suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the mixture and then separated mechanically.

Reaction of **4a**-PF_6 with nb. To a solution of **4a**-PF_6 (0.031 g, 0.05 mmol) in MeCN (30 mL) was added nb (0.045 g, 0.5 mmol). The resulting colourless solution was stirred for 2 days at room temperature then evaporated to dryness and extracted with diethyl ether. The extract was evaporated to dryness. A proton NMR spectrum in $CDCl_3$ showed the presence of 2,3-epoxynorbornane and small amounts of aldehydes **8** and **9**. A proton NMR spectrum of the residue insoluble in diethyl ether showed the presence of a 5:1 mixture of **3a** and **4a**.

Reaction of **4a**-PF_6 with $HBF_4 \cdot Et_2O$. To a solution of **4a**-PF_6 (0.031 g, 0.05 mmol) in CD_3COCD_3 (2.5 mL) was added nb (0.045 g, 0.5 mmol) and $HBF_4 \cdot Et_2O$ 0.029 M (85 μL, $2.5 \cdot 10^{-3}$ mmol). The reaction, monitored by ^{1}H NMR, was completed after 3 days yielding **3a**-PF_6 and 2,3-epoxynorbornane as the main organic product. Removal of the solvent under reduced pressure was followed by extraction with diethyl ether. The combined extracts were evaporated to dryness and analysed by GC-MS and LC-MS. GC-MS analysis (instrument B) showed the presence of a peak (RT = 5.58 min; relative abundance 100 %) with M^+ = 110, 2,3-epoxynorbornane (**6**); LC-MS analysis showed the presence of the protonated norbornanediol, $[M + H]^+$ = 129 (RT = 10.27 min).

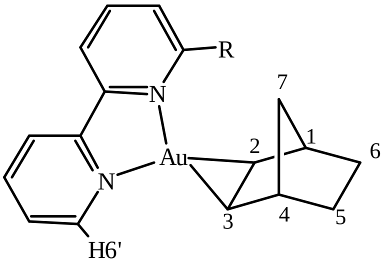
Analytical and spectroscopic data of the complexes



2a-PF_6 mp 130 °C (decomp.). Anal. Calcd for $C_{29}H_{28}Au_2F_{12}N_4P_2$: C, 31.19; H, 2.53; N, 5.02 %. Found C, 31.08; H, 2.54; N, 5.14 %. Λ_M (5 x 10^{-4} mol L^{-1}, Me_2CO) 170 $\Omega^{-1}cm^2mol^{-1}$. Selected IR bands: (ν/cm^{-1}, nujol mull): 1590 s, 1565 m, 1030 m, 850 vs (br), 785 s, 735 m. ^1H NMR (CD_3CN, 293 K): δ = 1.38 (s, 2H; CH_2-7), 2.99 (s, 6H; Me), 4.03 (s, 2H; CH-1,4), 4.59 (s, 4H; CH=CH), 7.80-8.49 (m, 12H; ArH), 8.91 (d, J = 4.5 Hz, 2H; H-6' bipy). $^{13}C\{^1H\}$ NMR (CD_3CN, 293 K): δ = 28.63 (Me), 49.57 (CH-1,4), 55.58 (CH_2-7), 85.24 (CH=CH), 122.07, 125.02, 128.71, 128.97, 142.77, 142.81, and 152.75 (ArCH) 153.00, 153.84, and 161.01 (ArC). Mass Spectrum (FAB+) *m*/*z*: 551 (50%) [Au(bipy^{Me})(nbd)$_2$], 457-461 ˜ [Au(bipy^{Me})(nbd)], 367 (100%) [Au(bipy^{Me})].

2b-PF_6 mp 141-142 °C. Calcd for $C_{33}H_{36}Au_2F_{12}N_4P_2$: C, 33.80; H, 3.09; N, 4.78 %. Found C, 33.45; H, 3.11; N, 4.65 %. Λ_M (5 x 10^{-4} mol L^{-1}, Me_2CO) 165 $\Omega^{-1}cm^2mol^{-1}$. Selected IR bands: (ν/cm^{-1}, nujol mull): 1585 s, 1560 m, 1020 m, 840 vs (br), 780 s. ^1H NMR ([D_6]acetone, 293 K): δ 1.52 (d, J = 6.8 Hz, 12H; CH_3), 1,55 (s, 2H; CH_2-7), 3.96 (sept, J = 6.8 Hz, 2H; C*H*Me_2), 4.84 (s, 4H; CH=CH), 8.03-8.90 (m, 12, ArH), 9.17 (d, J = 5.2 Hz, 2H, H-6' bipy). Mass Spectrum (FAB+) *m*/*z*: 487 (70%) [Au(bipy^{ip})(nbd)], 395 (50%) [Au(bipy^{ip})].

2c-PF_6 mp 147-148 °C. Calcd for $C_{37}H_{44}Au_2F_{12}N_4P_2$: C, 36.17; H, 3.61; N, 4.56 %. Found C, 35.98; H, 3.33; N, 4.48 %. Λ_M (5 x 10^{-4} mol L^{-1}, Me_2CO) 170 $\Omega^{-1}cm^2mol^{-1}$. Selected IR bands: (ν/cm^{-1}, nujol mull): 1600 s, 1573 m, 1228 m, 1026 m, 842 vs (br), 782 s, 740 m. ^1H NMR (CD_2Cl_2, 293 K): δ = 1.18 (s, 18H; CH_3), 1.43 (s, 2H; CH_2-7), 3.36 (s, 4H; C*H*$_2$CMe_3), 4.16 (br, 2H; CH-1,4), 4.68 (br, 4H; CH=CH), 7.75-8.41 (m, 12H, ArH), 8.98 (d, J = 4.7 Hz, 2H; H6' bipy).

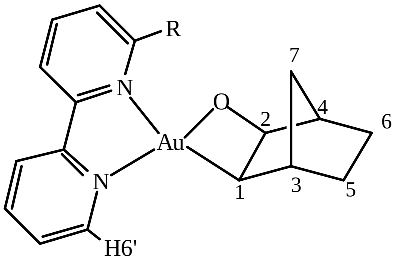


3a-PF_6 mp 206-207 °C. Calcd for $C_{18}H_{20}AuF_6N_2P$: C, 35.65; H, 3.32; N, 4.62 %. Found C, 35.71; H, 3.31; N, 4.55 %. Λ_M (5 x 10^{-4} mol L^{-1}, Me_2CO) 120 $\Omega^{-1}cm^2mol^{-1}$. Selected IR bands: (ν/cm^{-1}, nujol mull): 1597 s, 1575 m, 1561 m, 1125 m, 1027 m, 1011 m, 839 vs (br), 780 s, 741 m. ^{1}H NMR (CD_2Cl_2, 293 K): $\delta = 0.81$ (dt, *J* = 9.7, 1.5 Hz, 1H; CH*H*-7), 1.21 (2d overlapped, 3H; CH*H*-5,6 + C*H*H-7), 1.78 (dm, 2H; C*H*H-5,6), 3.04 (s, 3H; Me), 3.22 (s, 2H; CH-1,4), 4.22 (s, 2H; CH=CH), 7.75-8.45 (m, 6H, ArH), 8.86 (dd, *J* = 5.2, 1.7 Hz, 1H; H6' bipy); ([D_6]acetone, 293 K): δ = 0.77 (dt, *J* = 9.8 Hz, 1H; CH*H*-7), 1.18 (dm, *J* = 7.8, 2.4 Hz, 2H; CH*H*-5,6), 1.30 (dt, *J* = 9.5 Hz, 1H; C*H*H-7), 1.74 (dm, *J* = 7.4 Hz, 2H; C*H*H-5,6), 3.11 (s, 3H; Me), 3.25 (s, 2H; CH-1,4), 4.36 (s, 2H; CH=CH), 7.95-8.79 (m, 6H; ArH), 9.12 (d, *J* = 4.4 Hz, 1H; H6' bipy). $^{13}C\{^1H\}$ NMR (CD_3CN, 293 K): δ = 25.4 (CH_2-CH_2), 28.41 (Me), 42.8 (CH-1,4), 43.6 (CH_2-7), 83.3 (CH=CH), 121.3, 124.2, 128.0, 128.3, 141.9, 142.0, and 151.7 (ArCH), 152.1, 153.0, and 160.1 (ArC). Mass Spectrum (FAB+) *m/z*: 461 (100 %) [M^+], 367 (68 %) [*M* - nb].

3c-PF_6 mp 142-143 °C. Calcd for $C_{22}H_{28}AuF_6N_2P$: C, 39.89; H, 4.26; N, 4.23 %. Found C, 39.71; H, 4.16; N, 4.21 %. Λ_M (5 x 10^{-4} mol L^{-1}, Me_2CO) 124 $\Omega^{-1}cm^2mol^{-1}$. Selected IR bands: (ν/cm^{-1}, nujol mull): 1597 vs, 1573 s, 1307 s, 1227 s, 1167 m, 1128 m, 1025 s, 1009 s, 838 vs (br), 789 s, 765 s, 741 m, 723 m, 654 m, 639 m. ^{1}H NMR (CD_2Cl_2, 293 K): $\delta = 0.81$ (d, J = 9.7 Hz, 1H; CH*H*-7 *anti*), 1.09 (s, 9H; CH_2C*Me*$_3$), 1.18-1.23 (m, 3H; CH*H*-5,6 + C*H*H-7), 1.79 (d, *J* = 9.0 Hz, 2H; C*H*H-5,6), 3.26 (s, 2H; CH-1,4), 3.38 (s, 2H, C*H*$_2$CMe$_3$), 4.23 (s, 2H; CH=CH), 7.73-8.47 (m, 6H, ArH), 8.86 (d, *J* = 4.8 Hz, 1H; H6' bipy). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = 25.2 (CH_2-CH_2), 29.7 (CH_2C*Me*$_3$), 33.2 (CH_2*C*Me_3), 42.7 (CH-1,4), 43.4 (CH_2-7), 55.9 (*CH*$_2$CMe$_3$), 84.1 (CH=CH), 122.0, 124.2, 127.9, 129.1, 141.0, 141.9, and 151.4 (ArCH), 152.1, 153.5, and 161.5 (ArC). Mass Spectrum (FAB+) *m/z*: 553 (12 %) [*M* + O], 517 (100 %) [M^+], 423 (42 %) [*M* - nb], 227 (15 %) ($bipy^nH$).

3d-PF_6 mp 114-115 °C. Calcd for $C_{25}H_{26}AuF_6N_2P$: C, 43.12; H, 3.76; N, 4.02 %. Found C, 42.91; H, 3.78; N, 4.09 %. Λ_M (5 x 10^{-4} mol L^{-1}, Me_2CO) 120 $\Omega^{-1}cm^2mol^{-1}$. Selected IR bands: (ν/cm^{-1}, nujol mull): 1600 s, 1574 m, 1167 m, 1126 m, 1026 m, 1005 m, 842 vs (br), 778 s, 739 m, 722 m.

^{1}H NMR (CD_2Cl_2, 293 K): δ = 0.56 (d, *J* = 9.7 Hz, 1H; CH*H*-7), 0.85-0.91 (m, 3H; CH*H*-5,6 + C*H*H-7), 1.52 (d, *J* = 9.1 Hz, 2H; C*H*H-5,6), 2.07 (s, 6H; Me), 2.66 (s, 2H; CH-1,4), 3.46 (s, 2H; CH=CH), 7.31-8.55 (m, 9H; ArH), 8.80 (dd, *J* = 5.2, Hz, 1.7 1H; H6' bipy). Mass Spectrum (FAB+) *m*/*z*: 567 (5 %) [*M* + O], 551 (100 %) [M^+], 457 (30 %) [*M* - nb], 259 (15 %) (bipy^{oxyl} - H).



4a-PF_6 mp 129-130 °C. Calcd for $C_{18}H_{20}AuF_6N_2OP$: C, 34.74; H, 3.24; N, 4.50 %. Found C, 34.19; H, 3.15; N, 4.46 %. Λ_M (5 x 10^{-4} mol L^{-1}, Me_2CO) 125 $\Omega^{-1}cm^2mol^{-1}$. Selected IR bands: (ν/cm^{-1}, nujol mull): 1602 m, 1568 m, 1162 m, 1136 m, 1018 m, 998 m, 839 vs, 779 s, 723 s. ^{1}H NMR ([D_6]acetone, 293 K): δ = 1.04 (pseudo t, *J* = 8.5, 1.9 Hz, 1H; CH*H*-5), 1.33 (d, *J* = 10.2 Hz, 1H; CH*H*-7), 1.44 (pseudo t, *J* = 8.5 Hz, 1H; CH*H*-6), 1.58 (m, 2H; C*H*H-5,6), 1.96 (dd, *J* = 5.5, 1.9 Hz, 1H; CH-1), 2.16 (d, *J* = 1.9 Hz, 1H; CH-3), 2.49 (d, *J* = 10.2 Hz, 1H; C*H*H-7), 2.74 (s, 1H; CH-4), 2.82 (s, 3H; Me), 5.88 (d, *J* = 5.5 Hz, 1H; CH-2), 7.90-8.87 (m, 6H; ArH), 9.09 (d, *J* = 4.3 Hz, 1H; H6' bipy). $^{13}C\{^1H\}$ NMR ([D_6]acetone, 293 K): δ = 15.5 (CH-1), 21.1 (Me), 23.0 (CH_2-5), 35.4 (CH_2-7), 39.4 (CH-3), 44.4 (CH-4), 92.1 (CH-2), 122.4, 126.0, 129.9, 131.0, 142,8, 144.2, and 149.7 (ArCH), 152.3, 155.6, and 163.4 (ArC). Mass Spectrum (FAB+) *m*/*z*: 477 (100 %) [M^+], 461 (15 %) [M^+ **3a**], 367 (100 %) (M - nbO), 171 (80 %) (bipy^{Me}H), 107 (25 %) (nbO – H).

4a-BPh_4 mp 86-87 °C. Calcd for $C_{42}H_{40}AuBN_2O$: C, 63.33; H, 5.06; N, 3.52 %. Found C, 62.99; H, 4.91; N, 3.46 %. Λ_M (5 x 10^{-4} mol L^{-1}, Me_2CO) 128 $\Omega^{-1}cm^2mol^{-1}$. Selected IR bands: (ν/cm^{-1}, nujol mull): 1603 m, 1577 m, 1168 w, 1130 m, 1001 m, 772 s, 733 vs, 706 vs, 611 vs. ^{1}H NMR (CD_2Cl_2, 293 K): δ = 1.09 (pseudo t, br, 1H; CH*H*-5), 1.40 (d, br, *J* = 10.3 Hz, 1H; CH*H*-7), 1.44 (m, br, 1H; CH*H*-6), 1.58 (dd, *J* = 5.5, 2.2 Hz, 1H; CH-1), 1.65 (m, 2H; C*H*H-5,6), 2.24 (s, br, 1H; CH-3), 2.39 (d, br, *J* = 9.9 Hz, 1H; C*H*H-7), 2.54 (s, br, 1H; CH-4), 2.81 (s, 3H; Me), 5.89 (d, *J* = 5.5 Hz, 1H; CH-2), 6.86 (t, *J* = 7.3 Hz, 4H; H-*para* BPh_4), 7.01 (t, *J* = 7.3 Hz, 8H; H-*meta* BPh_4), 7.33-7.39 (m, br, 8H; H-*ortho* BPh_4), 7.42-7.92 (m, 6H; ArH bipy^{Me}), 8.31 (d, *J* = 4.8 Hz, 1H; H6' bipy^{Me}).

Spectroscopic and analytical data of organic products 6-11.

Organic products from the reaction in MeCN, [**1a**-PF_6] $3.75^{.}10^{-3}$ M: ^{1}H NMR ($CDCl_3$; 293 K): δ = 9.64 (d, *J* = 2.0 Hz, 2H; C*H*O **7**), 9.63 (d, *J* = 2.4 Hz, 1H; C*H*O **8** or **9**), 9.62 (d, *J* = 2.4 Hz, 1H; C*H*O **9** or **8**), 5.1-4.9 (broad m; **8** + **9**), 4.07 (broad s), 3.88 (m), 3.62 (m), 3.07 (s; 2H, C*H*-2,3 **6**), 2.87 and 2.78 (tt, *J* = 6.8, 2.0 Hz and broad tt, 2H; CH-1,3 **7**), 2.44 (s, 2H, CH-1,4 **6**), 2.26 (dt, *J* = 13.6, 6.8 Hz; **7**), 2.10-1.94 (m; **7**), 2.01 (s), 1.91 (m, **7**), 1.48 (dm, *J* = 9.5 Hz, 2H; C*H*H-5,6 **6**), 1.40 (m), 1.34 (dt, J = 5.6, 2.2 Hz, 1H; C*H*H-7 **6**), 1.30-1.18 (m; CH*H*-5,6 **6** + **8** or **9**), 0.70 (dm, *J* = 9.7 Hz, 1H; CH*H*-7 **6**). **7** = cyclopentane-1,3-dicarbaldehyde; **8**, **9** = 3-methylene-cyclopentane carbaldehyde, 3-methyl-2-cyclopentane carbaldehyde; **7**/(**8** + **9**) = 2; **7** ˜ **6**.

GC-MS analysis (apparatus A): RT = 4.89 (Rel. Ab. 100 %), M^{+} = 110, 2,3-epoxynorbornane, **6**; RT = 9.35 (85 %), M^{+} = 126, cyclopentane-1,3-dicarbaldehyde, **7**; RT = 10.31 (17 %), M^{+} = 110, **8** or **9**; 11.35 (10 %), M^{+} = 110, **9** or **8**.

[**1a**-PF_6] $7.5^{.}10^{-3}$ M: Same species; **7**/(**8** + **9)** = 1.33; **7** ˜ **6**.

Reaction in MeCN-H_2O (3 %); [**1a**-PF_6] $3.75^{.}10^{-3}$ M: same species with different integral ratios; **7** = (**8** + **9**); **6** = 2(**7**)

MeCN-H_2O (6 %); [**1a**-PF_6] $7.5^{.}10^{-3}$ M: **7**/(**8** + **9)** = 0.5; **6** ˜ 2(**7**)

When a larger amount of H_2O is used (12 %), in more diluted solution, 2,3-norbornanediols **10**, **11** are mainly obtained: ^{1}HNMR ($CDCl_3$, 273 K): d = 4.34 (broad s, **11**), 4.05 (d, *J* = 1.7 Hz; **10**), 3.88 (broad t, *J* = 4.6 Hz; **10**), 3.75 (dd, *J* = 8.5, 3.4 Hz, **11**), 2.19 (s), 2.11 (d, *J* = 4.2 Hz), 1.89 (d, *J* = 4.4 Hz), 1.70 (dd, J = 14.0, 8.0 Hz, **10**), 1.55 (m, **11**), 1.0 (m, **10**); **10**/**11** = 6/1. LC-MS analysis: $[M + H]^{+}$ = 129 (RT = 10.27 min).