

# Hydrochlorination of acetylene using a supported gold catalyst: A study of the reaction mechanism.

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## Abstract

A detailed study of the hydrochlorination of acetylene and higher alkynes using a supported gold catalyst is described and discussed. A series of reactions using sequential exposure of the catalysts to C<sub>2</sub>H<sub>2</sub> and HCl demonstrate that exposure to HCl prior to reaction of C<sub>2</sub>H<sub>2</sub>/HCl leads to enhanced activity whereas exposure to C<sub>2</sub>H<sub>2</sub> leads to deactivation. The reaction of higher alkynes is affected by steric factors with the trend in activity being: acetylene (*ca.* 40 % conversion)>> hex-1-yne (10 %)>phenylacetylene (7 %) > hex-2-yne (2 %) under standard reaction conditions. Using <sup>1</sup>H-NMR spectroscopy we have found that for hex-1-yne and phenyl acetylene the anti-Markovnikov product is formed by *anti* addition of HCl. However, the Markovnikov products are equivalent for *syn*- and *anti*-addition of HCl, and hence we investigated the reaction using deuterated substrates and confirmed the products are formed by the *anti* addition of HCl. The reaction mechanism is discussed in detail.

## 1. Introduction

Hydrochlorination of acetylene is one method by which vinyl chloride can be manufactured on a commercial scale. Industrial processes use mercuric chloride supported on carbon (1,2) but these catalysts can be short lived due to their instability with loss of mercuric chloride being a major catalyst deactivation mechanism, and this leads to environmental problems. In 1985 it was proposed (3) that supported  $\text{Au}^{3+}$  would be a viable catalyst for alkyne hydrochlorination and this was subsequently shown to be the case (4-7). These early studies largely predated the massive current interest in catalysis by gold (8-11), but it did show that gold could be the catalyst of choice for a specific reaction, whereas previously gold had been considered to be of little interest as a catalyst. In these earlier studies we studied the mechanism by which the gold catalysts deactivated during the hydrochlorination reaction (6) and also we explored means by which they could be reactivated (7). It is interesting that since these studies there have been no further investigations on the acetylene hydrochlorination reaction using supported gold catalysts. We have now revisited this reaction and in this paper we present a study of the reaction mechanism and also explore the reactivity of higher primary and internal alkynes for the hydrochlorination reaction.

## 2. Experimental

### 2.1 Catalyst preparation and characterisation

The carbon-supported gold catalyst (1 wt% Au/C) was prepared using an incipient wetness impregnation technique and aqua regia as solvent. The carbon (Aldrich, Darco 12-20 mesh) was initially washed with dilute aqueous HCl (1 mol L<sup>-1</sup>) at 70° C for 5 h to remove Na, Fe and Cu that are poisons for the hydrochlorination reaction (12). The carbon was filtered and washed with distilled water (2 L g<sup>-1</sup>) and dried at 140° C for 18 h. A solution of  $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$  (Strem, 82 mg, assay 49.7 %) in aqua regia (3.7 mL) was added dropwise to the acid-washed carbon (Aldrich, Darco 12-20 mesh, 4

g) with stirring. The product was then dried at 140° C for 18 h and used as a catalyst.

X-ray photoelectron spectroscopy spectra were recorded on a Kratos AXIS-Ultra spectrometer, using a monochromatic AlK<sub>α</sub> X-ray source (75-150 W) and an analyser pass energy of 160 eV (survey scans) or 20 eV (detailed scans). Binding energies are referenced to the C(1s) binding energy of carbon taken to be 284.7 eV.

Samples were prepared for transmission electron microscopy (TEM) analysis by dispersing the catalyst powders in high-purity ethanol and allowing a drop of the suspension to dry on a lacey-carbon film supported on a 300-mesh Cu TEM grid. Bright-field (BF) images were acquired using a JEOL 2000FX TEM operating at 200 keV with a LaB<sub>6</sub> filament.

## 2.2 Catalyst testing

Catalysts were tested for acetylene hydrochlorination in a fixed bed glass microreactor operating just above atmospheric pressure. Acetylene (5 mL min<sup>-1</sup>) and hydrogen chloride (5 mL min<sup>-1</sup>) were fed through a mixing vessel/preheater (70 °C) via calibrated mass flow controllers to a heated glass reactor containing catalyst (200 mg), giving a total GHSV of 870 h<sup>-1</sup>. Higher alkynes were used as liquids and were introduced by vaporisation in an inert gas. The pressure of the reactants, both HCl and C<sub>2</sub>H<sub>2</sub> was in the range of 1.1-1.2 bar. This value was chosen both for safety reasons, and to test the catalyst under mild conditions. The products were analysed in two ways. First, the exit gas mixture was passed through a Dreschel bottle containing NaOH at known concentration for a known time to determine the conversion of HCl. Alternatively, the gas stream could be analysed by GC. A reaction temperature of 180° C was chosen, and blank tests using an empty reactor filled with quartz wool did not display any catalytic activity, even at 250 °C with the reactants under these flow conditions.

## 2.3 DFT methodology

Calculations on the interaction between AuCl<sub>3</sub>, acetylene and HCl and the pathways to the formation of

chloroethene were carried out using the BHandH functional and a 6-31G(d,p) basis set (13) with the Gaussian03 program. (14). The core electrons of Au were represented using the relativistic effective core potential developed by Stoll *et al.* (15). Transition states were obtained by relaxed scans of the bond formed in the reaction, the maximum point was then used in a transition state optimisation. Transition states were confirmed by a frequency calculation to show only a single imaginary mode was present and this mode was animated to check that it linked reactants and products.

### 3. Results and Discussion

#### 3.1. Sequential HCl/C<sub>2</sub>H<sub>2</sub> during acetylene hydrochlorination

The activity of the supported gold catalyst decreases gradually during exposure to the C<sub>2</sub>H<sub>2</sub>/HCl reaction mixture under the standard reaction conditions (Fig. 1) and this was considered to be due to the reduction of Au<sup>3+</sup> and is consistent with our previous studies (3-7). Indeed, X-ray photoelectron spectroscopy of the fresh and deactivated catalyst confirmed this earlier conclusion (Fig. 2). C<sub>2</sub>H<sub>2</sub> is a well known reducing agent, and it is important to determine if the reduction in activity is an effect of the reaction or of acetylene only. In order to achieve this, a series of experiments have been carried out in which the catalyst is sequentially exposed to individual components of the reactants. To achieve this, an inert gas (He) was added to the reactants to ensure the overall flow rate could be maintained constant. Four sets of experiments were conducted, using a 1:1 molar reactant ratio (i.e. flow of 5mL·min<sup>-1</sup> for each reactant) at 180 °C, as follows:

- Experiment A: C<sub>2</sub>H<sub>2</sub>/HCl (2h) → He/HCl (2h) → C<sub>2</sub>H<sub>2</sub>/HCl (2h)
- Experiment B: He/HCl (2h) → C<sub>2</sub>H<sub>2</sub>/HCl (2h) → He/HCl (2h)
- Experiment C: C<sub>2</sub>H<sub>2</sub>/HCl (2h) → C<sub>2</sub>H<sub>2</sub>/He (2h) → C<sub>2</sub>H<sub>2</sub>/HCl (2h)
- Experiment D: C<sub>2</sub>H<sub>2</sub>/He (2h) → C<sub>2</sub>H<sub>2</sub>/HCl (2h) → C<sub>2</sub>H<sub>2</sub>/He (2h)

The results of these experiments are shown in Figs. 3. The role of HCl is clearly demonstrated in experiments A and B. In experiment A, where the intermediate step is He/HCl, the catalytic activity is maintained when the acetylene is reintroduced in the third phase of the experiment. In experiment B, where the initial treatment is with He/HCl, on introduction of the acetylene the formation of vinyl chloride is significantly enhanced. In this case, the initial HCl treatment oxidizes some  $\text{Au}^0$  and we have noted this previously in catalyst regeneration studies (7). Conversely, exposure to  $\text{C}_2\text{H}_2$  leads to catalyst deactivation in the absence of HCl (experiments C and D), and it is clear that, even if no reaction occurred initially (experiment D), the catalyst was deactivated by exposure to  $\text{C}_2\text{H}_2$ , and when the reaction was brought online again, the conversion to vinyl chloride was markedly lower when compared to a standard reaction without interruption of the reactants. From these experiments it is clear that both reactants are able to modify the final performance of the catalyst, but in opposing directions: a regeneration/activation role for HCl, while  $\text{C}_2\text{H}_2$  acts to decrease the activity of the catalyst, independent of whether the reaction is occurring.

In order to evaluate further the effects of the reactants, two additional tests, in which the molar ratios of HCl and  $\text{C}_2\text{H}_2$  were varied, were carried out:

- Experiment E:  $\text{C}_2\text{H}_2/\text{HCl}$  (2h) 1:1 →  $\text{C}_2\text{H}_2/\text{HCl}$  (2h) 1:1.5 →  $\text{C}_2\text{H}_2/\text{HCl}$  (2h) 1:1
- Experiment F:  $\text{C}_2\text{H}_2/\text{HCl}$  (2h) 1:1 →  $\text{C}_2\text{H}_2/\text{HCl}$  (2h) 1:0.5 →  $\text{C}_2\text{H}_2/\text{HCl}$  (2h) 1:1

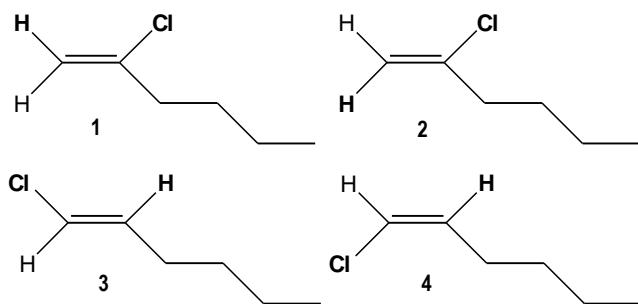
The results are shown in Fig. 4 and it is clear that the conversion increases and the rate of deactivation decreased when the molar ratio of the HCl is increased. Indeed, even when the standard flows of reactants are resumed the activity of the catalysts treated with the higher molar ratio of  $\text{HCl}/\text{C}_2\text{H}_2$  remains noticeably higher than that treated with the lower  $\text{HCl}/\text{C}_2\text{H}_2$  ratio.

### 3.2. Reaction of higher alkynes

In all our previous studies (4-7) we have only investigated the hydrochlorination of acetylene. Being a symmetrical molecule, the reaction of acetylene does not provide mechanistic data since only one product is possible. In view of this we wished to extend the reactant molecules to substituted alkynes, to answer two questions: (a) can higher alkynes be reacted with HCl under the same reaction conditions? and (b) what is the selectivity of the reaction?

#### 3.2.1. Hydrochlorination of hex-1-yne over Au/C catalyst

The reaction of hex-1-yne/HCl was studied using the Au/C catalyst and a reaction temperature of 180 °C with the standard reactant flow rates (HCl flow rate: 5 mL min<sup>-1</sup> and hex-1-yne introduced *via* a saturator with an He flow of 20 mL min<sup>-1</sup>, HCl:alkyne molar ratio = 0.74 *cf* 1.0 for acetylene). The products were analysed by gas chromatography to determine conversion. This was determined to be steady at 10% for hex-1-yne (as compared with *ca.* 40 % conversion for acetylene under the same conditions) hence the steric hindrance of the larger substrate significantly affects reactivity. We used <sup>1</sup>H-NMR spectroscopy to determine the nature of the product by collecting the reaction products in a chloroform trap at the outlet of the reactor for a time on line of 3 h (see supplementary data). Taking into account all the possible isomers, i.e. the Markovnikov and anti-Markovnikov and the *syn* or *anti* addition of HCl to the triple bond, the number of possible products that can be obtained is four, and they are shown in scheme 1 and table S1.



**Scheme 1:** possible regioselectivity and stereochemistry of the addition of HCl to hex-1-yne: **1** Markovnikov with *syn* HCl addition, **2** Markovnikov with *anti* HCl addition, **3** anti-Markovnikov with *syn* HCl addition and **4** anti-Markovnikov with *anti* HCl addition.

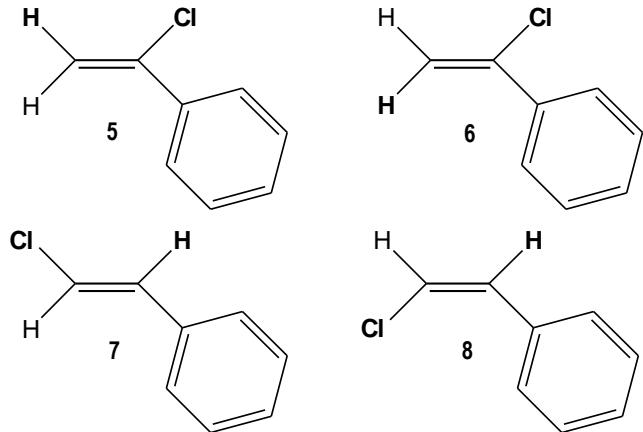
The reaction is found to display very high selectivity towards the Markovnikov products **1**, **2** (which are, unfortunately, NMR equivalent) and only traces (3.7 % of relative amount to the Markovnikov product) of the anti-Markovnikov product **4** were detected (see supplementary information, fig. S1 and scheme S1), while product **3** was absent.

Concerning the trace levels of the anti-Markovnikov products that were observed, the difference in terms of chemical shift between the HCl addition products with *syn* and *anti* stereochemistry is not significant for unambiguous characterization. However, at 6.03 ppm it is possible to observe a doublet of triplets, with a coupling constant  $J_{AB}$  equal to 6.7 Hz (see supplementary information, fig. S2 and table S1), which is a numerical value consistent with the HCl addition product with *anti* stereochemistry, expected to have a value in the range of 6-12 Hz (16), whereas the HCl addition product with *syn* stereochemistry is expected to have a value in the range 12-18 Hz

### 3.2.2 Hydrochlorination of phenyl-acetylene over Au/C catalyst

In order to collect further information on the reactivity towards different substrates, hydrochlorination of phenyl acetylene was studied using the same reaction conditions as those used for hex-1-yne, (180 °C, a flow of HCl of 5 mL min<sup>-1</sup> and phenyl acetylene introduced *via* a saturator with

an He flow of 20 mL min<sup>-1</sup>, HCl:alkyne molar ratio = 1.75 *cf* 1.0 for acetylene). The conversion of phenyl acetylene was determined using on-line gas chromatography as 7% under these conditions, and the difference in reactivity if compared with hex-1-yne, it could be explained with the fact that in phenyl-acetylene the triple bond is conjugated with the aromatic ring. The selectivity of the product was determined using <sup>1</sup>H-NMR spectroscopy (scheme 2 and see supplementary information, scheme S3) and the major product was determined to be the Markovnikov NMR equivalent products **5**, **6** (see supplementary information, fig. S3) and traces of the product for the *anti* addition of HCl (1.2% of relative amount) **8** (see supplementary information, fig. S4) were observed while the product for the *syn* addition **7** was absent



**Scheme 2:** possible regioselectivity and stereochemistry of the addition of HCl to phenyl-acetylene: **5** Markovnikov with *syn* HCl addition, **6** Markovnikov with *anti* HCl addition, **7** anti-Markovnikov with *syn* HCl addition and **8** anti-Markovnikov with *anti* HCl addition.

### 3.2.3 Hydrochlorination of hex-2-yne over Au/C catalyst and effects of terminal alkynes

In a catalytic test using hex-2-yne as a substrate using the same experimental conditions used for hex-1-yne (HCl:hex-2-yne molar ratio = 0.77 *cf* 1.0 for acetylene), very little conversion, below 2% was detected. In addition, in this case it was not possible to carry out assignments for the stereochemistry of the final products that are obtained. This is because the proton coupling constants of

the two Markovnikov isomers for the *syn* or *anti* addition of HCl were both in the same range (13) for an unambiguous determination of minor amounts of one isomer in the presence of the other. However, the very low reactivity of hex-2-yne in comparison with terminal alkynes shows the effects of steric hindrance on reactivity. Based on the reaction data obtained the trend in activity being: acetylene (*ca.* 40 % conversion)>> hex-1-yne (10 %)>phenylacetylene (7 %) > hex-2-yne (2 %). However, we must note that there are differences in the amounts of the alkyne fed to the reactor for the longer carbon chain alkynes since these are fed to the reactor using a saturator. Hence, the substrate:HCl ratio is different for the longer carbon chain alkynes as compared with acetylene. However, the ratios for the two hexynes we have studied are the same within experimental error (hex-1-yne, 0.74; hex-2-yne, 0.77) and hence the difference we observe in their reactivity is significant. We have shown that the rate of reaction is dependent on the alkyne:HCl molar ratio (Fig. 4) and the conversion increases and the rate of deactivation decreases when the molar ratio of the HCl is increased. Hence, this effect must be taken into account when considering the effect of the substrate structure on reactivity. However, as phenylacetylene is studied with a high HCl:alkyne molar ratio (1.175), the experiments will tend to overestimate its reactivity relative to acetylene. Similarly, we are underestimating by a small part the reactivity of the hexynes relative to acetylene. For acetylene when the molar ratio of acetylene:HCl is 1:0.5 the reactivity decreases by *ca.* 25%, and hence we can estimate that the effect of the molar ratio on the reactivity of hexenes will be *ca.* 10-15%. Taking these factors into account we consider that the relative order of reactivity we describe based on the reaction data is substantiated

### 3.3. Hydrochlorination using deuterated reactants

Using  $^1\text{H-NMR}$  spectroscopy we have found that for hex-1-yne and phenyl acetylene the anti-Markovnikov is formed by *anti* addition of HCl. However, as the Markovnikov products are equivalent for *syn*- and *anti*- addition of HCl, we investigated the reaction using deuterated substrates.

### 3.4.1 Hydrochlorination of hex-1-yne with DCl

The hydrochlorination reaction was carried out with hex-1-yne and DCl. The DCl was used in a diethylether solution ( $1 \text{ mol}\cdot\text{L}^{-1}$ ) and fed to the reactor *via* a saturator. The effect of the presence of the diethylether was tested separately and no reaction occurred with this molecule nor did it affect the reaction. The reaction products were collected in deuterated chloroform and  $^1\text{H-NMR}$  revealed the presence of only one deuterated Markovnikov product (see supplementary information, fig. S5) with *anti* stereochemistry, and it was concluded that this product is formed *via anti* addition of DCl to hex-1-yne. However, traces of  $\text{H}_2\text{O}$  were found to be present in the He carrier gas and hence traces of HCl could be present. In view of this we reacted deuterated hex-1-yne.

### 3.3.2 Hydrochlorination using D-hex-1-yne and HCl

In order to collect further mechanistic information, a catalytic test using deuterated D-hex-1-yne was carried using the same experimental conditions described for the other tests involving hex-1-yne. In contrast with the experiment where DCl was used, the deuterated product was that formed by *syn* addition of the HCl (see supplementary information, fig. S6), and this discrepancy could be related to an isotope effect involving D-Cl cleavage, effect which is not operating in presence of deuterated D-hex-1-yne. Hydrochlorination of phenyl-acetylene using DCl was also investigated but no reaction was observed.

## 3.4 Investigation of the catalysts using transmission electron microscopy

In section 3.1 we demonstrated that the deactivation of the catalyst that we observe can be ascribed to loss of  $\text{Au}^{3+}$  during use. This is consistent with our previous studies (6,7). However, it is feasible that some deactivation could be caused by sintering of the metallic gold nanoparticles, since

this is the predominant form of the metal that is present on the catalyst during the reaction. In view of this we studied the catalyst before and after use for acetylene hydrochlorination using transmission electron microscopy (Fig. 5). There is a small amount of sintering that occurs on use and the mean gold nanoparticles size increases from 4.8 nm to 5.9 nm, which we do not consider to be particularly significant with respect to the overall deactivation of the catalyst.

### 3.5 DFT studies

To aid our understanding of the reaction mechanism of alkyne hydrochlorination using supported gold catalysts we have carried out a series of theoretical studies. The  $\text{AuCl}_3$  structure geometry optimisation gave a T-shaped complex with a largest Cl-Au-Cl angle of  $169^\circ$ . The lowest unoccupied molecular orbital (LUMO) of this structure has a large lobe in the plane of the complex between the two *trans* Cl ligands, Fig. 6. This is consistent with the well known electrophilic nature of Au(III) and would suggest complexation of a nucleophilic reactant in a square planar geometry.

The overall calculated reaction energy profile is shown in Fig. 7. The energy scale shown takes the sum of the calculated energies for the individual components of the reaction,  $\text{AuCl}_3$ ,  $\text{C}_2\text{H}_2$  and  $\text{HCl}$  as the arbitrary zero (labelled level **1** in Fig. 7). Initially the complexation of  $\text{HCl}$  and acetylene were compared, both have a favourable interaction with the Au centre in the position expected from the shape of the  $\text{AuCl}_3$  LUMO. Initial co-ordination of  $\text{HCl}$  results in a calculated energy of  $-105 \text{ kJ mol}^{-1}$  with respect to the reference state (level **2**) whereas placing  $\text{C}_2\text{H}_2$  into the vacant co-ordination site of  $\text{AuCl}_3$  gave structure **3** with a relative energy of  $-168 \text{ kJ mol}^{-1}$ . This indicates that the alkyne is a better ligand than  $\text{HCl}$ . Further calculations based on the co-ordinated  $\text{HCl}$  structure reacting with acetylene did not identify any low energy route to chlorinated products. Indeed introduction of acetylene in an axial position over the Au centre in complex **2** gave only a very weak interaction.

In the absence of  $\text{HCl}$  the structure of the co-ordinated acetylene, **3**, shows an angle of  $59^\circ$  between the C-C bond and the  $\text{AuCl}_3$  plane. This twisted arrangement gives a better overlap of the

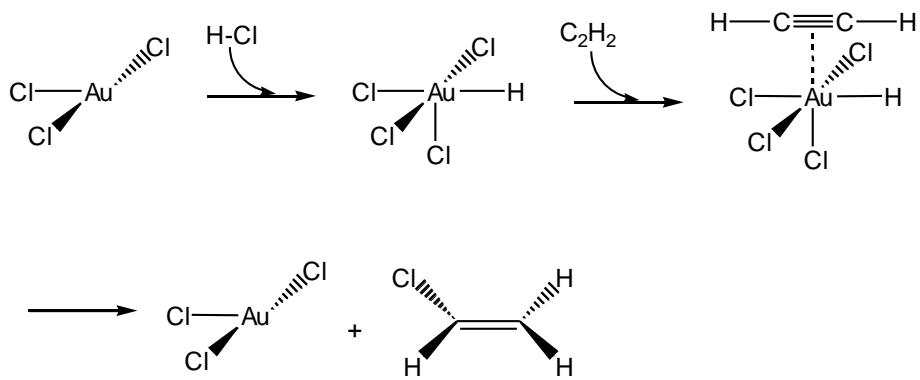
$\text{C}_2\text{H}_2$  HOMO  $\pi$ -orbital with the LUMO state shown in fig.6. Using constrained optimisations we calculated the energy of the complex as a function of this twist angle and found the low lying intermediate **5** (energy -213 kJ mol<sup>-1</sup>) via transition state **4**. The calculated barrier between the  $\pi$ -complex, **3**, and metallocycle, **5**, is 69 kJ mol<sup>-1</sup>. However attempting to find transition states involving addition of HCl to the C-C bond in **5** resulted in barriers considerably higher than reported in fig. 6. This may indicate that the co-ordination of acetylene in the absence of HCl results in site blocking via the formation of this stable metallocycle structure.

Returning to the  $\pi$ -complex, **3**, HCl was introduced with the Cl atom close to an axial site at the Au centre. However on relaxation the HCl molecule moved away to the position shown in structure **6**, and a Bader analysis of the charge density confirmed that the main interaction between HCl and the complex is via a HCl..HC hydrogen bond. To search for a transition state for HCl addition the Cl atom was stepped toward the nearest C atom in a series of constrained optimisations. This resulted in Cl addition via the transition state shown as structure **7**. At this point in the reaction the HCl bond is cleaved to add Cl to the alkyne with the H(Cl) atom leaving to one of the Cl ligands on Au. In addition the second carbon atom has a  $\sigma$ -bond to the Au centre which is *anti* to the forming Cl-C bond. The final stereochemistry is set by this transition state since transfer of the H atom to replace the Au centre is facile and results in a complex with the product alkene in a  $\pi$ -complex akin to **3**.

### 3.6. Comments on the reaction mechanism

Based on the preceding experimental evidence and discussion it is possible to comment on the reaction mechanism by which alkyne hydrochlorination occurs using the gold catalyst. One possibility can be based on an analogy with the mechanism of hydrogenation using Wilkinson's catalyst (17) with Rh and Ir analogues complexes, in which the initial step is oxidative addition of  $\text{H}_2$  followed by coordination of an alkene, transfer of the hydrogen to form an alkyl group initially and subsequently an

alkane and thereby regenerating the catalytic complex. Such a mechanism based on  $\text{AuCl}_3$  is shown in scheme 3 which involves the formation of an octahedral intermediate.

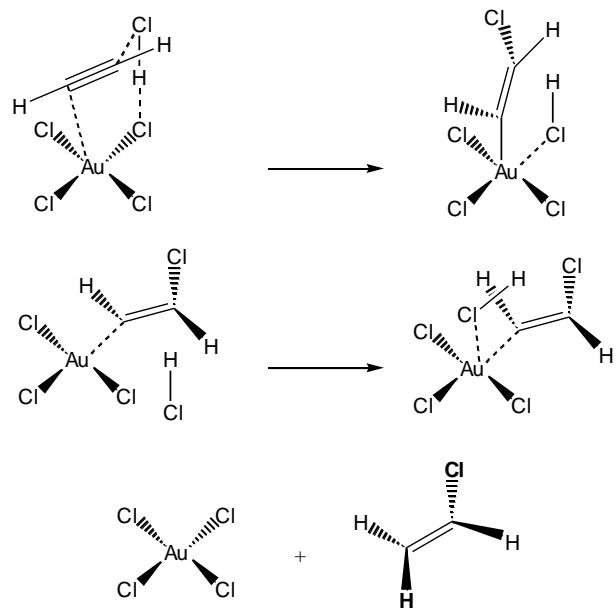


**Scheme 3 :** Proposed model for the hydrochlorination of acetylene over  $\text{Au}/\text{C}$  catalyst, assuming an oxidative addition pathway

This mechanism involves oxidative addition of  $\text{HCl}$  followed by coordination of acetylene and then reductive elimination. A point for debate is whether  $\text{Au}^{3+}$  can act in this way, and it is more likely that such a mechanism could operate with  $\text{Au}^+$ , and this could be present in the operating catalyst. However, the mechanism denoted in scheme 3 could be a viable reaction pathway for terminal alkynes while it is unlikely that internal alkynes could undergo reaction *via* the oxidative addition mechanism shown in scheme 3. Since internal alkynes are not reactive with the supported gold catalyst this may demonstrate that the mechanism shown in scheme 3 may be possible. However, the theoretical studies indicate that the formation of an intermediate in which both the alkyne and  $\text{HCl}$  are adsorbed together results in only a weak interaction, and hence this may mitigate against this mechanistic proposal.

It is therefore necessary to consider other potential reaction pathways. The reactivity of gold, especially  $\text{Au}^{3+}$  towards alkynes is usually explained in two ways: one is a nucleophilic-electrophilic interaction between the  $\text{Au}^{3+}$  centre and the triple bond *via*  $\pi$ -coordination (18). The second, observed for gold(I)-alkynyl complexes (19) uses the acidity of the acid protons of the terminal alkyne to give a  $\sigma$ -coordination. In addition, sometimes both  $\pi$ - and  $\sigma$ - coordination can also be observed (20) using two gold centres. It should be noted that  $\pi$ - and  $\sigma$ - coordination of alkynes (10) have been observed for homogenous catalysis reactions, and these previous studies show a possible pathway that could explain the observed reactivity for primary alkynes and the absence towards secondary alkynes that could be operating for the systems studied in this work. This could indirectly support a mechanism involving a  $\text{C}_2\text{H}_2/\text{Au}/\text{HCl}$  complex. The key piece of mechanistic information is that HCl adds in accordance with the Markovnikov rule and in an *anti* configuration to the alkyne. This *anti* addition has also been observed in the hydrochlorination of acetylene using mechanically activated  $\text{K}_2\text{PtCl}_6$  (21) for which it is proposed that the reaction could occur *via* a complex formed by adsorption of acetylene at a defect site on the surface of the mechanically activated  $\text{K}_2\text{PtCl}_6$  and HCl adsorbed *via* hydrogen bonding with the surface Cl. It is feasible that a similar mechanism could operate with supported the gold catalysts *via* the mechanism shown in scheme 4 with gold tetrachloroaurate as the active species. The hypothesis of the  $\text{C}_2\text{H}_2/\text{Au}/\text{HCl}$  complex, is consistent with the high selectivity; the regeneration effect of HCl and the deleterious effect of  $\text{C}_2\text{H}_2$ , and can explain polymerisation which is one of the mechanisms by which catalyst deactivation occurs. However, this mechanism requires the presence of both reactants to give an initial six member ring in which the alkyne co-ordinates axially to the Au centre. In our DFT studies we found only weak co-ordination of either alkyne or HCl in this position and would expect the resulting penta-coordinated complex to be unstable. It worth noting, that if  $\text{C}_2\text{H}_2$  is present instead of HCl on the regeneration step, it is possible to obtain a conjugate polymer with an even number of

carbon atoms. This could also be true in the case of our DFT generated transition state (**7**, Fig 7) which does not require axial co-ordination of the alkyne.



**Scheme 4:** Proposed model for the hydrochlorination of acetylene over Au/C catalyst, assuming a C<sub>2</sub>H<sub>2</sub>/Au/HCl complex formation

Although the cationic active gold species is represented in both of these reaction mechanisms as a single site, and the computational studies we have carried out use this as a basis, we consider that the active centre is associated with the surface of a gold nanoparticle. In particular, it might be interesting to consider that the reaction takes place in an analogous manner to a homogeneous catalyst and that the cationic gold species is not associated with the surface of the heterogeneous catalyst. Such effects are well known in palladium catalysts, e.g. for the Heck reaction (22,23) where attempts to heterogenise the catalyst have not succeeded and the catalysis continues to result from Pd<sup>2+</sup> that leaches from the catalyst surface. However, this analogy does not work well in the present case since there is no fluid phase in which the leached cationic gold species could be stabilised. Of course the reaction could

proceed in the gas phase but there are two pieces of evidence against this possibility. First, gold compounds are not particularly volatile under the reaction conditions used, indeed gold chlorides decompose at elevated temperatures and they do not sublime( Au(I) chloride decomposes at 289 °C and gold (III) chloride decomposes at >160 °C) hence any gas phase gold chloride species, if formed, would not be stable, and we consider that such species are stabilized on the surface of the catalyst and can be expected to be formed as intermediates. Secondly, if the reaction occurred in the gas phase then in the flow reactor gold would be continually redispersed down the catalyst bed and then out of the reactor. This would severely affect the lifetime of the catalyst, an effect that is observed when the markedly more volatile HgCl<sub>2</sub> is used as a catalyst (1,2). We do not observe any loss of gold in this study or in our previous extensive studies (4-7) and hence we do not consider that the reaction occurs via a gas phase species.

#### 4. Conclusions

In the hydrochlorination of acetylene and higher alkynes using deuterated reactants with supported gold catalysts the addition of HCl has been shown to occur in the *anti* stereochemistry configuration and in accordance with Markovnikov rule for the formation of the main product. However, with higher alkynes trace amounts of minor products formed *via* anti-Markovnikov addition can be observed. The reactivity of higher primary alkynes decreases with their steric bulk, and internal alkynes are unreactive. DFT calculations indicate that the simultaneous co-ordination of alkyne and HCl to the Au(III) centre of AuCl<sub>3</sub> is unlikely. The calculated transition state for HCl addition to the  $\pi$ -complex of C<sub>2</sub>H<sub>2</sub> with AuCl<sub>3</sub> shows that a hydrogen bond between HCl and a Cl ligand of Au controls the stereochemistry of Cl addition. The *anti*-addition of HCl experimentally observed is then a consequence of a sequential addition of Cl and H to the alkyne. This scheme is similar to that proposed

for hydrochlorination using mechanically activated  $K_2PtCl_6$  but takes note of the preference for square planar geometries in Au(III) complexes.

### **Acknowledgements**

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## Captions for Figures

**Fig. 1** – Acetylene hydrochlorination using Au/C catalyst at 180 °C, HCl/C<sub>2</sub>H<sub>2</sub> mol ratio = 1:1, reactant flow rates 5 mL min<sup>-1</sup>.

**Fig. 2** – Au 4f XPS spectra of Au/C catalysts, (a) before reaction it is possible to detect the presence of Au<sup>3+</sup> while (b) after reaction Au<sup>3+</sup> is reduced.

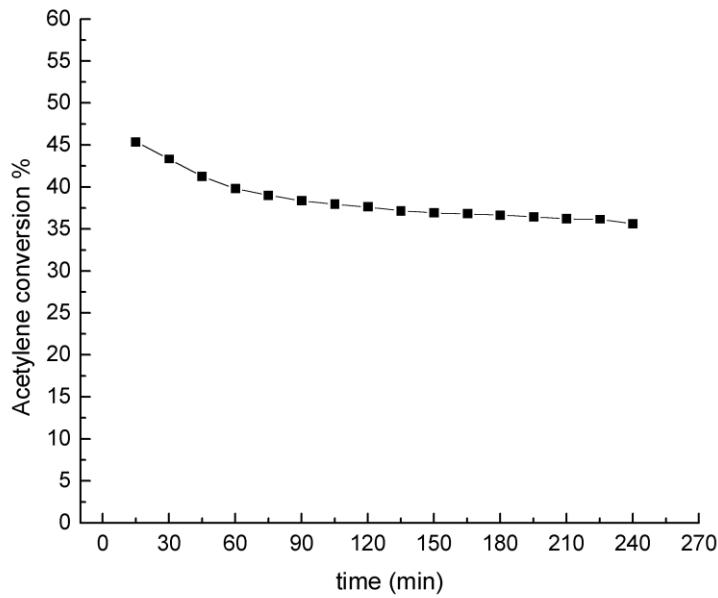
**Fig. 3** – Sequential flow experiments to evaluate the effect of each reactant for the hydrochlorination reaction of acetylene over Au/C catalyst. (Experiment A: ■) C<sub>2</sub>H<sub>2</sub>/HCl (2h) → He/HCl (2h) → C<sub>2</sub>H<sub>2</sub>/HCl (2h); (Experiment B: ●) He/HCl (2h) → C<sub>2</sub>H<sub>2</sub>/HCl (2h) → He/HCl (2h) (Experiment C: ▼) C<sub>2</sub>H<sub>2</sub>/HCl (2h) → C<sub>2</sub>H<sub>2</sub>/He (2h) → C<sub>2</sub>H<sub>2</sub>/HCl (2h) and (Experiment D: ◆) C<sub>2</sub>H<sub>2</sub>/He (2h) → C<sub>2</sub>H<sub>2</sub>/HCl (2h) → C<sub>2</sub>H<sub>2</sub>/He (2h).

**Fig. 4** – Hydrochlorination reaction of acetylene with varying molar ratios of HCl, (Experiment E: ■) C<sub>2</sub>H<sub>2</sub>/HCl (2h) 1:1 → C<sub>2</sub>H<sub>2</sub>/HCl (2h) 1:1.5 → C<sub>2</sub>H<sub>2</sub>/HCl (2h) 1:1 and (Experiment F: ●) C<sub>2</sub>H<sub>2</sub>/HCl (2h) 1:1 → C<sub>2</sub>H<sub>2</sub>/HCl (2h) 1:0.5 → C<sub>2</sub>H<sub>2</sub>/HCl (2h) 1:1

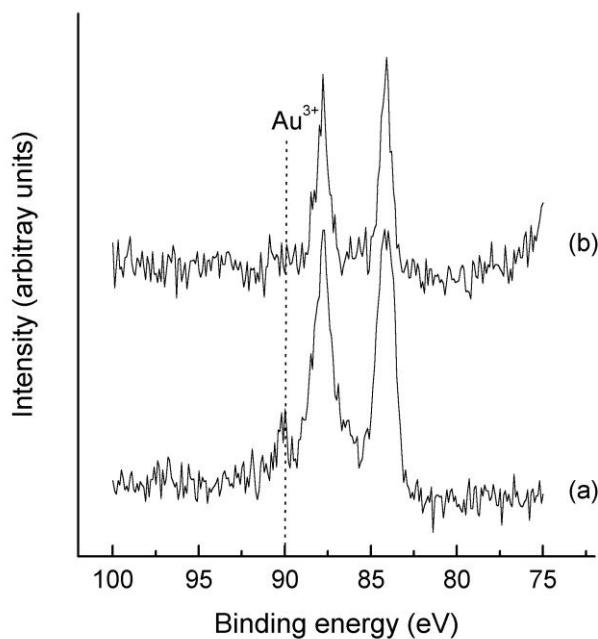
**Fig. 5** – Representative TEM micrographs of the Au/C catalyst before (a) and after (b) reaction; mean particle sizes were 4.8 and 5.9 nm, respectively. Also shown are the Au particle size distributions (c) of these catalysts, filled columns pre-reaction and open columns post-reaction, showing a slight increase in the particle size after the reaction.

Fig. 6 – The calculated LUMO state for AuCl<sub>3</sub> at the BHandH/6-31(d,p) level.

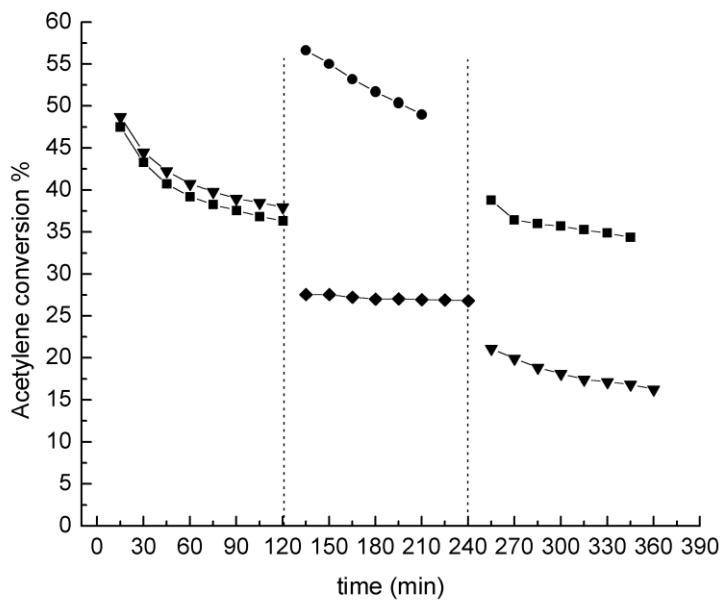
Fig. 7 - Reaction energy profile for hydrochlorination of acetylene, all energies in kJ mol<sup>-1</sup>, transition states marked; ‡.



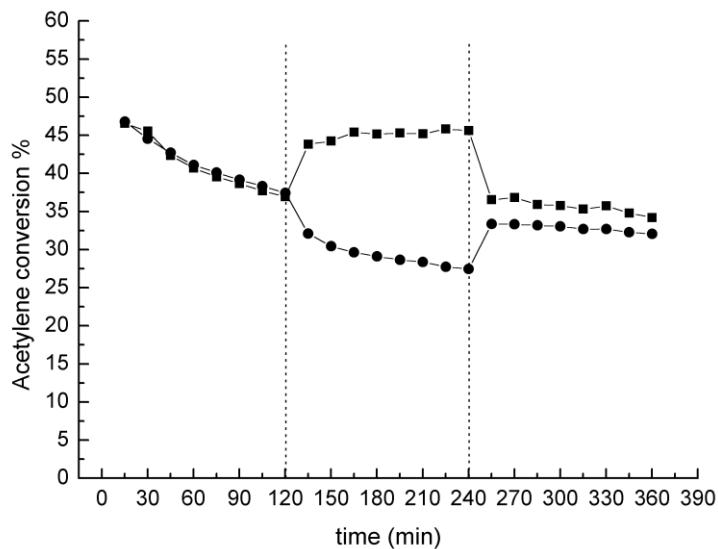
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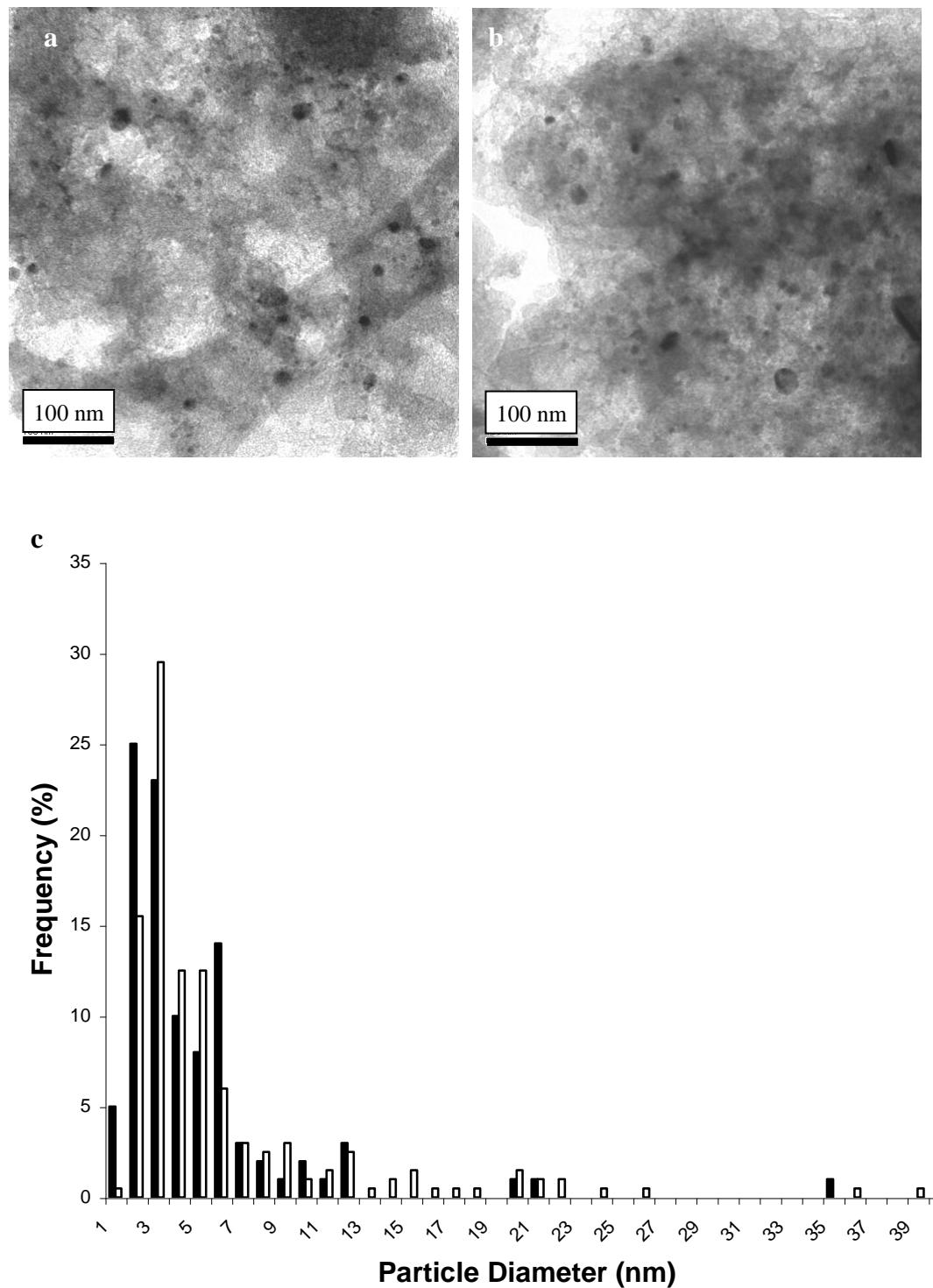
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**Fig. 4:** hydrochlorination reaction of acetylene with varying molar ratios of HCl, (Experiment E: ■)  $\text{C}_2\text{H}_2/\text{HCl}$  (2h) 1:1 →  $\text{C}_2\text{H}_2/\text{HCl}$  (2h) 1:1.5 →  $\text{C}_2\text{H}_2/\text{HCl}$  (2h) 1:1 and (Experiment F: ●)  $\text{C}_2\text{H}_2/\text{HCl}$  (2h) 1:1 →  $\text{C}_2\text{H}_2/\text{HCl}$  (2h) 1:0.5 →  $\text{C}_2\text{H}_2/\text{HCl}$  (2h) 1:1



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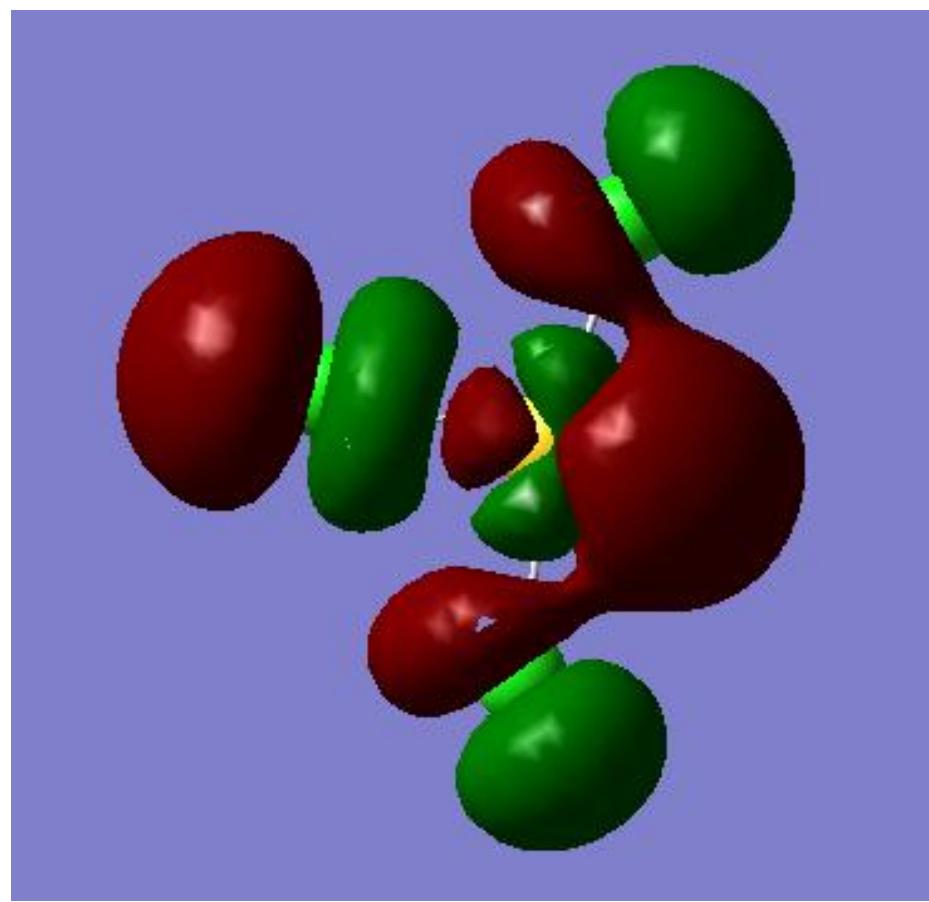


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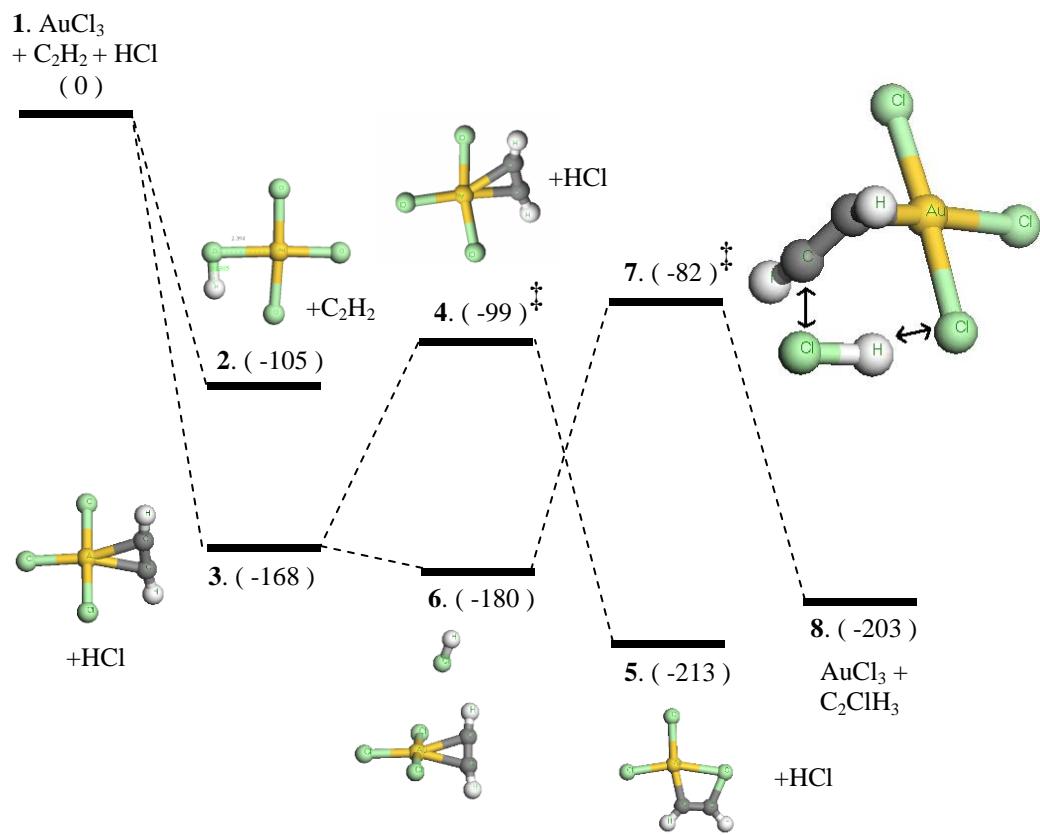


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