Direct Evidence for the Origin of Bis-Gold Intermediates: Probing Gold Catalysis with Mass Spectrometry

Mei Lu  
*Ohio University*

Yijin Su  
*University of South Florida*

Pengyi Zhao  
*Ohio University*

Xiaohan Ye  
*University of South Florida, xye1@usf.edu*

Yi Cai  
*Ohio University*

*See next page for additional authors*

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Direct Evidence for the Origin of Bis-Gold Intermediates: Probing Gold Catalysis with Mass Spectrometry

Mei Lu, Dr. Yijin Su, Pengyi Zhao, Dr. Xiaohan Ye, Yi Cai, Prof. Xiaodong Shi, Prof. Eric Masson, Fengyao Li, J. Larry Campbell, and Prof. Hao Chen

Center for Intelligent Chemical Instrumentation, Department of Chemistry and Biochemistry & Edison Institute of Biology, Ohio University, Athens, OH 45701 (USA)
Department of Chemistry, University of South Florida, Tampa, FL 33620 (USA)
AB Sciex, 71 Four Valley Drive, Concord, Ontario, L4K 4V8 (Canada)

Abstract
Gold-catalyzed alkyne hydration was studied by using in situ reacting mass spectrometry (MS) technology. By monitoring the reaction process in solution under different conditions (regular and very diluted catalyst concentrations, different pH values) and examining the reaction occurrence in the early reaction stage (1–2 ms after mixing) with MS, we collected a series of experimental evidence to support that the bis-gold complex is a potential key reaction intermediate. Furthermore, both experimental and computational studies confirmed that the \( \sigma, \pi \)-bis-gold complexes are not active intermediates toward nucleophilic addition. Instead, formation of geminally diaurated complex C is crucial for this catalytic process.

Keywords
desorption electrospray ionization mass spectrometry (DESI-MS); gold catalysis; hydration; mass spectrometry

Introduction
The rapid growth of homogeneous gold catalysis during the last decade puts gold complexes under the spotlight in synthetic and organometallic chemistry research.\(^1\) Although the superior reactivity of gold cations toward unsaturated C-C bonds has been clearly demonstrated during the last decade, studying gold reaction mechanism remains a challenging task owing to A) involvement of multiple gold-containing intermediates in the catalytic cycle, and B) experimental difficulty in isolating and monitoring these highly reactive intermediates during reactions.\(^2\)

Compared with earlier discovered/proposed gold-containing intermediates, such as gold-alkyne \( \pi \)-complexes\(^3\) and vinyl gold derivatives,\(^4\) the dinuclear gold complexes (bis-gold)
have received sustained attention only recently. Based on NMR analysis, Gagné and co-workers identified the existence of dinuclear gold intermediates in intramolecular hydroarylation reactions.\(^5\) The viability of these geminally diaurated intermediates was reinforced by recent studies from Ferstner’s and Hashmi’s groups (Figure 1A).\(^6\) These studies revealed that gem-diaurated intermediates were generated by nucleophilic attack on gold π-allene and alkyne complexes, followed by addition of [L-Au]\(^+\) to the corresponding vinyl gold. Another possible origin of geminally diaurated intermediates could be initiated by C–H activation of a terminal acetylene, reported by Russell, Widenhoefer, Finzed, Corma, Echavarren, etc. (Figure 1B).\(^7\) Although gold acetylides can be readily prepared from terminal alkyne under various conditions,\(^8\) one critical question is whether the gold-catalyzed terminal alkyne activation takes place through σ,π-dual activation instead of simple π-activation.\(^9\)

Mass spectrometry (MS) is a valuable tool in elucidating reaction mechanisms owing to its high detection sensitivity and specificity.\(^10\) With the ability to isolate specific gold cations, MS provides the opportunity to evaluate the reactivity of certain gold-containing cations, which will greatly help the elucidation of the reaction mechanism.\(^11\) The reaction we selected for this investigation was the hydration of propargyl acetate alkyne 1 owing to the existence of both a terminal alkyne (formation of s,p-diaurated gold acetylides) and the intramolecular nucleoside (acetate).\(^12\) Based on this reaction, herein, we report the application of reactive MS and NMR spectroscopy in obtaining direct evidence of the involvement of bis-gold complex C (with the retention of alkyne terminal C–H) in the catalytic cycle and the significantly lower reactivity of σ,π-diaurated gold acetylides over gold-alkyne π-complex, which offers intriguing mechanistic insights for better understanding of gold catalysis (Figure 1C).

Results and Discussion

We first evaluated the solution of the Gagosz catalyst\(^13\) (PPh\(_3\)AuNTf\(_2\)) in acetonitrile (MeCN) by using electrospray ionization mass spectrometry (ESI-MS) (Figure 2A). Some key gold-containing ions are identified, including [LAu]\(^+\) (m/z=459) (L=Ph\(_3\)P) and [LAu+MeCN]\(^+\) (m/z=500). Notably, bis-gold ion [L\(_2\)Au\(_2\)OH]\(^+\) (m/z=935) and triple gold ion [L\(_3\)Au\(_3\)O]\(^+\) (m/z= 1393) were also observed with high intensity. To explore gold cation reactivity, we studied the gold-catalyzed hydration of propargyl acetate alkyne 1 (\(M_W=174\) Da) by monitoring the reaction process with both NMR spectroscopy and MS. By using ESI-MS (Figure 2B–D), the reaction mixture of 1 and Gagosz catalyst (PPh\(_3\)AuNTf\(_2\)) was studied over time. After 5 min of the reaction, the mono-gold L-Au\(^+\) cations with m/z=459 ([LAu]\(^+\)) and 500 ([LAu+MeCN]\(^+\)) decreased significantly, likely owing to their involvement in the reaction. Interestingly, only a small amount of mono-gold ion [LAu+1+ H\(_2\)O]\(^+\) (m/z=651, theoretical mass=651.13635, measured mass=651.13622, mass error=0.20 ppm) was detected. One interesting observation was the formation of [L\(_2\)Au\(_2\) +1+ H\(_2\)O–H]\(^+\) (m/z=1109, theoretical mass=1109.18623, measured mass=1109.18614, mass error=0.08 ppm) ion as the key intermediate throughout the reaction with significantly higher intensity than the mono-gold species (m/z=651). This complex ion [L\(_2\)Au\(_2\) +1+H\(_2\)O–H]\(^+\) (m/z=1109) contained two gold cations, propargyl...
acetate alkyne 1, and water. The loss of one proton in the notation was to keep the complex at the +1 charge state as it has two cationic golds. Considering that both ions (m/z=651 and 1109) contain all the reactants (catalyst, alkyne, and water nucleophile), it is highly likely that they might be reactive intermediates in the catalytic cycle. It is interesting to note that the intensity of m/z=1109 decreased over time, and almost disappeared after 30 min. Analogously, the corresponding NMR experiments indicated that the reaction was nearly completed after 30 min (Figure 1S in the Supporting Information). By contrast, the m/z=651 intensity increased at 15 min and did not decrease much at 30 min, indicating that m/z=1109 rather than m/z=651 is the crucial reaction intermediate. Upon reaction completion (30 min, Figure 2D), the intensities of simple gold adduct ions such as m/z=459 and 500 were recovered, which was consistent with the proposed involvement of [L-Au]^+ in the catalytic cycle.

Besides monitoring the catalyst ions, the product [P+H]^+ (P=product) at m/z=193 was also monitored over time; results were consistent with NMR experiments (increase of signal intensity over time). Subsequent MS/MS analysis of the product ion of m/z=193 reveals a fragment ion at m/z=133 by loss of HOAc, which is characteristic and readily occurring neutral loss for this product ion (the fragment ion m/z=133 was also seen in Figure 2B–D owing to in-source ion fragmentation); this product ion was verified by performing MS/MS analysis on an authentic hydrated propargyl acetate 2 (synthesized and purified).

To further demonstrate whether the bis-gold ion [L2Au2 + 1+H2O−H]^+ is the key reactive intermediate, we conducted the reaction in a very short timescale (1–2 ms) by using online reactive desorption electrospray ionization mass spectrometry (DESI-MS). To acquire the MS data, a home-made liquid sample DESI apparatus was used. Briefly, one reagent (e.g., Au catalyst) was infused from the DESI spray probe, whereas the other reactant (e.g., propargyl acetate alkyne 1) was infused from another fused silica capillary. As liquid emerged from the capillary tip, charged microdroplets from the DESI spray mixed with the capillary liquid, allowing reactions to occur at the tip. This workflow has the advantage to monitor reaction products (and their kinetics) at very short mixing times. Figure 3 shows the online reactive DESI spectra of spraying 100 mm Au with a) MeCN and b) 20 mm propargyl acetate alkyne 1 in MeCN. As indicated in Figure 3B (inset), even when the gold catalyst and neutral propargyl acetate alkyne 1 were reacted during the DESI ionization process for only a brief interaction time (ca. 1– 2 ms) before being analyzed by MS, the bis-gold complex (m/z=1109) could also be detected. In addition to the bis-gold intermediate, the protonated product ion of m/z=193, was also detected (compared with a MeCN solvent blank), suggesting that the hydrolysis reaction takes place rapidly. The observation of m/z=1109 in the reactive DESI experiment also indicates that the formation of this species is very fast. In addition, when another gold catalyst with a slightly different ligand, (pCH3Ph)3PAuNTf2 (L*==(pCH3Ph)3P), was doped in the DESI spray, three bis-gold intermediate ions, ion [L2Au2 + 1+H2O−H]^+ (m/z=1109), [LL*Au2 + 1+H2O−H]^+ (m/z=1151), and [L*2Au2 + 1+H2O−H]^+ (m/z=1193) were observed, as expected (Figure 8S in the Supporting Information).

Recently, there has been debate on whether or not the bisgold intermediate is inside or outside the catalytic cycle. Maier and Zhdanko’s study suggested gem-diaurated species
cannot directly undergo protodeauration, which is not directly involved in the catalytic cycle, whereas Roithova and co-worker’s results showed the alkyne could assist the dissociation of diaurated species, which was involved in the reaction cycle.\textsuperscript{[16,17]} Houk, Vilhelmsen, and Hashmi computed that in some reactions the gem-diaurated species is in the catalytic cycle.\textsuperscript{[6g,h]} Inspired by the previous work, we hypothesize that the bis-gold intermediate would be more difficult to form if the gold catalyst concentration is reduced.\textsuperscript{[18]} In our case, we further tested this dilution effect. In our experiment, the concentration of gold catalyst Ph$_3$PAuNTf$_2$ was lowered from 4 mm to 40 μm (0.02% load) and the concentration of propargyl acetate alkyne 1 (200 mm) was kept the same. To our surprise, the ion of m/z=1109 still could be seen in high abundance (Figure 6S in the Supporting Information), in addition to the product ion detected at m/z=193. This result indicates that the bis-gold intermediate ion of m/z 1109 is not a gas-phase artifact generated from the ionization process.

To identify the exact structure of ion [L$_2$Au$_2$ + I+H$_2$O−H]$^+$ (m/z=1109), isotope-labeling experiments were first carried out. As shown in Figure 2Sa (in the Supporting Information), when using H$_2^{18}$O, an ion of m/z=1111 [L$_2$Au$_2$ + I+H$_2$^{18}O−H]$^+$ was detected (2 Da heavier than m/z=1109), which confirmed the incorporation of water. Moreover, a product ion of m/z= 195 was detected (Figure 2Sa in the Supporting Information), analogous to the product ion of m/z=193 for non-labeled H$_2$O. The MS/MS fragment of m/z=195 gave rise to a fragment ion of m/z=133, thereby indicating the loss of H$_{18}$OAc and suggesting that O scrambling occurred. This result confirmed the formation of intermediate A as the initiation step, just as proposed in previous reports (Scheme 1A).\textsuperscript{[19]}

Switching the nucleophile to D$_2$O (Figure 2Sb in the Supporting Information) gave an ion of m/z=1110 [L$_2$Au$_2$ + I+ D$_2$O−D]$^+$, implying hydrogen loss (deuterium loss for this D$_2$O reaction; Scheme 1B). To verify this result, methanol was used as the nucleophile. As expected, the corresponding methanol adduct ion [L$_2$Au$_2$ + I+CH$_3$OH−H]$^+$ (m/z=1123, Figure 4Sa in the Supporting Information) was detected with high intensity soon after mixing. When d$_4$-labeled methanol was used, formation of [L$_2$Au$_2$ + I+CD$_3$OD−D]$^+$ (m/ z=1126) with a mass shift of +3 Da strongly suggested that the lost proton was from the nucleophile instead of alkyne. Finally, reaction of C–D bond labeled terminal alkyne and H$_2$O gave an ion of m/z= 1110, as [L$_2$Au$_2$ +(1D)+H$_2$O−H]$^+$, thereby confirming the retention of the C–D bond in this key intermediate ion (Figure 2Sc in the Supporting Information; also see m/z=1110 fragmentation in Figure 3Sb). Therefore, structure D in Scheme 1D is ruled out based on these isotope-labeling experiments.

The MS/MS fragmentation of ion m/z=1109 was also conducted (see details in Figure 3Sa in the Supporting Information). According to the spectrum, [L$_2$Au$_2$ + I+H$_2$O−H]$^+$ (m/z= 1109) mainly dissociates into m/z=1021 by consecutive losses of HOAc and CO, which confirmed the formation of geminally diaurated complexes. The proposed fragmentation pathway is shown in Scheme 3Sa (in the Supporting Information).

Notably, besides the formation of bis-gold [L$_2$Au$_2$ + I+ H$_2$O−H]$^+$ (m/z=1109), another important observation is the formation of dehydrated bis-gold ion (m/z=1091, Figure 2B).
The complex E was proposed initially. However, this structure was quickly ruled out based on the designated ion/molecule reaction experiments.

As illustrated in Figure 4A, by using our home-made modified Qtrap MS instrument, the gold-containing ion \( m/z=1091 \) was isolated and transferred into another chamber to react with water (see spectra in the Supporting Information, Scheme 2S). This ion/molecule reaction method was very powerful as it provided the direct measurement of the reactivity of specific gold cations toward certain substrates. Interestingly, no bis-gold ion of \( m/z=1109 \) was observed at all, which suggested that the proposed structure E (Figure 4B) was not the structure of ion \( m/z=1091 \). In fact, density functional theory (DFT) calculations with the dispersion-corrected TPSS-D3(BJ) functional (well suited for 5d transition metals),\(^{[20]}\) and triple-\( \Sigma \) basis sets def2-TZVP showed that structure E could not be optimized into a valid intermediate, but relaxed into adduct F (see details in the Supporting Information).

According to the computational result, the C/C bond length of ion F was 1.25 Å, longer than a typical C/C bond (1.20 a). This result greatly supported the observed low reactivity of ion \( m/z=1091 \), the \( \sigma,\pi \)-diaurated complex. It is very important to notice here that the formation of gold-acetylide (terminal alkyne–Au bond) is a rapid process. It has been assumed that the formation of \( \sigma,\pi \)-diaurated complexes occurs in many gold-promoted terminal alkyne activation reactions. However, this DFT computational result provides clear evidence that \( \sigma,\pi \)-diaurated complexes were not the active intermediate at least in this terminal propargyl ester case. Consequently, bis-gold C (Scheme 1D) was the only plausible structure of ion \( m/z=1109 \) that matched all the experimental data.

With the structure of the \( m/z=1109 \) ion confirmed, the origin of complex C became extremely important to uncover the actual reaction mechanism. One possible route to complex C was the alkyne activation by dinuclear gold \([\text{L}_2\text{Au}_2\text{OH}]^+ \) (\( m/z=935 \)). However, this pathway is unlikely, as there was no consumption of \([\text{L}_2\text{Au}_2\text{OH}]^+ \) (\( m/z=935 \)) during the short interaction time, whereas \([\text{L}_2\text{Au}_2 +\text{I}+\text{H}_2\text{O}+\text{H}^+] \) (\( m/z=1109 \)) was detected as shown in Figure 3. To confirm this, we conducted another ion/molecule reaction by using the \([\text{L}_2\text{Au}_2\text{OH}]^+ \) ion (\( m/z=935 \)) to react with volatile propargyl acetate 3 (AcOCH=CH, Figure 5S in the Supporting Information). As expected, no alkyne addition \([\text{L}_2\text{Au}_2 +\text{I}+\text{H}_2\text{O}+\text{H}^+] \) (\( m/z=1033 \), similar to \( m/z=1109 \)) was observed (Figure 4A). Instead, \([\text{L}_2\text{Au}_2 +\text{I}+\text{H}^+] \) (\( F^+ \) \( m/z=1015 \), similar to F \( m/z=1091 \)) was detected as the dominant product, which confirmed that \([\text{L}_2\text{Au}_2\text{OH}]^+ \) (\( m/z=935 \)) was not responsible for the formation of the \( m/z=1109 \) species.

Nolan and co-workers have reported the enhanced reactivity of L-Au-OH as the improved nucleophile (compared with H\(_2\)O) toward alkyne hydration. Thus, another plausible mechanism is the L-Au-OH addition toward mono-gold activated alkyne A (formation of structure B, Scheme 1D). Owing to the poor volatility of both reaction partners (complexes A and L-Au-OH), direct ion/molecule reactions cannot be used here to explore this step.

However, we hypothesize that the reaction may not occur if acid is present as it would reduce or eliminate the species of L-Au-OH. In our experiment, when formic acid was added to the reaction mixture containing 4 mm Ph\(_3\)PAuNTf\(_2\) and 200 mm propargyl acetate alkyne I to adjust the solution pH to 4.5, the reaction occurred and ions of \( m/z=193 \) and 1109 were...
all observed (Figure 7S in the Supporting Information), thereby excluding the possibility of involvement of L-Au-OH species in the reaction. Such an acid effect was also noted in the recent report by Roithova et al.\textsuperscript{[17]}

Based on these phenomena and results, we proposed that mono-gold intermediate \textbf{A} undergoes addition with H\textsubscript{2}O first, which is then followed with proton exchange with another LAu\textsuperscript{+} ion to form the bis-gold intermediate. The question was how is bis-gold complex \textbf{B} converted into the detected germinal bis-gold \textbf{C}? To understand this step, we conducted DFT computational studies. To our surprise (at least not obvious), the DFT computational studies confirmed that bis-gold \textbf{C} was much more stable than ion \textbf{B} (\(\Delta G = -18.7 \text{ kcalmol}^{-1}\)). Moreover, the isomerization barrier between ion \textbf{B} to the observed key complex \textbf{C} (\(m/z=1109\)) is very low (\(\Delta G^\ddagger = 4.1 \text{ kcalmol}^{-1}\)) with the reaction proceeding via a six-membered ring transition state (Figure 5).

Thus, we summarize all the experimental results:

1. Results from reaction MS, NMR spectroscopy, and online reactive DESI-MS confirmed the formation of \([\text{L}_2\text{Au}_2 + 1 + \text{H}_2\text{O} - \text{H}]^+\) (\(m/z=1109\)) as one key intermediate during alkyne 1 hydration;
2. MS/MS, isotope-labeling, and ion/molecule reaction experiments confirmed the structure \textbf{C} as the composition of this ion;
3. Based on all these studies, the likely reaction mechanism is proposed in Figure 5.

Notably, the fact that geminally diaurated complex \textbf{C} was determined during the reaction process strongly suggested that the rate-determining step of this reaction was the protodeauration of complex \textbf{C}, which could not be explored by this MS method. However, with the direct evidence for the formation of bis-gold intermediate \textbf{C} in the reaction process and observed poor reactivity of \(\sigma,\pi\)-diaurated complex \textbf{F} provided some really interesting new mechanistic insight toward gold-catalyzed terminal alkyne activation.

Conclusion

In short, by using the combination of reactive MS, NMR spectroscopy, and DFT calculations, we unveiled the reaction mechanism of the hydration of terminal propargyl ester 1. Several unexpected but very interesting mechanistic insights were disclosed, including the high stability of the \(\sigma,\pi\)-diaurated complex (\textbf{F}), and the formation of C-H containing bis-gold \textbf{C} as a potential key intermediate in reaction process. These mechanistic insights are intriguing and will certainly benefit the understating of the rapidly growing area of gold catalysis research.

Experimental Section

General methods and materials

Methanol (MeOH), acetonitrile (MeCN), and isotope-labeled water (H\textsubscript{2}\textsuperscript{18}O and D\textsubscript{2}O) were purchased from Sigma–Aldrich (St. Louis, MO). Methanol-d\textsubscript{4} was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). The gold catalyst and propargyl
acetate alkyne 1 were synthesized based on published methods.\cite{13,21} The deionized water used for sample preparation was obtained by using a Nanopure Diamond Barnstead purification system (Barnstead International, Dubuque, IA).

**Electrospray ionization mass spectrometry (ESI-MS)**

ESI-MS spectra for monitoring reactions with time were collected by using either a Thermo Fischer Orbitrap Q-Exactive Plus or a Waters Xevo QTof mass spectrometer (Milford, MA, USA) in the positive ion mode. A solution containing 4 mm Ph₃PAuNTf₂, 200 mm propargyl acetate alkyne 1, and 600 mm H₂O was infused directly into the ESI source for ionization, immediately after mixing the reactants. The injection flow rate was 2 μLmin⁻¹ and the applied potential for ionization was 5 kV. High-resolution MS data was obtained by using the Orbitrap mass spectrometer and collision-induced dissociation (CID) was carried out by using nitrogen as the collision gas.

**Reactive desorption electrospray ionization mass spectrometry (DESI-MS) measurements**

A home-made reactive DESI-MS apparatus was used (Scheme 1S in the Supporting Information) and this has been described previously in detail. Briefly, one reagent (e.g., Au catalyst) was sprayed via the DESI spray probe applied with a high voltage of 5 kV and high pressure N₂ nebulization gas (≈170 psi) to generate charged microdroplets. The other reagent (e.g., propargyl acetate alkyne 1) was infused from a piece of fused silica sample capillary (i.d. 0.1 mm) and underwent interactions with the charged microdroplets generated from the DESI spray for simultaneous reaction and ionization. The resulting ions can be detected by the nearby mass spectrometer. The reaction time in this reactive DESI is short (ca. 1–2 ms) because of the momentary interaction of the charged microdroplets containing one reactant from the DESI spray and the solution of the other reagent introduced from the sample capillary,\cite{15g} thus allowing detection of transient reaction intermediates.\cite{10g} The capillary outlet was placed about 1 mm downstream from the DESI spray probe tip and held, both being directly in line with the sprayer tip and the mass spectrometer’s inlet. The injection flow rates for both the DESI spray and capillary-infused sample were 5 μLmin⁻¹.

**Ion/molecule reactions**

Ion/molecule reaction experiments were performed with a triple quadrupole linear ion-trap mass spectrometer (2000 QTrap; AB Sciex, Canada). A scheme of the instrument set up is shown in Scheme 2S (in the Supporting Information). The gold catalyst sample solutions were introduced to the ESI ion source to generate reactant ions. Reactant ions of interest were then mass-selected in Q1 and trapped in q2. Reagent gases were introduced through a gas line into q2, where they reacted with the selected reactant ion. After reaction, the product ions were transferred from q2 into Q3, where they were analyzed by mass-selective axial ejection in Q3.

**Supplementary Material**

Refer to Web version on PubMed Central for supplementary material.
Acknowledgments

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References


[14]. The highest intensity peak could even be a resting state. Peak m/z= 1109 is dominant but m/z=651 is quite small. When we repeated the experiment as shown in Figure 2, we noticed that the m/z=1109 intensity change with time is consistent with the product formation rate. However, the m/z=651 intensity increased at 15 min and did not decrease much at 30 min (NMR results showed that the reaction nearly was completed at 30 min), providing an evidence that m/z=1109 rather than m/z=651 is the key reaction intermediate.


[18]. Unlike the digold species in Figure 1A, which are product-derived and already have been shown to be part of the catalytic cycle, the digold species we detected in this system is starting material-derived and more investigation is necessary to identify whether it will be involved in the catalytic cycle.


Figure 1.
Geminally diaurated complexes.

(A) Geminally diaurated vinyl complexes

(B) Reported α,ω-diaurated complexes from terminal alkynes

(C) This work: Formation of geminal bis-gold revealed by reactive-MS

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Figure 2.
ESI-MS spectra of A) 4 mm Ph₃PAuNTf₂ with 600 mm H₂O in MeCN and B–D) reaction mixture of 4 mm Ph₃PAuNTf₂, 200 mm propargyl acetate alkyne 1, and 600 mm H₂O in MeCN at different reaction times (as indicated).
Figure 3.
Online reactive DESI-MS spectra upon spraying a Ph₃PAuNTf₂ solution mixed with A) MeCN and B) 20 mm propargyl acetate alkyne 1 in MeCN. The inset shows the zoomed-in product and intermediate ion.
Figure 4.
Summary of selected ion/molecule reactions with the modified Qtrap MS set-up; optimized geometry of intermediate F.
Figure 5. Proposed mechanism and DFT-optimized structure of the transition state leading to bis-gold C.
Scheme 1.
Structural information from isotope-labeling experiments.