Reactions of gold(III) complexes with alkenes in aqueous media: generation of bis-(β-hydroxyalkyl)gold(III) complexes

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Reactions of gold(III) complexes with alkenes in aqueous media: generation of bis-(*β*-hydroxyalkyl)gold(III) complexes

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Reactions of gold(III) complexes with ethylene and propylene in water provide the first such examples not accompanied by reduction of the gold. HAuCl$_4$ and AuCl$_3$(TPPTS) produce organic products (alcohol, aldehyde/ketone, etc.) with gold reduction to the metal. However, [Au(bipy)Cl$_2$] Cl in water produces the gold(III) *β*-hydroxy complexes, [Au(bipy)(CH$_2$CH$_2$OH)$_2$]X (X = Cl$^-$, PF$_6$$^-$) and [Au(bipy)(CH$_2$CH(OH)CH$_3$]Cl, which are stable in solution. These complexes could not be isolated, but were characterized by NMR and high-resolution mass spectra. [Au(terpy)Cl]Cl$_2$ fails to react with ethylene in water, even at elevated temperatures. DFT computations were performed to investigate the reaction mechanism.

Keywords: Gold(III); Alkenes; Water solution; DFT calculations

Introduction

Activation of alkenes, although the basis of many industrial processes, remains a challenge in terms of activity and especially selectivity. Homogeneous transition metal systems for addition of hydrogen atom, hydrogen halides, formaldehyde (H$_2$ + CO), silanes, alcohols, etc. have been developed [1]. Surprisingly, little has been reported on systems for addition of water to an alkene [1].

Metal complexes with *β*-hydroxyalkyl ligands have been investigated as intermediates in a variety of organometallic reactions. The first such examples were intermediates in the oxidation of alkenes by mercury(II), thallium(III), and lead(IV) [2, 3], with *β*-hydroxyethylthallate(III) complexes isolated and characterized [4–6]. *β*-Hydroxyalkyl metal complexes played a central role in mechanistic investigations into the Wacker process, in which the *β*-hydroxyethylpalladium(II) intermediate was too unstable to be isolated [7–12]. Other reactions involving *β*-hydroxyalkyl intermediates include the Shilov system (based on Pt(II)/Pt(IV)) and the action of the biologically active Vitamin-B$_{12}$ coenzyme (based on Co (III)) [13–30]. The *β*-hydroxyalkyl complexes are prepared by a variety of processes,

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including nucleophilic attack on coordinated alkene, S_N2 reactions, and photolysis involving metals of the first transition period [31–37].

Stable β-hydroxyalkyl transition metal complexes are generally achieved by blocking coordination sites required for β-hydride elimination. Palladium(II) and platinum(II) mono-β-hydroxyethyl complexes were prepared using the tridentate ligand, PNP (PNP = 2,6-bis (diphenylphosphinomethyl)pyridine), and were characterized by ^{1}H NMR [38, 39]. In both cases, the dimer ([M(PNP)CH$_2$CH$_2$OCH$_2$CH$_2$(PNP)M]) was also produced; the reaction could be reversed upon treatment with HBF$_4$, yielding the alkene complex quantitatively. For palladium, displacement of the olefin by water was a competing reaction, though addition of NaBH$_4$ to the product β-hydroxyethyl complexes (in CD$_2$Cl$_2$) cleaved the organic fragments and produced free ethanol and ethyl ether [38]. Similar observations have been reported for [PtCl(tmen)(C$_2$H$_4$)]$^+$ (tmen = N,N,N^{-1},N^{-1}-tetramethylethylenediamine) with the observation that the condensation can be prevented in pure water as solvent [40, 41]. Recently, generation of β-hydroxyalkyl complexes by reaction of a Rh(III)-porphyrin complex (which is structurally similar to the Co(III)-B$_{12}$ coenzyme) with alkenes in aqueous solution was reported [42]; the β-hydroxylalkyl complexes can form ketones in aqueous media, or epoxides in organic solvents. The stability of the hydrocarbon ligand for the Rh(III)-phorphyrin complex is attributed to the porphyrin blocking all *cis*-coordination sites usually required for β-hydride elimination [42].

The important roles of β-hydroxyalkyl intermediates in various reactions provide impetus for further investigations. As an alternative to blocking coordination sites, gold complexes are less susceptible to β-hydride elimination. This difference in reactivity should allow for β-hydroxyalkylgold(III) complexes to be more stable than those of Pt(II) and Pd(II), even without using tri or tetradentate ligands.

There are myriad reports in the literature of catalytic gold(I) systems capable of adding a variety of nucleophiles to unsaturated hydrocarbons, mostly alkynes, though alkenes have also been investigated [43]. While gold(I) has received a majority of the attention to date, similar processes with gold(III) have also been reported with both alkynes and alkenes. The most common example of these reactions is gold(I) mediating an oxygen-based nucleophile attack on an alkyne, which forms the corresponding diether or vinyl ether [44–47]. Reactions of gold complexes with alkenes generally give ethers, ketones, and aldehydes; gold(III) can be substituted for gold(I) in most cases, though it is typically less active with alkynes [48]. In one particular instance, a gold(III) bipyridine oxo complex was reacted with norbornene to yield the auroxetane, [Au(bipy)(κ^2-*O,C*-2-oxynorbornyl)] PF$_6$ [49]. This complex undergoes further reactions: in organic/hybrid organic systems, it reacts to form the epoxide, which subsequently produces a variety of aldehydes, while addition of water leads to the glycol.

Herein, we report the reactions of gold(III) complexes with ethylene and propylene in water that lead to moderately stable β-hydroxyalkyl complexes of gold(III).

Results

Finding little mention of reactions of Au(III) complexes with simple alkenes in the literature [50], we examined the reaction of HAuCl$_4$ with ethylene (1 atm) in water at room temperature and 70 °C. A number of signals (triplets) appeared in the NMR spectrum, the primary ones at 2.06 and 3.56 ppm, which integrated at 1 : 1 and were coupled to each other. From later discussion, this will be assigned to β-hydroxyethylgold(III) complex. Ethylene

Table 1. Products for reactions of ethylene with Au(III) complexes.

Compound	Temperature (time)	Product (%)
$HAuCl_4$	22 °C (24 h)	Au–CH_2CH_2OH (54%)
		$HOCH_2CH_2OH$ (24%)
		$ClCH_2CH_2OH$ (16%)
$HAuCl_4$	70 °C (48 h)	Au–CH_2CH_2OH (7%)
		$HOCH_2CH_2OH$ (59%)
		$ClCH_2CH_2OH$ (29%)
$AuCl_3TPPTS$	12 °C (18 h)	Au–CH_2CH_2OH (100%)
$AuCl_3TPPTS$	22 °C (18 h)	Au–CH_2CH_2OH (77%)
		$HOCH_2CH_2OH$ (23%)
$AuCl_3TPPTS$	22 °C (215 h)	Au–CH_2CH_2OH (22%)
		$HOCH_2CH_2OH$ (48%)
		Acetaldehyde + hydrate (29%)
$AuCl_3(py)$	22 °C (72 h)	Au–CH_2CH_2OH (major)
		$HOCH_2CH_2OH$ (minor)
$Au(bipy)Cl_2^+$	50 °C (48 h)	Au–CH_2CH_2OH (100%)
$Au(terpy)Cl^{2+}$	22–70 °C	No reaction

glycol was a product producing NMR resonances of less intensity than the two triplets at room temperature (see table 1), but the dominant product at 70 °C. Chloroethanol is also a significant product in this reaction. The yields of these products as calculated by NMR integration are given in table 1. A dark precipitate of metallic gold was observed at room temperature and prominent at 70 °C, suggesting that the amounts of ethylene glycol and gold precipitate are related. Examining this reaction under pressure of ethylene shows no change in amounts or ratios of products.

Another resonance appears as a shoulder to the upfield triplet, at approximately 2.07 ppm. Tetrachloroaurate(III) salts undergo slow hydrolysis in aqueous solution to obtain the aquatrichloroaurate(III) species, which immediately deprotonates to give tricholorohydroxoaurate(III) [51]. A solution of $HAuCl_4$ was prepared in water and left for 24 h, at which point the ^{1}H NMR showed a sharp peak at 2.08 ppm, indicating that the shoulder to the upfield triplet may be attributed to hydrolysis of the gold(III) complex.

Encouraged by the obvious activation of ethylene by $HAuCl_4$ at mild conditions, we prepared $AuCl_3$(TPPTS) (TPPTS = P(m-$C_6H_4SO_3Na$)$_3$) with the water-soluble phosphine replacing a chloride. This complex (and all of the Au(III) complexes we prepared) was very sensitive to metal objects (steel spatulas, syringes, etc.) in the presence of water which caused reduction to gold nanoparticles with characteristic purple color [52]. Avoiding the use of metal objects gave a clean ^{1}H NMR spectrum exhibiting two triplets at 2.12 and 3.59 ppm upon reaction with ethylene at one atmosphere and room temperature for the first several hours. COZY experiments confirmed that these triplets were coupled with a 7 Hz coupling, typical for XCH_2CH_2Y. In longer times (more than 12 h), the TPPTS showed as the oxide and ethylene glycol (singlet 3.52) was observed. This was confirmed by an ethylene glycol spike in the ^{1}H NMR. Attempts to isolate the product exhibiting the two triplets by distillation, extraction or protonation were unsuccessful. Reaction up to 18 h showed formation of acetaldehyde and its hydrate. The ^{1}H NMR spectrum is shown in figure S1 (Supplementary material) with the signals labeled for the different products. figure 5 gives the products and labels of the protons. Reducing the temperature to 10 °C for the reaction of $AuCl_3$(TPPTS) with C_2H_4 suppressed decomposition to ethylene glycol and acetaldehyde with only the two triplets at 2.12 and 3.59 ppm observed in the NMR spectrum. The amounts of products at various times are provided in table 1.

The pyridine analog, $AuCl_3(py)$, was prepared to remove the problem of phosphine oxidation. Solubility in water posed some problems, but (table 1) after 72 h at 22 °C, no decomposition to metallic gold was observed upon reaction with ethylene in water. The major product is $Au(CH_2CH_2OH)_n(py)$ with a small amount of ethylene glycol. In contrast to the reaction of $AuCl_3(TPPTS)$, no gold decomposition products were observed.

To occupy another coordination site at gold(III), we examined the reaction of $[Au(bipy)Cl_2]X$ ($X = Cl^-$ and PF_6^-) with ethylene in water. At 22 °C, no reaction was observed but at 50 °C, $[Au(bipy)Cl_2]Cl$ gave two triplets at 3.72 and 2.30 ppm and no other product was observed. High-resolution mass spectroscopy gave a molecular ion with a mass of 433.1037 amu, consistent with $C_{14}H_{18}O_2N_2Au$ or $Au(bipy(CH_2CH_2OH)_2^+$. This product is also consistent with the ^1H NMR spectrum (figure S2). The NMR assignments were confirmed by HSQC which showed that the ^1H triplet at 3.72 ppm was coupled to the ^{13}C signal at 38.6 and 2.30 ppm was coupled to 7.8 ppm [53]. Changing to the PF_6^- salt decreased the solubility in water, but did not affect the formation of $Au(bipy))(CH_2CH_2OH)_2^+$. To increase the solubility in water of $[Au(bipy)Cl_2]PF_6$, it was heated to 70 °C. The ^1H NMR indicated hydrolysis of an N–C bond of bipyridine [54], but the hydrolysis is reversed over time and the pure bidentate $[Au(bipy)Cl_2]PF_6$ was observed. The synthetic method was improved using a high-pressure apparatus, resulting in a yield of 75%. The same process was observed for $[Au(bipy)Cl_2]Cl$ when heated to 70 °C.

The terpy complex $[Au(terpy)Cl]Cl_2$ showed no reaction with C_2H_4, even to temperatures above 70 °C. The results for reactions of four Au(III) complexes with ethylene are shown in table 1.

Reactions with propylene

Propylene offers stereochemical information about the site of attack. Reaction of $HAuCl_4$ with propylene in water for 18 h results in acetone (32%), i-PrOH (51%), and other minor, unidentified products (table 2). Both acetone and i-PrOH result from Markovnikov attack of $OH^-(H_2O)$ on coordinated propylene leading to $AuCH_2CH(OH)CH_3$ which can then be hydrolyzed to i-PrOH or from β-hydride eliminations result in acetone. There seems to be no significant time dependence of the acetone/i-PrOH ratio; thus, it is most likely they both result from the common intermediate. For the reaction with propylene, products analogous to ethylene glycol and chloroethanol are not observed. The gold product was not characterized, but looks similar to the ethylene reaction with $HAuCl_4$.

Reaction of $AuCl_3(TPPTS)$ with propylene (table 2) in water leads to the same products as for $HAuCl_4$ but with much more acetone. As for the ethylene reactions, phosphine oxide is observed in the propylene reaction. $[Au(bipy)Cl_2]Cl$, when reacted with propylene

Table 2. Products for reactions of propylene with Au(III) complexes.

Compound	Temperature (time)	Product (%)
$HAuCl_4$	22 °C (24 h)	$CH_3CH(OH)CH_3$ (51%) $CH_3C(O)CH_3$ (32%)
$AuCl_3TPPTS$	22 °C (68 h)	$CH_3CH(OH)CH_3$ (19%) $CH_3C(O)CH_3$ (81%)
$Au(bipy)Cl_2^+$	70 °C (24 h)	$AuCH_2CH(OH)CH_3$ (100%)
$Au(terpy)Cl^{2+}$	No reaction	
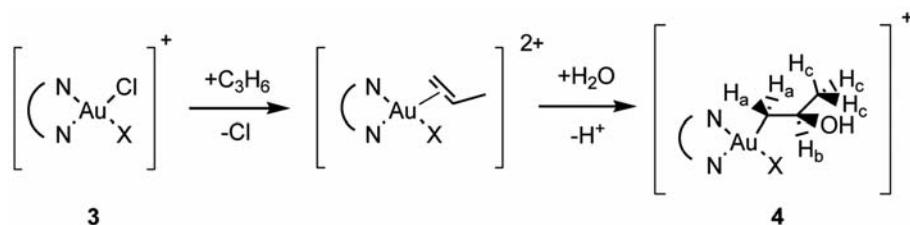
Scheme 1. Reaction of **3** with propylene. Labels on hydrogen atoms refer to the ^{1}H NMR in figure 1.
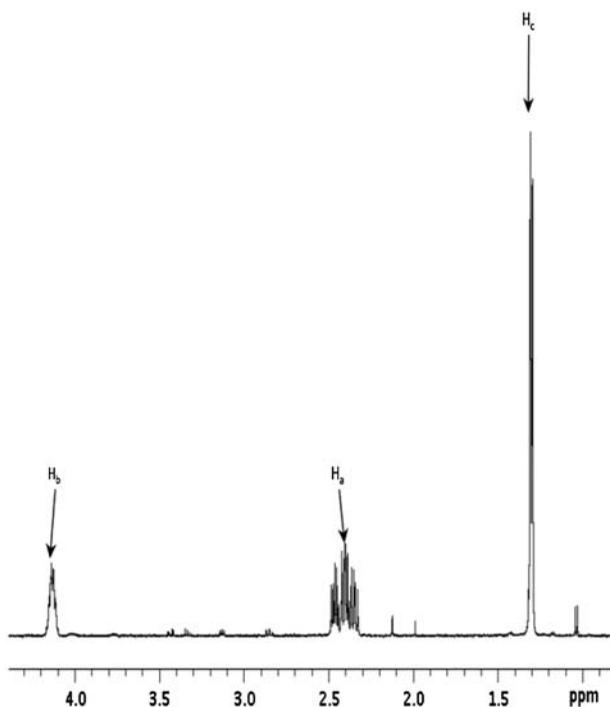
Figure 1. ^{1}H NMR (at 500 MHz) of the downfield products resulting from the reaction of **3** with propylene. Upfield peaks are omitted for clarity.

at 50 °C, shows Markovnikov addition (scheme 1 and figure 1). The NMR quartet at 4.08 ppm corresponds to Hb and the doublet at 1.23 to the methyl; the multiplet at 2.34, shown in detail as the insert to figure 2, corresponds to the diastereotopic Ha's. A detailed analysis is presented in the Supplementary material. A high-resolution mass spectrum of this product gave a mass of 471.1357 amu, corresponding to a molecular formula of $C_{16}H_{22}O_2N_2Au$ or $Au(bipy)(CH_2CHOHCH_3)_2^+$.

Discussion

The growing use of gold in organic synthesis has been phenomenal. Nucleophilic attack on coordinated alkenes (and alkynes) is a key aspect for continued development of this
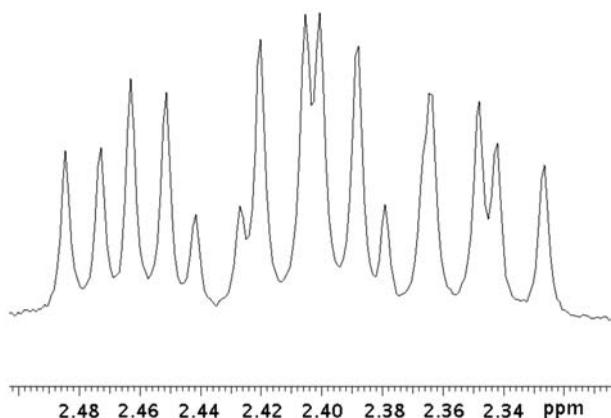
Figure 2.   Expansion of the signal at 2.4 ppm from figure 1.

field. Our studies of simple Au(III) complexes with ethylene and propylene in water demonstrate that such reactions occur at moderate temperatures and pressures less than 1 atm.

Obviously, the results show that simple alkenes can be coordinated to Au(III) and are susceptible to attack by water (or OH^-) at mild conditions. The Au(III) alkene complex appears to be more susceptible to nucleophilic attack than platinum analogs with reaction occurring at much lower pH [55]. The nucleophilic attack on propylene is selective to the Markovnikov product as shown in figure 1.

$HAuCl_4$ was previously reacted with some alkenes with the most relevant being 1-octene [56]. By refluxing in CH_3OH for 24 h, 1-octene was converted to 2-octanone (36%), 3-chloro, 2-octanone (17%), 1-chloro, 2-methoxy-octane (5%), and 1,2-dimethoxyoctane (12%); gold metal was produced in this reaction. This reaction, which also features Markovnikov attack of MeOH on the coordinated alkene, is similar in the formation of gold metal and the 2-ketone to our reaction with propylene, but not in the other products. Norman *et al.* do not report the simple methoxy analog of *i*-PrOH that we observe and we do not see any evidence for chloride incorporation. Likely, the Cl^- is better solvated in water and less available for reaction. Similarly, water may provide more facile hydrolysis of $Au-CH_2CH(OH)CH_3$ than methanol does for $Au-CH_2CH(OMe)C_6H_{13}$. Both reactions have a $Au–CH_2CH(OR)R'$ intermediate as the key to the products.

The selectivity of $AuCl_2(bipy)^+$ to $Au(bipy)(CH_2CH_2OH)_2^+$ and $Au(bipy)(CH_2CH(OH)CH_3)_2^+$ speaks to an unusual stability of the bis(β-hydroxy alkyl) over the mono β-hydroxy alkyl complexes which are not observed, even at short times. With the reasonable assumption that coordination of alkene to Au(III) is rate-determining (gold(III) alkene complexes are not common), then replacement of a chloride by the β-hydroxyalkyl should increase electron density on gold(III), thus increasing the coordination of alkene through increased back bonding. However, further experiments are necessary to confirm this interpretation.

In the experiments described here, we have examined four square planar gold(III) complexes with one to four chloride ligands. With the exception of $Au(terpy)Cl^{2+}$, the complexes all show reactions with ethylene and propylene. $HAuCl_4$ produces the difunctionalized products, ethylene glycol and chloroethanol, but in a mixture of other products.

$AuCl_3(TPPTS)$ initially produces a product that is likely $AuCl_2(CH_2CH_2OH)(TPPTS)$, but loss of TPPTS ultimately leads to products similar to those of $HAuCl_4$. The pyridine analog,
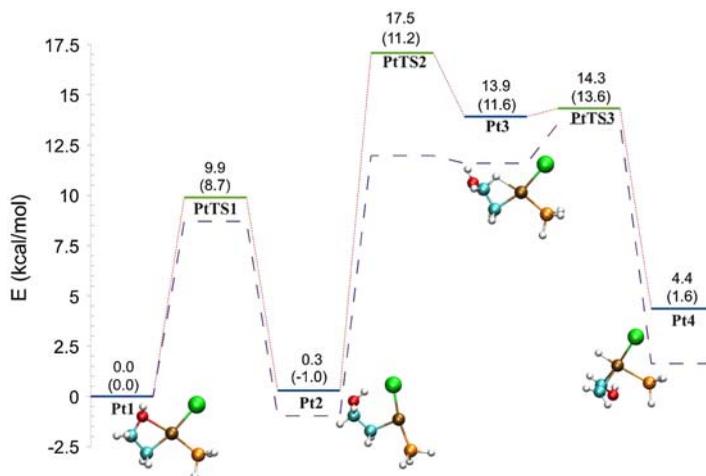
Figure 3. Reaction profile for Pt complexes. Written energies are gas-phase potential energies of TS (green) and minima (blue). Dashed purple line shows the Gibbs energies (energies in parentheses).
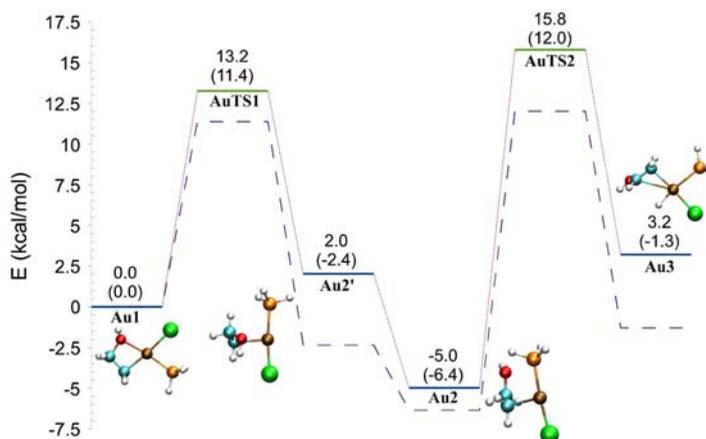
Figure 4. Reaction profile for Au complexes. Written energies are gas-phase potential energies of TS (green) and minima (blue). Dashed purple line shows the Gibbs energies (energies in parentheses).
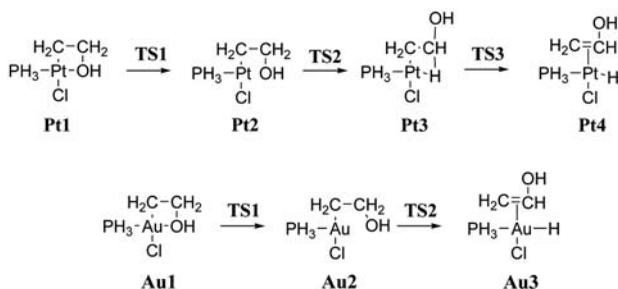
Scheme 2. Labeling of the intermediates and transition states for the calculations in reactions with ethylene.

$AuCl_3(py)$, produces primarily $AuCl_2(CH_2CH_2OH)(py)$ with only a small amount of ethylene glycol, supporting that oxidation of the phosphine is important in the decomposition.

To better understand the isolation of the gold β-hydroxyethyl complex, we performed calculations on the stability of the model complexes $Pt(Cl)(PH_3)(CH_2CH_2OH)$ and $Au(Cl)(PH_3)(CH_2CH_2OH)^+$ prior to a carbon–hydrogen activation step that could lead to decomposition. The reaction coordinates for each are shown in figures 3 and 4. For the Pt model, the mechanism is divided in three elementary steps: decoordination of the oxygen (transition state **TSl**), formation of a β agostic hydrogen (**TS2**), and C–H activation (**TS3**), as shown in scheme 2. From the computed potential energies (see figure 3), the rate-determining step is the formation of the agostic intermediate (**Pt3**), with a relative barrier of 17.5 kcal/mol (from the initial O-coordinated species **Pt1**).

For the Au model, only two steps are needed, since no agostic intermediate has been found (scheme 2, figure 4). The primary difference is that a conformation of intermediate **Au2** has been obtained that is more stable than the O-coordinated species; hence, it can be expected to be the resting state of 2-hydroxyethyl-gold. A transition state connecting the two minima obtained from transition states (**Au2′** and **Au2**) has not been found. However, these species only differ by the orientation of the oxygen and can be considered two conformations of a single species with a fast and easy interconversion. A comparison of the energy barriers suggests that the reaction may be faster for Pt, but the differences are small: despite the TS energy being lower for the Au main step, the relative barrier is higher because of stability of the **Au2** intermediate. The difference among relative barriers is 20.8 *versus* 17.5 kcal/mol. The calculations may be further improved by explicitly including bulky phosphine ligands and, potentially, solvent effects. However, already at the present level of theory, the calculations support the extra stability of $AuCH_2CH_2OH$ over $PtCH_2CH_2OH$, consistent with the experimental observations.

Only $Au(bipy)Cl_2^+$ produced selective products on reactions with ethylene and propylene. These products showed that $Au(III)(CH_2CH_2OH)_2$ is less susceptible to β-hydride elimination. $Au(bipy)))(CH_2CH_2OH)_2^+$ is also not susceptible to reductive elimination (unfortunately, since this would lead to production of 1,4-butanediol from ethylene and water!). These β-hydroxy alkyls are neither susceptible to protonation at low pH nor hydroxide cleavage at high pH (above pH = 8 the products decompose).

Despite the rapidly increasing number of applications of gold complexes to synthesis and catalysis, direct reactions of alkenes with gold(III), leading to a gold(III) product, has apparently not been reported [50]. Thus, our reactions of $Au(bipy)Cl_3$ with ethylene and propylene producing $[Au(bipy)(CH_2CH_2OH)_2]X$ ($X = Cl^-$, PF_6) and $[Au(bipy)(CH_2CH(OH)CH_3)_2]X$ provide the first examples of reactions of gold(III) with simple alkenes that occur without reduction of the gold(III).

Conclusion

The nucleophilic addition of water to ethylene and propylene mediated by gold(III) complexes produces β-hydroxyalkylgold(III) complexes. Depending on the ligand, this complex can undergo hydrolysis to produce ethylene glycol or β-hydride elimination to produce acetaldehyde. In the case of bipyridine, these decomposition pathways are suppressed and the bis-β-hydroxyalkylgold(III) complex remains stable in solution. The tridentate terpyridine does not allow for the reaction to occur, leading to the conclusion that the reaction requires at least two coordination sites to proceed. The nature of the counter ion

does not seem to have an appreciable effect on the outcome of the reaction. Hydration of propylene proceeds similarly to ethylene, in accordance with Markovnikov's rule.

Experimental

Materials

The following materials were used in the syntheses: $H[AuCl_4] \cdot 3H_2O$ was purchased from Alfa Aesar. 2,2′-Bipyridine (bipy) and 2,2′:6′,2″-terpyridine (terpy) were purchased from Strem Chemical. Celite, potassium hexafluorophosphate, and tetrahydrothiophene were available from Aldrich. Potassium hydroxide, acetone, and acetonitrile were purchased from Fisher Scientific. Deuterium oxide and d_3-acetonitrile were purchased from Cambridge Isotope Laboratories. Ethylene and chlorine gasses were purchased from Matheson. Propylene gas was purchased from Irish. Methanol was obtained from EMD. Anhydrous ethanol was available from Pharmco. Ethyl ether, pyridine, and NaOH were available from J.T. Baker. TPPTS was prepared and used after analysis by $^{31}P\{^1H\}$ NMR to confirm purity (the phosphorus resonance of TPPTS occurs at -4.8 ppm, whereas its oxide appears at 34.2 ppm) [57].

Instrumentation

All ^1H and ^{31}P NMR spectra were recorded on a Varian Inova 400 MHz NMR spectrometer unless otherwise indicated. ^{31}P NMR spectra were ^1H decoupled and referenced to an external reference of 85% H_3PO_4 in D_2O (reference set as 0.00 ppm). ^1H-^{13}C HSQC experiment was run on a Varian 500 MHz spectrometer. All chemical shifts (δ) are reported in parts per million (ppm) and all coupling constants (J) are reported in Hz. When appropriate, proton signals for products were integrated and their values established relative to the known number of protons in the aromatic region of the ligand. Mass spectra were run on a ThermoFinnigan MAT 95XL high-resolution magnetic sector (San Jose, CA) with electrospray source (3.3 kV) in positive ionization mode. Samples were run in 100% water.

Syntheses

Chloro(2,2′:6′,2″-terpyridine)gold(III) chloride trihydrate ($[Au(C_{15}H_{11}N_3)Cl]Cl_2 \cdot 3H_2O$); [Au(terpy)Cl]Cl$_2$·3H$_2$O) [58]. A mixture of $H[AuCl_4] \cdot 3H_2O$ (0.970 g, 2.46 mM) and 2,2′:6′,2″-terpyridine (0.633 g, 2.71 mM) was placed in 75 mL of water, and the solution was adjusted to a pH of 4 with a NaOH solution. The resulting mixture, a yellow-orange solution and a purple solid, was brought to reflux and within 1.5 h the solid dissolved producing a dark red solution. After being refluxed for 24 h, the solution was filtered to remove small amounts of a purple solid and the filtrate was evaporated to dryness under reduced pressure. The complex was then recrystallized from water. Yield: 889 mg (60.2%). ^1H NMR (D_2O): δ 9.14 (d), 8.59-8.53 (m), 8.01–7.94 (m).

Dichloro(2,2′bipyridine)gold(III) chloride ($[Au(C_{10}H_8N_2)Cl_2]Cl$); [Au(bipy)Cl$_2$]Cl [59]. An aqueous solution of $H[AuCl_4] \cdot 3H_2O$ (396 mg, 1.01 mM) in 10 mL of water was adjusted to an approximate pH of 3 with a NaOH solution. The solution was then heated to boiling, at which point 2,2′-bipyridine (325 mg, 2.08 mM) was added with stirring. The yellow precipitate of [Au(bipy)Cl$_2$][AuCl$_4$], which was first deposited, dissolved on boiling

for a few minutes. Sodium chloride (NaCl; 5.844 g, 100.0 mM) was stirred in and the clear solution was left overnight in the refrigerator. The orange needles were washed with a large excess of anhydrous acetone followed by anhydrous ether. Yield: 209 mg (45.2%). ^{1}H NMR (D_2O): δ 9.35 (d), 8.53–8.40 (m), 7.91 (t).

Dichloro(2,2′bipyridine)gold(III) hexafluorophosphate ([Au($C_{10}H_8N_2$)Cl_2]Cl); [Au(bipy)Cl_2]PF_6) [60]. The ligand (0.100 mM), KPF_6 (0.300 mM), H[$AuCl_4$]·$3H_2O$ (0.100 mM), 0.500 mL CH_3CN, and 2.50 mL of H_2O were combined in a 5 mL microwave reaction vessel. The reaction mixture was heated at 110 °C for 10 min in a microwave reactor. While still warm, the vessel was placed in a cold water bath for 60 min. After cooling, the product was collected on a fine frit and washed with 2 × 5 mL portions each of water and ethyl ether and allowed to dry. Yield: 47.7 mg (83.8%). ^{1}H NMR (CD_3CN): δ 9.45 (d), 8.61-8.54 (m), 8.04 (t).

Chloro(tetrahydrothiophene)gold(I) (AuCl(SC_4H_8); AuCl(tht)) [61]. A 100 mL flask fitted with a Teflon-coated magnetic stirring bar is charged with a solution of hydrogentetra-chloroaurate(III) tetrahydrate (H[$AuCl_4$]·$4H_2O$; 3.09 g, 7.50 mM) in a mixture of 5.00 mL water and 25.0 mL of ethanol. Dropwise addition of tetrahydrothiophene (tht; 1.40 mL, 16.0 mM) gives a bulky yellow precipitate $AuCl_3$(tht), which is transformed into the white solid of AuCl(tht) while the addition is continued. The mixture is stirred for 15 min at room temperature and the white precipitate is filtered, washed with two 5 mL portions of ethanol and vacuum dried. Yield: 2.38 g (98.9%).

Chloro(tri *m*-sulfonatophenylphosphine trisodium salt)gold(I) (AuCl(P(*m*-$C_6H_4SO_3Na$)$_3$); AuClTPPTS) [45]. To a solution of AuCl(tht) (417 mg, 1.30 mM) in 70 mL methanol was added TPPTS (738.9 mg, 1.30 mM). After being stirred for approximately 40 min, the solution was filtered through Celite and the filtrate was concentrated under vacuum to about 3 mL. Addition of diethyl ether precipitated the colorless complex, which was isolated by filtration, washed with diethyl ether, and dried in vacuum. Yield: 1.00 g (95.7%). ^{1}H NMR (D_2O): δ 7.54–7.65 (m), 7.87–7.91 (m). ^{31}P{^{1}H} NMR (D_2O): δ 33.73 (s).

Trichloro(tri *m*-sulfonatophenylphosphine trisodium salt)gold(III) (AuCl$_3$(P(*m*-$C_6H_4$$SO_3Na$)$_3$); AuCl$_3$TPPTS) [62]. Chlorine gas was slowly bubbled through an aqueous solution of AuClTPPTS (400.4 mg, 0.5000 mM) in 20 mL of water while the solution was magnetically stirred. The original colorless solution turned bright yellow within a few seconds. The addition of chlorine continued for about one minute, after which the solution was filtered, and the solvent was removed by rotary evaporation. Yield: 358.5 mg (82.25%). ^{1}H NMR (D_2O): δ 7.58–7.69 (m), 7.89–7.98 (m).

Trichloro(pyridine)gold(III) (Au(C_5H_5N)Cl_3; Au(py)Cl_3) [63]. H[$AuCl_4$]·$3H_2O$ (48.7 mg, 0.124 mM) was dissolved in water (2.0 mL) and a stoichiometric amount of pyridine, dissolved in water, was added dropwise while stirring. The yellow precipitate formed almost immediately was filtered off, washed three times with water (1.0 mL), and dried in vacuo. Yield: 35.7 mg (75.5%). ^{1}H NMR (D_2O, sparingly soluble): δ 8.643 (m), 8.487 (m), 7.926 (m).

Reactions with alkenes

For [AuCl₄]⁻ and AuCl₃L (L = TPPTS or pyridine), 0.1 mmol of the appropriate complex was dissolved in 20 mL of D_2O. The reactant gas was then bubbled through a Pasteur pipet into the solution for at least an hour, at which point the flask was stoppered with an atmosphere of the gas still in the flask.

For [Au(bipy)Cl₂]⁺, 0.1 mM of the appropriate complex was dissolved in 20 mL of D_2O in a lipless beaker. The beaker was placed in a high-pressure reactor, which was charged with 100 psi of the reactant gas and then sealed. The reactor was immersed in an oil bath at 50 °C and stirred for the duration of the experiment.

(2,2′bipyridine)bis-*β*-hydroxyethylgold(III) ([Au(C₁₀H₈N₂)(C₂H₅O)₂]⁺; [Au(bipy)(CH₂ CH₂OH)₂]⁺. 0.100 mmol of a [Au(bipy)Cl₂]⁺ salt was dissolved in 20.0 mL of D_2O and reacted with ethylene gas according to the above procedure. ¹H NMR (D_2O): δ 3.705 (t), 2.287 (t). MS ESI: 443.1037 amu (M).

(2,2′bipyridine)bis-*β*-hydroxypropylgold(III) ([Au(C₁₀H₈N₂)(C₂H₇O)₂]⁺; [Au(bipy)(CH₂CH (OH)CH₃)₂]⁺. 0.100 mmol of a [Au(bipy)Cl₂]⁺ salt was dissolved in 20.0 mL of D_2O and reacted with propylene gas according to the above procedure. ¹H NMR (D_2O): δ 4.054 (m), 2.353 (m), 1.226 (d). MS ESI: 471.1357 amu (M).

Computational details

All calculations have been performed with the Gaussian03 Rev. C.02 software package [64] using Density Functional Theory with the hybrid functional B3LYP. Transition metals (Au and Pt) were described with the Los Alamos pseudopotential with its associated double-zeta basis set for the valence electrons (LANL2DZ). A set of polarization *f* functions was added with exponents 1.050 and 0.993 for Au and Pt, respectively. The 6–31G(d) basis set was used for C, P, O, and Cl. Hydrogen atoms were described with a 31+G(p) basis set originating from 6–31++G(d,p), including a set of p polarization functions and diffuse functions. All energies reported here are in units of kcal/mol and if not stated otherwise the energies are gas-phase internal energies. However, Gibbs energies including entropic terms are also included in the graphics. Minima and transition states were characterized by the presence of zero or one imaginary frequency, respectively. Transition states were related to minima using IRC calculations.

Supplementary material

Additional NMR spectra (including COZY and HSQC) are available in the supplementary material.

Acknowledgments

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