JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by United Arab Emirates University | Libraries Deanship

Article

#-Hydride Elimination at Low-Coordinate Gold(III) Centers

Feriel Rekhroukh, Laura Estévez, Sonia Mallet-Ladeira, Karinne
Miqueu, Abderrahmane Amgoune, and Didier Bourissou

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.6b07035 • Publication Date (Web): 17 Aug 2016

Downloaded from http://pubs.acs.org on August 17, 2016

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

β-Hydride Elimination at Low-Coordinate Gold(III) Centers

Feriel Rekhroukh,[a] *Laura Estevez,*[b,c] *Sonia Mallet–Ladeira,*[d] *Karinne Miqueu,*[b]* *Abderrahmane Amgoune,*[a]* *Didier Bourissou*[a]*

[a]Université de Toulouse, UPS, Laboratoire Hétérochimie Fondamentale Appliquée, 118 route de Narbonne, F-31062 Toulouse, France;
CNRS, LHFA UMR 5069, F-31062 Toulouse, France;

[b]Université de Pau et des Pays de l'Adour, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux. Hélioparc, 2 Avenue du Président Angot, 64053 Pau cedex 09, France.
CNRS, IPREM UMR 5254, F-64053 Pau, France;

[c]Departamento de Química Física, Facultade de Química, Universidade de Vigo. Lagoas-Marcosende s/n, 36310 Vigo, Galicia, Spain

[d]Institut de Chimie de Toulouse (FR 2599), 118 Route de Narbonne, 31062 Toulouse Cedex 09, France

E–mails karinne.miqueu@univ-pau.fr, amgoune@chimie.ups-tlse.fr, dbouriss@chimie.ups–tlse.fr

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

ABSTRACT

This article reports the first comprehensive study of β-hydride elimination at gold(III). The stability/fate of gold(III) alkyl species have been investigated experimentally and computationally. A series of well–defined cationic cyclometallated gold(III) alkyl complexes [(P,C)gold(III)(R)][NTf_2] [(P,C) = 8-diisopropylphosphino-naphthyl; R = Me, *n*Pr, *n*Bu] have been synthesized and spectroscopically characterized. While the cationic gold(III) methyl derivative **3c** is stable for days at room temperature, the gold(III) *n*-propyl and *n*-butyl complexes **3a,b** readily undergo β-hydride elimination at low temperature to generate propylene and 2-butenes, respectively. The formation of internal olefins from the gold(III) *n*-butyl complex **3b** shows that olefin isomerization takes place after β-hydride elimination. Computational studies indicate that this isomerization proceeds through a *chain walking* mechanism involving a highly reactive gold(III) hydride intermediate and a sequence of β-hydride elimination / re-insertion into the Au–H bond. The reaction of the cationic gold(III) methyl complex **3c** with ethylene was also explored. According to ^1H and ^{13}C NMR spectroscopy, a mixture of propylene, 1-butene and 2-butenes is formed. DFT calculations provide detailed mechanistic insights and support the occurrence of migratory insertion of ethylene, β-hydride elimination and olefin exchange at gold(III).

INTRODUCTION

β-Hydride elimination is a key organometallic transformation in which a metal alkyl complex is converted into a metal hydride olefin species (Chart 1).[1] It is the microscopic reverse of olefin insertion into a M–H bond. β-Hydride elimination plays a major role on the stability/reactivity of metal alkyl complexes. It is also one of the preparative routes to metal hydride species. In catalytic cycles, β-hydride elimination may be a key step or a side reaction. For example, products of Mizoroki-Heck coupling or Shell higher olefin process are released *via* β-hydride elimination, while C–C coupling of alkyl fragments and linear polymerization of ethylene often suffer from the occurrence of undesirable β-hydride elimination (resulting in lower yields and/or side products). It is therefore critical to understand precisely the parameters affecting the reactivity and selectivity of transition metals towards β-hydride elimination if highly efficient and selective transformations involving alkyl complexes are to be developed.

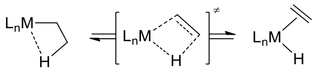


Chart 1. Schematic representation of β-hydride elimination.

In contrast with the other transition metals, very little is known about β-hydride eliminations at gold. The transformation of gold alkyl complexes in gold hydride olefin species is considered to be highly disfavored, and the reluctance to undergo β-hydride elimination is regularly pointed out as a distinctive feature of gold in catalysis.[2,3] However, the reactivity of alkyl complexes has been much less investigated with gold than with the other transition metals. To the best of our knowledge, the only study devoted to β-hydride elimination at gold is a joint experimental/computational investigation carried out by Köppel and Hashmi on an NHC gold(I) ethyl complex (NHC = IPr).[4] DFT calculations predicted a prohibitively high barrier ($\Delta G^{\neq}$: 49.7 kcal·mol^{-1}) for β-hydride elimination, with formation of a high-energy 3-coordinate gold(I) hydride ethylene species (ΔG : 33.0 kcal·mol^{-1}). Consistently, the (IPr)Au(Et) complex was found experimentally to decompose only at ca. 180 °C, and it showed no tendency to eliminate ethylene.[5] The huge activation barrier computed for the β-hydride elimination was attributed to the filled 5d shell of gold(I) complexes, which makes the interaction of the β C–H bonds with gold unfavorable. Nevertheless, as suggested by the authors, gold in higher oxidation states may behave differently and gold(III) alkyl complexes are certainly worthwhile candidates.

Over the last 15 years, homogenous gold catalysis has developed tremendously.[6] The field has been largely dominated by gold(I) catalysis, but recent contributions have highlighted the catalytic interest and potential of gold(III) complexes.[7,8] These landmark achievements have sparked renewed interest in gold(III) complexes and our knowledge of gold(III) organometallic chemistry has significantly progressed over the last few years.[9,10] The reactivity of gold(III) species towards reductive elimination,[11] transmetallation[12] and migratory insertion[13,14] reactions has been documented and thoroughly investigated. But comparatively, β-hydride elimination reactions at gold(III) remain very seldom. In a seminal study, Kochi *et al.* reported in the 1970's a spontaneous *tert*-butyl → *iso*-butyl isomerization at gold(III) [upon attempts to purify (*t*-Bu)AuMe$_2$(PPh$_3$)] that was proposed to proceed *via* β-hydride elimination, but no olefin, free or coordinated, could be detected.[15] More recently, Toste investigated C$_{sp3}$–F bond-forming reductive elimination from NHC gold(III) alkyl difluoride complexes and observed the formation of alkenes as side-products, suggesting that β-hydride elimination may occur and compete with C–F reductive elimination.[16]

The studies of Kochi and Toste suggest that β-hydride elimination reactions can take place with gold(III) species and thus may occur in catalytic transformations involving gold(III) alkyl intermediates. Given the increasing role and huge potential of gold(III) catalysis, it is highly desirable to gain better knowledge on this elementary reaction and to determine the factors controlling its occurrence. So far, this has been largely hampered by the lack of suitable gold(III) alkyl complexes. In the course of our studies on oxidative addition to gold,[17] we recently gained access to well–defined cyclometallated (P,C) gold(III) complexes which are stable towards reductive elimination. This robustness allowed us to evidence hitherto unknown migratory insertion of olefins at gold[13a,b] and also to characterize the first agostic complex with gold.[18] As a step forward, we envisioned to take advantage of the stability of the cyclometallated (P,C) gold(III) complexes to thoroughly investigate the stability/reactivity of gold(III) alkyl species towards β-hydride elimination (Chart 2). Herein we report well–defined cationic gold(III) alkyl complexes that readily undergo β-hydride elimination at low temperature. According to detailed mechanistic studies combining multinuclear NMR experiments and DFT calculations, β-hydride elimination was shown to be a very facile process from cationic gold(III) alkyl species, and the generated gold(III) hydride species was found to readily insert olefins. Other key processes commonly observed with Ni/Pd/Pt alkyl complexes, namely olefin isomerization and olefin exchange have also been evidenced with gold and are discussed hereafter.

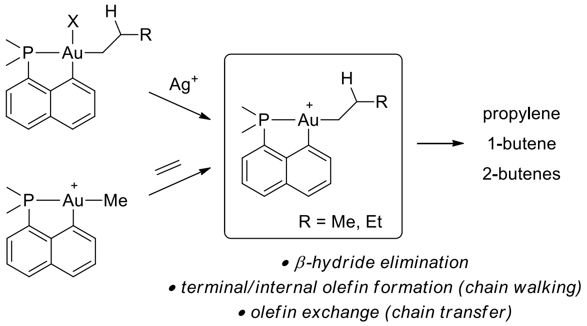


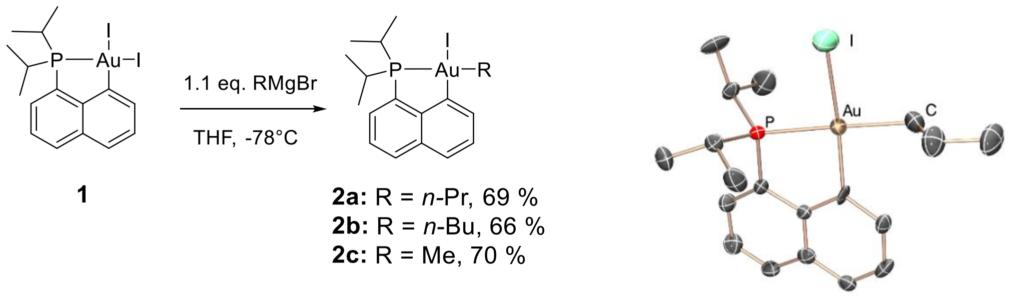
Chart 2. Formation of cationic gold(III) alkyl complexes and β-hydride elimination.

COMPUTATIONAL METHODS

All calculations were performed using the Gaussian 09 package[19] and the B3PW91 hybrid functional.[20] The gold atom was described with the relativistic electron core potential SDD and associated basis,[21] augmented by a set of f-orbital polarization functions.[22] 6-31G** basis sets were employed for the other atoms. All stationary points involved were fully optimized. Optimizations were carried out taking into account the counter-anion NTf_2 and solvent effect (DCM : CH_2Cl_2) by means of the dielectric continuum standard SMD model.[23] Frequency calculations were undertaken to confirm the nature of the stationary points, yielding one imaginary frequency for transition states (TS), corresponding to the expected process, and all of them positive for *minima*. The connectivity of the transition states and their adjacent *minima* was confirmed by intrinsic reaction coordinate (IRC)[24] calculations. Natural Bond Orbital[25] calculations (NBO, 5.9 version)[26] have been carried on solvent-optimized geometries to analyze the bonding situation, in particular for the description of agostic interactions. Natural Localized Molecular Orbital (NLMO) were plotted with Molekel 4.3[27] and all the geometrical structures with Gaussview 5.0.[28]

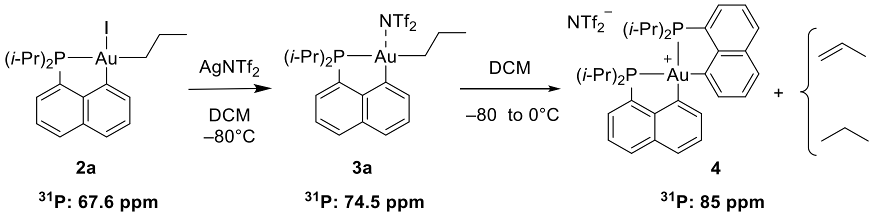
RESULTS AND DISCUSSION

Synthesis and reactivity of model cationic gold(III) alkyl complexes. Selective mono–alkylation of the cyclometallated [(P,C)gold(III)I_2] complex **1** was successfully achieved using 1.2 equiv. of Grignard reagents RMgBr (R = Me, *n*-Pr, *n*-Bu) in THF at – 78 °C (Scheme 1).[29] After workup, the targeted [(P,C)gold(III)] complexes **2a-c** were isolated as thermally stable yellow powders in good yields (~70 %). They were characterized by multinuclear NMR spectroscopy and high-resolution mass spectrometry.[30] In all cases, the carbon atom of the alkyl group bound to gold resonates as a doublet with a large J_{PC} coupling constant ($\geq$ 100 Hz), indicating that the alkyl chain sits in *trans* position to phosphorus. The structures of complexes **2a,c** were further confirmed by single crystal X-ray diffraction analyses (Scheme 1, right and Figure S32).



Scheme 1. Preparation of the mono-alkylated [(P,C)Au(III)] complex **2a-c**, molecular view of **2a** with thermal ellipsoids drawn at 50% probability level.

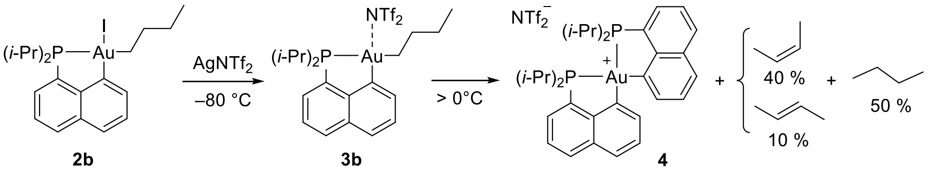
We then studied the generation and behavior of the corresponding cationic gold(III) alkyl complexes. To start with, the gold(III) *n*-propyl complex **2a** was reacted with $AgNTf_2$ in dichloromethane (Scheme 2). According to NMR monitoring, the silver salt immediately abstracts the iodide from gold at – 80 °C to form the corresponding [(P,C)Au(*n*-propyl)][NTf_2] complex **3a** (δ ^{31}P: 74.5 ppm). The structure of **3a** was ascertained by multinuclear NMR spectroscopy at low temperature (– 50 °C). The ^{1}H and ^{13}C NMR signals of the *n*-propyl chain were unequivocally assigned thanks to 2D HSQC and HMBC experiments. The large coupling constant between the α–carbon atom and phosphorus (J_{PC} = 102.7 Hz) indicates that the propyl chain remains in a *trans* position to the phosphine moiety. The spectroscopic data were carefully analyzed to detect a possible agostic interaction between the gold center and the hydrogen atoms (in α, β or γ position). However, no sign of such an interaction was found for **3a**, in contrast with what we recently observed in a related gold(III) bis(norbornyl) complex.[18] For all the CH_2 and CH_3 groups of the *n*-propyl chain, the $^{1}J_{CH}$ coupling constant is of about 130 Hz, in the normal range for C_{sp3}–H bonds.



Scheme 2. β-Hydride elimination from the cationic gold(III) *n*-propyl complex **3a**.

Upon warming the temperature to 0 °C, complex **3a** was rapidly converted into a new species **4** displaying a ^{31}P NMR signal at δ 85 ppm. Compound **4** was unambiguously assigned as a cationic bis-cyclometallated gold(III) complex based on NMR spectroscopy and mass spectrometry.[31] In addition, ^{1}H NMR spectroscopy indicates concomitant formation of propylene and propane.[32] The formation of propene from the (P,C)Au(III) *n*-propyl complex **3a** is a strong evidence for the occurrence of a β-hydride elimination process. The concomitant formation of propane is likely to result from a bimolecular pathway[33] involving **3a** and the corresponding gold(III) hydride species (generated by β-H elimination), by analogy with that recently proposed to account for the deactivation of neutral palladium(II) and nickel(II) alkyl species.[34] To further substantiate the occurrence of β-hydride elimination at gold(III), we then investigated the behavior of the gold(III) *n*-butyl complex **3b**. The formation of butene (and butane) was anticipated to facilitate quantification (the boiling points of butenes fall between -6 and +4 °C, *vs* –47 °C for propene). Furthermore, the *n*-butyl chain allows to investigate possible re–insertion and isomerization reactions, which would result in the formation of 2-butenes along with or instead of 1-butene.

As for **2a**, the gold(III) *n*-butyl complex **2b** rapidly and cleanly reacts with $AgNTf_2$ at low temperature (Scheme 3). The ensuing cationic gold(III) complex **3b** is stable up to 0 °C and shows no sign of agostic interaction by NMR. Increasing the temperature above 0 °C afforded directly the bis(cyclometallated) complex **4** as indicated by ^{31}P NMR spectroscopy. In addition, GC–MS analyses and ^{1}H/^{13}C NMR spectroscopy reveal concomitant formation of 2–butene (*cis* and *trans* isomers) and butane. The relative integration of the ^{1}H NMR signals for the organic products *vs.* the signals of the naphthyl ligand backbone indicates complete conversion of the *n*-butyl chain into 50 % of butane and 50% of 2–butene (40 % of *cis* isomer and 10 % of *trans* isomer).[30]

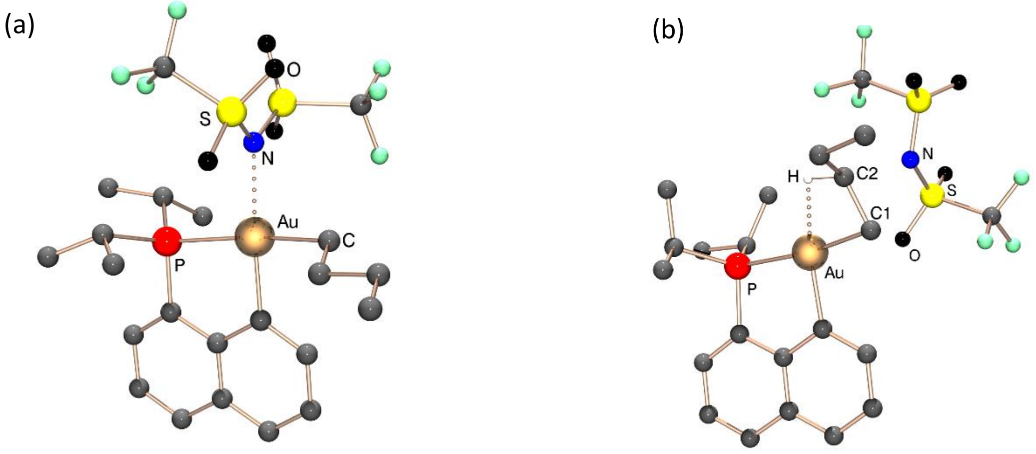


Scheme 3. β-Hydride elimination from the cationic gold(III)-butyl complex **3b** with formation of complex **4**, 2-butenes (*cis* and *trans* isomers) and butane.

The formation of the internal alkene (no trace of 1-butene is detected) from the gold(III) *n*-butyl complex **3b** shows that olefin isomerization takes place after β-hydride elimination. By analogy with that observed with Pd/Ni(II) alkyl intermediates, the isomerization process is likely to proceed through a *chain walking* mechanism involving a sequence of β-hydride elimination/re–insertion reactions.[35] This suggests that the highly reactive gold(III) hydride intermediate[36] rapidly re-inserts 1-butene before decomposition.

To probe the stability of cationic gold(III) alkyl complexes without hydrogen atom in β position, we also studied the reaction of the methyl complex **2c** with $AgNTf_2$. The resulting complex $[(P,C)gold(III)(methyl)][NTf_2]$ **3c** is much more stable than the corresponding *n*-propyl and *n*-butyl species. Compound **3c** is stable at room temperature (only traces of decomposition are observed after 2 days) and was isolated as a white powder (77% yield). The increased stability of **3c** shows that the high reactivity of **3a** and **3b** is not due to their cationic gold(III) alkyl structures, but to the occurrence and facility of β-hydride elimination processes.

Computational studies on the β-hydride elimination from complex 3b. To gain more insight into the mechanism and energetic parameters of the β-hydride elimination process, DFT calculations were carried out on the real complex *cis*–**3b** taking into account the $[NTf_2]$ counter–anion. The ground state structure corresponds to a tight ion pair with a Au•••N contact of 2.228 Å (Figure 1a).[37] The $[NTf_2]$ counter–anion can be readily displaced from the coordination sphere by the *n*–butyl chain to give structures such as *cis*–$\mathbf{3b}_\beta$ (Figure 1b), which is only slightly uphill in energy ($\Delta G = +\ 6.5\ kcal{\cdot}mol^{-1}$). Detailed examination of the optimized geometry of *cis*–$\mathbf{3b}_\beta$ indicates the presence of a short contact between gold and one of the hydrogen atoms in a β-position ($Au{\cdots}H_\beta = 1.954$ Å; $AuH_\beta C_\beta = 99.0^o$), which is located in the coordination plane of the gold center, in a *trans* position to $C_{naphthyl}$ (Figure 1, right). The corresponding C_β–H bond is significantly elongated compared to the other C–H bonds of the *n*-butyl chain (1.184 *vs.* 1.089–1.097 Å). These geometric features are in line with the presence of a β–agostic interaction. The bonding situation in *cis*–$\mathbf{3b}_\beta$ was confirmed by NBO analyses. A $\sigma_{C-H}{\rightarrow}\sigma^*_{AuCnaphthyl}$ donor-acceptor interaction was found at the second-order perturbation level with a stabilizing energy $\Delta E(2)$ of 29.1 $kcal{\cdot}mol^{-1}$ (Figure 1c). The nature of the C–H•••Au interaction is similar to that we recently reported in the (P,C) gold(III) bis(norbornyl) complex, albeit with a β instead of γ-CH bond (the NBO stabilizing energy associated with the γ(C–H)•••Au interaction was 18.6 kcal/mol).[18] Energy *minima* displaying contacts between gold and H_γ/H_δ atoms were also located on the potential energy surface, they are 3-6 kcal·mol^{-1} higher in energy than *cis*–**3b**$_\beta$ (Figure S35). The cationic gold(III) *n*-butyl complex free of agostic interaction is also 4 kcal·mol^{-1} higher in energy than *cis*–**3b**$_\beta$, indicating the stabilizing character of the β(C–H)•••Au bonding.



cis–**3b** *cis*–**3b**$_\beta$

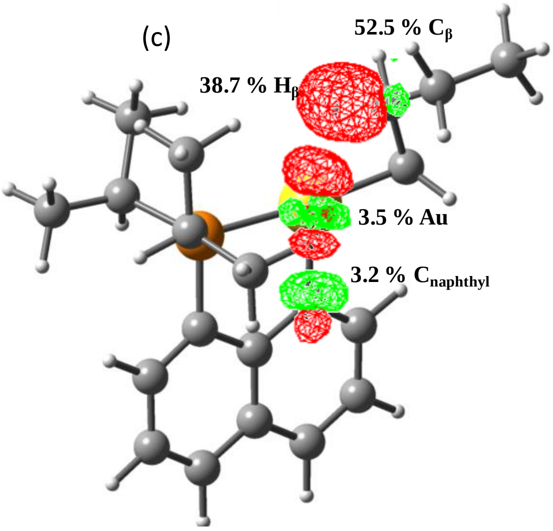


Figure 1. DFT–Optimized structures of the [(P,C)gold(III)(*n*-butyl)][NTf_2] complex *cis*–**3b** (a) and ***cis***–**3b**$_\beta$ (b) [B3PW91(SMD-CH_2Cl_2)/SDD+f(Au)/6-31G**(other atoms)]: Au•••NTf_2 (2.228 Å) *vs.* Au•••H_β (1.954 Å) contact. (c) NBO/NLMO analysis. Superposition of the donor $\sigma_{C–H\beta}$ and acceptor $\sigma^*_{C–Au}$ (chicken-wire) NBOs (cutoff: 0.07 au) associated with the β-agostic interaction in complex ***cis***–**3b**$_\beta$.

β–Hydride elimination from **3b** and formation of 2-butene (*cis* and *trans* isomers) were then studied theoretically. The agostic complex *cis*–**3b**$_\beta$ was found to readily undergo β–hydride elimination, which proceeds *via* a late transition state **TS(3b**$_\beta$–**3b**$_H$**)** (Figure 2 and Figure S33). The associated activation barrier is remarkably low ($\Delta G^{\neq}$ = 7.1 kcal·mol^{-1} from *cis*–**3b**$_\beta$) and following the intrinsic reaction coordinate, **TS(3b**$_\beta$–**3b**$_H$**)** leads to the 4–coordinate 1-butene gold(III) hydride complex *trans*–**3b**$_H$. The hydrogen atom sits *trans* to the $C_{naphthyl}$ atom and 1-butene is in-plane coordinated to gold with the ethyl group in *cis* position to the hydride at gold (Figure S36)[38] The formation of the 1-butene gold(III) hydride species from the *n*-butyl complex **3b** is endergonic (ΔG = 5.6 kcal·mol^{-1} from *cis*–**3b**$_\beta$, ΔG = 12.1 kcal·mol^{-1} from *cis*–**3b**), explaining why *trans*–**3b**$_H$ (as *cis*–**3b**$_\beta$) is not observed experimentally.

After β-hydride elimination, 1-butene can reinsert into the Au–H bond with a very low reverse barrier ($\Delta G^{\neq}$ = 1.5 kcal·mol^{-1} from *trans*–**3b**$_H$). However, the formation of internal olefins (*cis* and *trans* 2–butene) suggests that re-insertion can also occur with opposite regiochemistry to give a branched gold(III) butyl complex that would release 2–butenes after β-hydride elimination. DFT calculations indicate that this pathway is also a favorable process. Indeed, starting from *trans*–**3b**$_H$, 180° rotation of 1-butene is very easy (activation barrier of less than 5 kcal·mol^{-1}, Figure S37) [38] and gives *trans*–**3'b**$_H$ which is only 2.0 kcal·mol^{-1} uphill in energy. The low energy required for rotation around the olefin-gold axis is consistent with the low bonding energies of alkenes to gold(III), primarily due to weak Au→π* back-donation.[10d,13a] From *trans*–**3'b**$_H$, 2,1-insertion of 1–butene into the Au–H bond then proceeds spontaneously (the corresponding activation barrier is very low, $\Delta G^{\neq} = 1.9$ kcal·mol^{-1}) to give the corresponding gold(III) *sec*-butyl complex *cis*–**3’b**$_{\beta}$, which is downhill in energy ($\Delta G = -6.2$ kcal·mol^{-1} from *trans*–**3b**$_{H}$) and features a β agostic interaction. Finally, rotation of the alkyl group followed by β-hydride elimination (with an activation barrier of 8 kcal·mol^{-1}) afford 2-butene gold(III) hydride species. For sake of clarity, Figure 2 shows only the formation of the *cis* 2-butene complex, *trans*–**3”b**$_{H}$, the complete energy profile including *trans* 2-butene species is provided in the Supporting Information (Figure S33). As for 1-butene, the β-H elimination process requires only a low activation barrier, but the formation of the 2-butene gold(III) hydride complexes from **3b** is endergonic. The driving force of the overall transformation is the displacement of butene by triflimidate at gold (which is predicted to be downhill in energy by about 30 kcal·mol^{-1}, see Figure S33) and the decomposition of the ensuing gold(III) hydride species, resulting ultimately in the formation of the bis(cyclometallated) complex **4**.

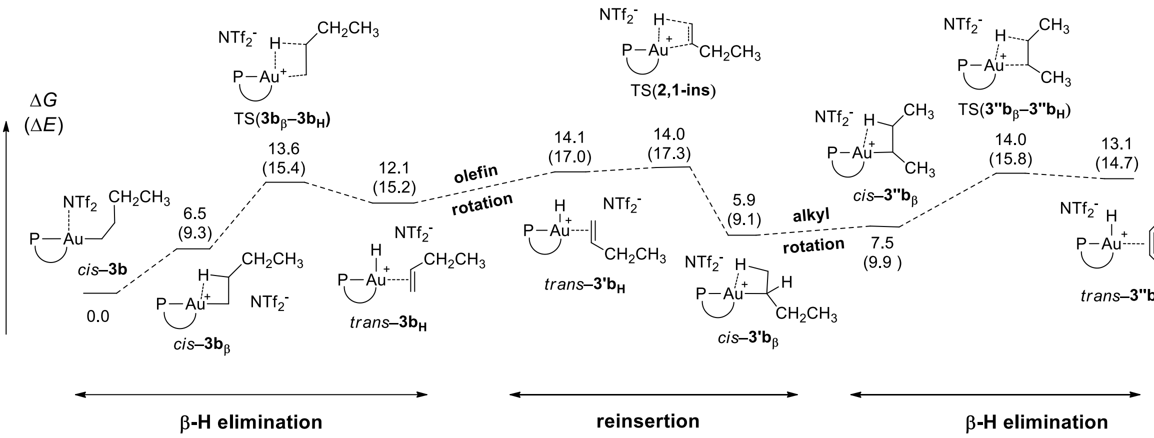
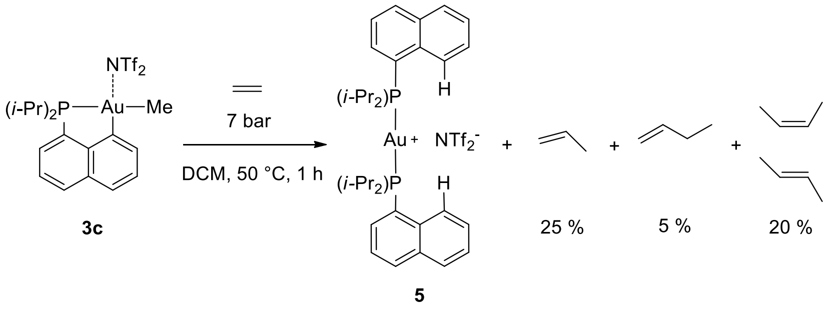


Figure 2. Energy profile (ΔG and ΔE values in kcal·mol^{-1}) computed at the B3PW91(SMD-CH_2Cl_2)/SDD+f(Au)/6-31G**(other atoms) level of theory for β–hydride elimination from the [(P,C)gold(III)(*n*-butyl)][NTf_2] complex *cis*-**3b**, as well as subsequent olefin rotation and 2,1-insertion of 1–butene into the Au–H bond.

Note that due to the unsymmetrical character of the (P,C) bidentate ligand, *cis*/*trans* isomers have in principle to be considered for all reaction intermediates.[39] However, in line with the higher *trans* influence of the $C_{naphthyl}$ *vs*. phosphorus, the isomer of gold complexes with the alkyl / hydride in *trans* position to phosphorus is lower in energy by about 6–7 kcal·mol^{-1} (than the isomer with the alkyl / hydride in *trans* position to $C_{naphthyl}$). The whole reaction profile from the *n*-butyl gold(III) complex **3b** to the 2-butene gold(III) hydride species has also been computed for the *trans* isomer (Figure S38).[30] It involves the same reaction sequence but the associated energetic span is significantly larger (ΔG ~31.6 kcal·mol^{-1} *vs.* 14 kcal·mol^{-1} for *cis*–**3b**).[40]

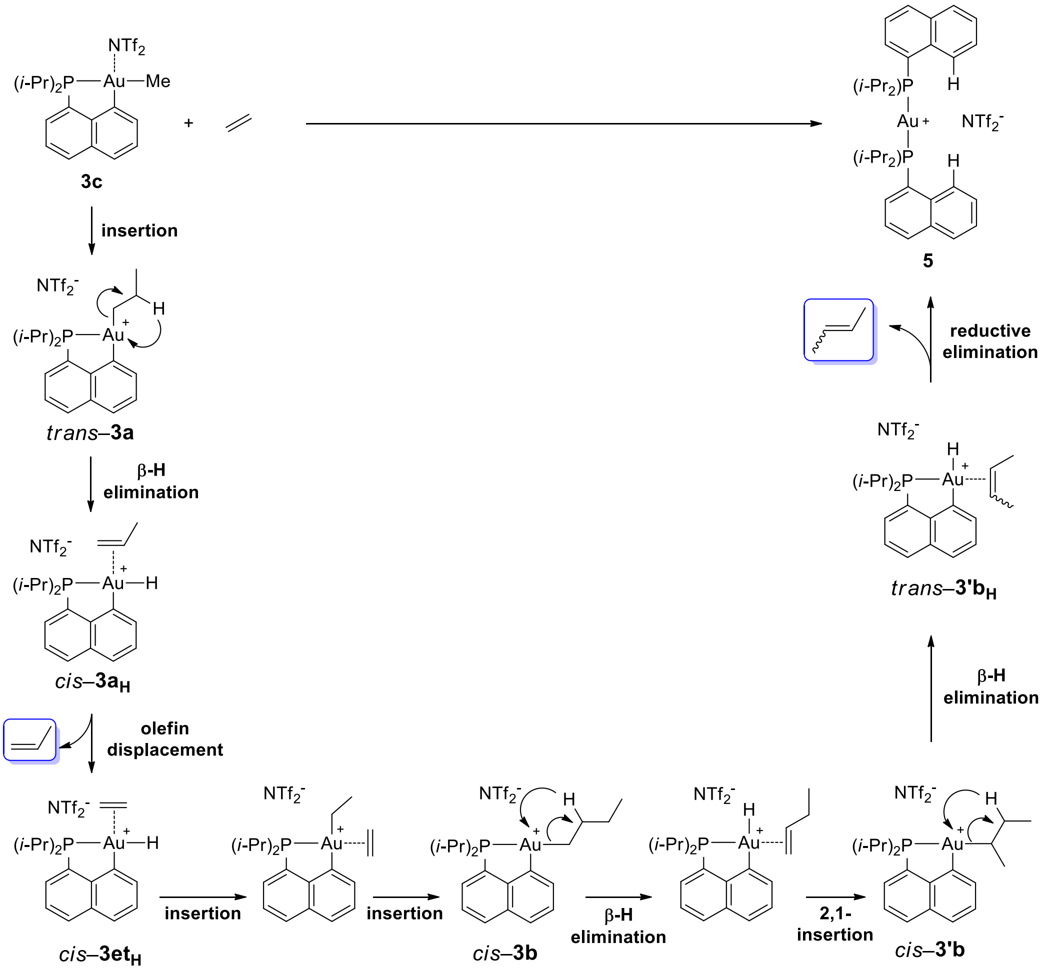
The reactions observed with the cationic gold(III) *n*-propyl and *n*-butyl complexes substantiate that (*i*) β–hydride elimination is a very facile process and (*ii*) the formed alkene readily reinserts into the Au–H bond, giving access to internal alkenes *via* a chain-walking mechanism. These two elementary reactions are well-established and play a major role in many organometallic transformations involving olefins and metal alkyl species, but they were unprecedented with gold. To advance further our understanding of gold complexes, we then investigated the reactivity of the stable [(P,C)gold(III)(methyl)][NTf_2] complex **3c** towards ethylene with the aim to assess whether migratory insertion and β-hydride elimination may compete and/or combine with each other.

Reaction of the [(P,C)gold(III)(methyl)][NTf_2] complex 3c with ethylene. A CD_2Cl_2 solution of the methyl complex **3c** was reacted with ethylene at room temperature in a J. Young NMR tube. ^{1}H NMR spectroscopy indicates slow formation of a mixture of alkenes (complete conversion after 12 h at 7 bar). ^{31}P NMR monitoring shows concomitant conversion of **3c** into a new species (δ 60 ppm) which was unequivocally identified as the cationic 2-coordinate bis(phosphine) gold(I) complex **5** based on multi-nuclear NMR and HRMS (Scheme 4).[30] When the reaction of **3c** with ethylene is performed at 50 °C, complete conversion is achieved within 1 h. All the ^{1}H NMR signals of the formed alkenes were unambiguously assigned by COSY and 2D ^{1}H–^{13}C NMR analyses. The signals of the naphthyl moiety were again used as internal reference to determine the relative amounts of propylene (25 %), 1-butene (5 %) and 2-butenes (20 %) in solution. No traces of higher olefins nor alkanes were detected in this case.



Scheme 4. Reaction of the gold(III) methyl complex **3c** with ethylene, formation of the bis(phosphine) gold(I) complex **5**, propylene, 1- and 2-butenes.

Insertion of olefins into Au–C bonds is extremely rare and was so far limited to our recent work on norbornene insertion.[13a,b] The formation of propylene and butenes from **3c** provides evidence for the first time of migratory insertion of ethylene into Au–C bonds. A recent computational study suggested that insertion of ethylene into Au(III)–C bonds may be feasible,[38] but the instability of low-coordinate gold(III) alkyl species has so far prevented the study and experimental evidence of such olefin insertion. In this respect, the rigid phosphino-naphthyl chelate is very valuable, granting enhanced stability to gold(III) alkyl species. After ethylene insertion, propylene is formed by β-hydride elimination from the gold(III) *n*-propyl intermediate. The generation of 1–butene most likely results from two successive insertions of ethylene into Au–H and then Au–Et bonds, followed by β-hydride elimination. A small amount of 1-butene was detected in this case, which may be explained by displacement of the coordinated 1–butene by ethylene which is present in large excess. But as in the case of the gold(III) *n*-butyl complex **3b**, 2-butenes are formed predominantly, indicating that under these conditions, the olefin exchange at gold hardly competes with the 2,1-insertion of 1-butene and subsequent β-hydride elimination (Scheme 5). The formation of the gold(I) complex **5** can be explained by Csp^2–H bond reductive elimination from the unstable (P,C)gold(III) hydride species followed by ligand redistribution, as commonly observed with cationic LAu$^+$ fragments.[41]



Scheme 5. Mechanism proposed to account for the formation of propylene, 1- and 2-butenes.

The mechanism of the reaction between complex **3c** and ethylene was thoroughly investigated by DFT. The study addressed: *(i)* the insertion of ethylene into the Au–Me bond of complex **3c**, *(ii)* the β-hydride elimination from the ensuing *n*-propyl complex *trans*–**3a** and subsequent olefin displacement, (*iii*) the double insertion of ethylene into the Au–H and then Au–Et bonds to form complex *cis*–**3b**, and *(iv)* the C$_{sp2}$–H bond reductive elimination from the *trans* (P,C)gold(III) hydride species (*cis*–**3$_H$**). The calculations were carried out on the real system, taking into account the triflimidate counter–anion and solvent effects.

(i) Coordination-insertion of ethylene (Figure 3): The reaction starts by the displacement of NTf_2^- for ethylene at gold to give the π–olefin complex *cis*–**3cπ**, which is 14.3 kcal·mol^{-1} uphill in energy (ΔE = 6.5 kcal·mol^{-1}). Then, migratory insertion of ethylene into the Au–Me bond proceeds through an in–plane 4–center transition state **TSins(***cis*–**3cπ→** *trans*–**3a)** leading to the cationic gold(III) *n*-propyl intermediate *trans*–**3a** (*trans* arrangement of the naphthyl and *n*-propyl groups). Coordination of a C–H bond in β-position to give the agostic complex *trans*–**3a**$_\beta$ is exothermic by 6.5 kcal·mol^{-1}, which makes the overall insertion reaction quasi thermoneutral (ΔG = 2.2 kcal·mol^{-1} from *cis*–**3c**). The corresponding energy barrier ($\Delta G^{\neq}$ = 30.5 kcal·mol^{-1}, $\Delta E^{\neq}$ = 22.3 kcal·mol^{-1}) is significant but accessible under the experimental conditions (50 °C, 7 bar).

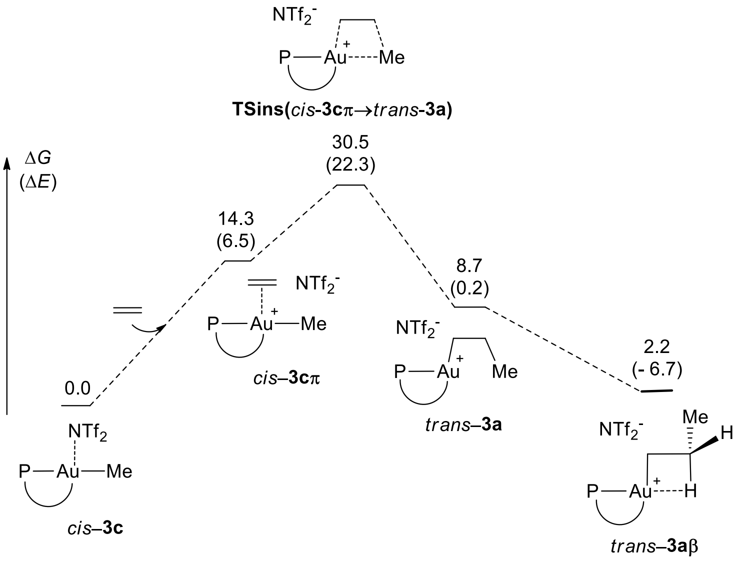


Figure 3. Energy profile (ΔG and ΔE values in kcal·mol^{-1}) computed at the B3PW91(SMD-CH_2Cl_2)/SDD+f(Au)/6-31G**(other atoms) level of theory for the insertion of ethylene into the Au–Me bond of complex *cis*–**3c**.

*(ii) β–hydride elimination of complex trans–***3a**$_{\beta}$ *and subsequent propylene→ethylene displacement* (Figure 4): The β–agostic intermediate *trans*–**3a**$_{\beta}$ readily undergoes β–hydride elimination. The associated activation barrier is much lower than that predicted for the Au(III) *n*-butyl complex *cis*–**3b**$_{\beta}$ ($\Delta G^{\neq} = 0.6$ *vs.* 7.1 kcal·mol^{-1}). This difference can be explained by the configuration of the starting *n*-propyl complex and the stronger *trans* effect of the naphthyl carbon atom *vs.* phosphorus. In the case of *trans*–**3a**$_{\beta}$, the β-hydride elimination reaction is slightly exergonic (by 2.6 kcal·mol^{-1}). The ensuing propylene hydride complex *cis*–**3a**$_{\mathbf{H}}$ then undergoes olefin exchange in the presence of the large excess of ethylene (chain transfer). The formed ethylene adduct *cis*–**3et**$_{\mathbf{H}}$ is quasi isoenergetic with the propylene complex *cis*–**3a**$_{\mathbf{H}}$ (ΔG = 0.5 kcal·mol^{-1}, ΔE = 0.2 kcal·mol^{-1}).

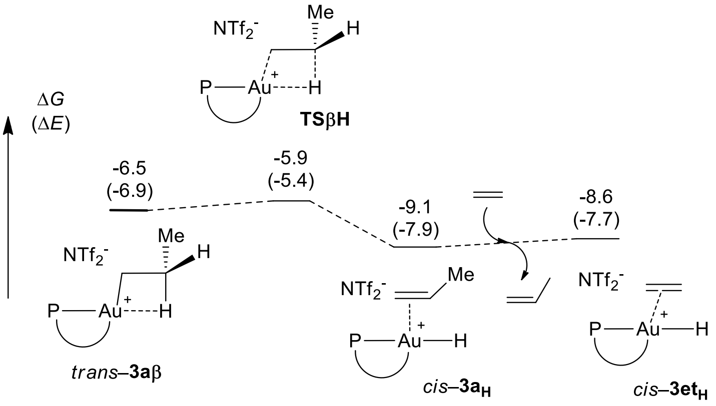


Figure 4. Energy profile (ΔG and ΔE values in kcal·mol^{-1}) computed at the B3PW91(SMD-CH_2Cl_2)/SDD+f(Au)/6-31G**(other atoms) level of theory for the β-hydride elimination reaction from complex *trans*–**3a**$_{\beta}$ and subsequent olefin displacement.

(iii) Double insertion of ethylene (Figure 5): Starting from *cis*–**3et**$_{\mathbf{H}}$, insertion of ethylene into the Au–H bond is predicted to be very facile (with a low activation barrier of $\Delta G^{\neq}$ = 1.8 kcal·mol^{-1}) giving the *trans* gold ethyl complex *trans*–**3d**$_{\beta}$, which is stabilized by β-agostic interaction. Then, a second molecule of ethylene coordinates to give the olefin complex *trans*–

$3d_{\pi}$ (ΔG = 3.2 kcal·mol^{-1}), followed by insertion into the Au–Et bond. The strong *trans* effect of the naphthyl carbon enhances the migrating ability of the ethyl group and facilitates the insertion of ethylene compared to that observed for complex *cis*–**$3c_{\pi}$** ($\Delta G^{\neq}$ = 12.9 *vs.* 16.2 kcal·mol^{-1}). The double coordination–insertion of ethylene is thermodynamically favorable (ΔG = - 21.6 kcal·mol^{-1} from *cis*-**$3et_{H}$**) and leads to the gold *n*-butyl complex *cis*–**$3b_{\beta}$** (which is stabilized by β agostic interaction and which is slightly more stable than the initially formed γ agostic complex *cis*–**$3b_{\gamma}$** around 4.4 kcal·mol^{-1}). As discussed in the previous section, *cis*–**$3b_{\beta}$** easily undergoes β-hydride elimination and re–insertion reactions to release butenes. The formation of 2-butenes is predominant, but a small amount of 1-butene is observed in this case, due to olefin exchange with ethylene before 2,1-insertion occurs.

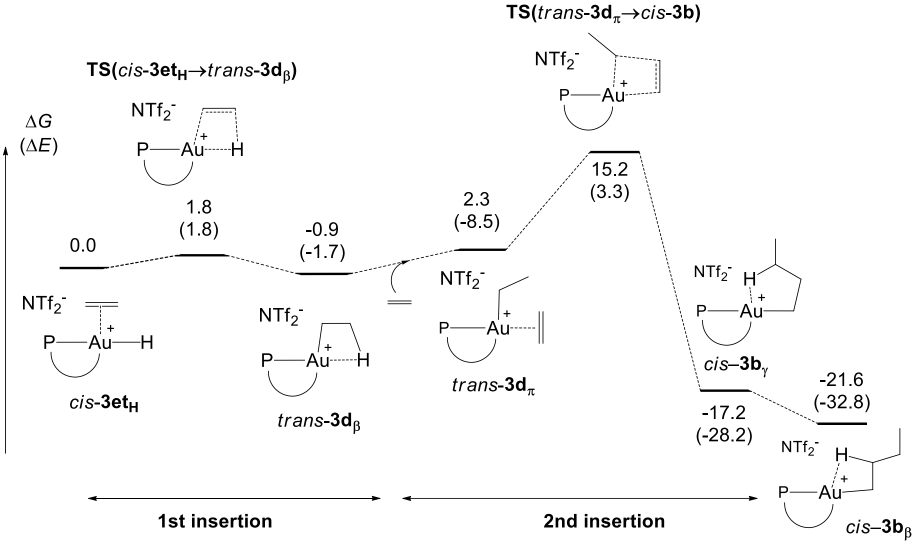
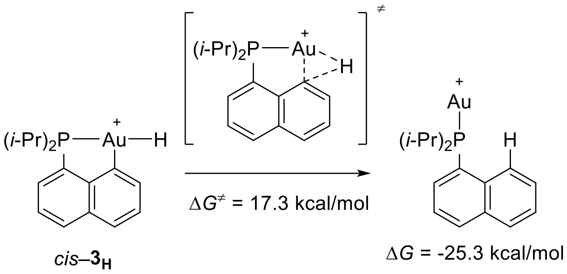


Figure 5. Energy profile (ΔG and ΔE values in kcal·mol^{-1}) computed at the B3PW91(SMD-CH_2Cl_2)/SDD+f(Au)/6-31G**(other atoms) level of theory for the double insertion of ethylene leading to the gold(III) *n*-butyl complex *cis*–**$3b_{\beta}$**.

(iv) C_{sp2}–H bond forming reductive elimination (Scheme 6): Finally, the formation of the naphthylphosphine gold(I) complex (C_{sp2}–H coupling) was investigated computationally. The reaction most likely involves reductive elimination from unstable gold(III) hydride species.

From the 3-coordinated cationic complex *cis*–$\mathbf{3}_\mathrm{H}$ (readily accessible by dissociation of ethylene, propylene or butene), reductive elimination with $C_{sp}{}^2$–H bond formation is thermodynamically favored (ΔG = –25.3 kcal·mol^{-1}; ΔE = –25.0 kcal·mol^{-1}) and the corresponding activation barrier is readily accessible ($\Delta G^{\neq}$ = 17.3 kcal·mol^{-1}; $\Delta E^{\neq}$ = 17.1 kcal·mol^{-1}). The ensuing phoshine gold(I) complex then evolves into **5** by ligand redistribution, following the classical decomposition pathway of monocoordinate cationic gold(I) species.[41]



Scheme 6. Reductive elimination (C_{sp2}–H coupling) of the gold(III) hydride complex *cis*–$\mathbf{3}_\mathbf{H}$.

CONCLUSION

This experimental / theoretical study evidences and provides a comprehensive picture of β–hydride elimination at gold(III). Taking advantage of the phosphino-naphthyl (P,C) chelate, cationic gold(III) alkyl complexes **3a-c** have been generated and characterized. Their fate was thoroughly investigated by multi-nuclear variable-temperature NMR spectroscopy. The occurrence of β-hydride elimination was demonstrated and detailed DFT studies have shed light into the reaction mechanism. Moreover, the fate of the gold(III) *n*-butyl complex **3b** and the reaction of the gold(III) methyl complex **3c** with ethylene have afforded several major insights into the stability/reactivity of gold(III) alkyl complexes: *(i)* migratory insertions of ethylene into Au(III)–C and Au(III)–H bonds have been evidenced for the first time; *(ii)* β–hydride elimination reactions readily proceed even in the presence of a large excess of ethylene; *(iii)* though very unstable, the generated gold(III) hydride species readily insert olefins. In addition, other transformations typically observed during coordination–insertion at Ni/Pd/Pt(II) alkyl complexes, such as olefin isomerization (chain walking) and olefin exchange (chain transfer) have been evidenced with gold(III) complexes.

In the end, if not favored with gold(I), β–hydride elimination appears as a very easy process for gold(III) alkyl species that definitely deserves to be considered in the development of homogeneous Au(III) and Au(I)/Au(III) catalysis. Future work from our group will seek to take advantage of our increasing knowledge of the reactivity of gold(III) complexes to develop new valuable synthetic transformations.

ACKNOWLEDGMENT

Financial support from the Centre National de la Recherche Scientifique, the Université de Toulouse, and the Agence Nationale de la Recherche (ANR-JCJC-2012-POGO) is gratefully acknowledged. Umicore AG & Co is acknowledged for a generous gift of gold precursors. We thank Hélène Olivier-Bourbigou (IFP Energies Nouvelles) for fruitful discussions. Université de Pau et des Pays de l'Adour, MCIA (Mésocentre de Calcul Intensif Aquitain) and IDRIS under Allocation 2016 (i2016080045) made by Grand Equipement National de Calcul Intensif (GENCI) are also acknowledged for computational facilities. L. Estévez thanks the Xunta de Galicia for the postdoctoral contract under the I2C program.

ASSOCIATED CONTENT

Detailed experimental conditions and procedures, theoretical details, analytical data (PDF), crystallographic data for compounds **2a,c**, CCDC numbers, optimized structures (XYZ). "This material is available free of charge via the Internet at http://pubs.acs.org."

REFERENCES

1. Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*, University Science Books, Sausalito, CA, **2009.**
2. Corma, A.; Leyva-Pérèz, A.; Sabater, M. J. *Chem. Rev.* **2011**, *111*, 1657.
3. For a very rare example in which β-hydride eliminations at gold have been proposed, see: Alcaide, B.; Almendros, P.; del Campo, T. M.; Fernández, I. *Chem. Comm.* **2011**, *47*, 9054.
4. Klatt, G.; Xu, R.; Pernpointner, M.; Molinari, L.; Quang Hung, T.; Rominger, F.; Hashmi, A. S.; Köppel, H. *Chem. Eur. J.* **2013**, *19*, 3954.
5. In contrast to β-hydride elimination, α- and β-hydride abstractions have been shown by Bertrand to readily occur upon treatment of CAAC gold(I) alkyl complexes with Ph_3C^+,BF_4^-: Ung, G.; Bertrand, G. *Angew. Chem. Int. Ed.* **2013**, *52*, 11388.
6. (a) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896; (b) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180; (c) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239; (d) Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266; (e) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351; (f) Jimenez-Nunez, E.; Echavarren, A. M. *Chem. Rev.* **2008**, *108*, 3326; (g) Fürstner, A. *Chem. Soc. Rev.* **2009**, *38*, 3208; (h) Corma, A.; Leyva-Perez, A.; Sabater, M. J. *Chem. Rev.* **2011**, *111*, 1657; (i) Boorman, T. C.; Larrosa, I.; *Chem. Soc. Rev.* **2011**, *40*, 1910. (i) Bandini, M. *Chem. Soc. Rev.* **2011**, *40*, 1358; (j) Hashmi, A. S. K.; Toste, F. D. *Modern Gold Catalyzed Synthesis, First Edition;* Wiley-VCH Verlag GmBH & Co. KGaA: Weinheim, **2012**; (k) *Acc. Chem. Res.* **2014**, *issue 3*. Special issue edited by Friend, C. M. and Hashmi, A. S. K. on gold catalysis.
7. For reviews on the use of gold(III) compounds in catalysis, see: (a) Schmidbaur, H.; Schier, A. *Arab. J. Sci. Eng.* **2012**, *37*, 1187; (b) Boorman, T. C.; Larrosa, I. *Chem. Soc. Rev.* **2011**, *40*, 1910.
8. Wu, C. Y.; Horibe, T.; Jacobsen, C. B.; Toste, F. D. *Nature* **2015**, *517*, 449.
9. For a recent review on the reactivity of gold complexes towards elementary organometallic reactions, see: Joost, M.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2015**, *54*, 15022.
10. For selected examples reporting the isolation of organometallic gold(III) compounds, see: (a) Rosca, D. A.; Fernandez-Cestau, J.; Morris, J.; Wright, J. A.; Bochmann, M. *Science Adv.* **2015**, *1;* e1500761; (b) Kumar, R.; Linden, A.; Nevado, C. *Angew. Chem. Int. Ed.* **2015**, *54*, 14287; (c) Rosca, D. A.; Wright, J. A.; Hughes, D. L.; Bochmann, M. *Nat. Commun.* **2013**, *4*, 2167; (d) Savjani, N.; Rosca, D.; Schormann, M.; Bochmann, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 874; (e) Langseth, E.; Scheuermann, M. L.; Balcells, D.; Kaminsky, W.; Goldberg, K. I.; Eisenstein, O.; Heyn, R. H.; Tilset, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 1660; (f) Rosca, D. A.; Smith, D. A.; Hughes, D. L.; Bochmann, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 10643; (g) Rosca, D. A.; Smith, D. A.; Bochmann, M. *Chem. Commun.* **2012**, *48*, 7247; (h) Cinellu, M. A.; Minghetti, G.; Cocco, F.; Stoccoro, S.; Zucca, A.; Manassero, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 6892.
11. (a) Kawai, H.; Wolf, W. J.; DiPasquale, A. G.; Winston, M. S.; Toste, F. D. *J. Am. Chem. Soc.* **2016**, *138*, 587; (b) Winston, M. S.; Wolf, W. J.; Toste, F. D. *J. Am. Chem. Soc.* **2015**, *137*, 7921; (c) Winston, M. S.; Wolf, W. J.; Toste, F. D. *J. Am. Chem. Soc.* **2014**, *136*, 7777 ; (d) Wolf, W. J.; Winston, M. S.; Toste, F. D. *Nat. Chem.* **2014**, *6*, 159; (e) Vicente, J.; Bermùdez, M. D.; Carrión, F. J. *Inorg. Chim. Act.* **1994**, *220*, 1; (f) Vicente, J.; Dolores Bermudez, M.; Escribano, J. *Organometallics* **1991**, *10*, 3380; (g) Vicente, J.; Bermudez, M. D.; Escribano, J.; Carrillo, M. P.; Jones, P. G. *J. Chem. Soc., Dalton. Trans.* **1990**, 3083.
12. (a) Browne, A. R.; Deligonul, N.; Anderson, B. L.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Chem. Commun.* **2015**, *51*, 15800; (b) Wu, Q.; Du, C.; Huang, Y.; Liu, X.; Long, Z.; Song, F.; You, J. *Chem. Sci.* **2015**, *6*, 288; (c) Maity, A.; Sulicz, A. N.; Deligonul, N.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Chem. Sci.* **2015**, *6*, 981; (d) Hofer, M.; Gomez-Bengoa, E.; Nevado, C. *Organometallics* **2014**, *33*, 1328; (e) Smith, D. A.; Rosca, D. A.; Bochmann, M. *Organometallics* **2012**, *31*, 5998.
13. (a) Rekhroukh, F.; Estevez, L.; Bijani, C.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Organometallics* **2016**, *35*, 995; (b) Rekhroukh, F.; Brousses, R.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2015**, *54*, 1266; (c) Joost, M.; Estevez, L.; Mallet-Ladeira, S.; Miqueu,

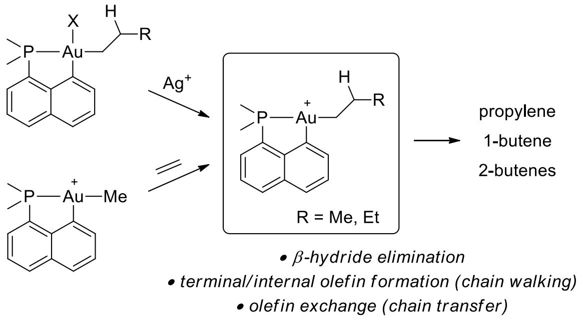
K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.* **2014**, *136*, 10373; (d) Joost, M.; Gualco, P.; Mallet-Ladeira, S.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 7160.

14. For examples of formal insertion of alkenes into gold(III)-oxygen bonds, see: Langseth, E.; Nova, A.; Tråseth, E. A.; Rise, F.; Øien, S.; Heyn, R. H.; Tilset, M. *J. Am. Chem. Soc.* **2014**, *136*, 10104, and references 10d,f.
15. Tamaki, A.; Magennis, S. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6140.
16. Mankad, N. P.; Toste, F. D. *Chem. Sci.* **2012**, *3*, 72.
17. (a) Joost, M.; Estévez, L.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2015**, *54*, 5236; (b) Joost, M.; Zeineddine, A.; Estévez, L.; Mallet Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.* **2014**, *136*, 14654; (c) Joost, M.; Gualco, P.; Coppel, Y.; Miqueu, K.; Kefalidis, C. E.; Maron, L.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2014**, *53*, 747; (d) Guenther, J.; Mallet-Ladeira, S.; Estevez, L.; Miqueu, K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.* **2014**, *136*, 1778; (e) Lassauque, N.; Gualco, P.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.* **2013**, *135*, 13827; (f) Gualco, P.; Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Organometallics* **2012**, *31*, 6001; (g) Gualco, P.; Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 8320.
18. Rekhroukh, F.; Estévez, L.; Bijani, C.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2016**, *55*, 3414.
19. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.
20. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652; (b) Perdew, J. P. in *Electronic Structure of Solids '91*, Ed. P. Ziesche and H. Eschrig, Akademie Verlag, Berlin, **1991**, 11.
21. Andrae, D. U. Häussermann, M. Dolg, H. Stoll, Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
22. Ehlers, A. W.; Biihme, M.; Dapprich, S.; Gobbi, A.; Hijllwarth, A.; Jonas, V.; Kiihler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Letters*, **1993**, *208*, 111.
23. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.
24. (a) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 36. (b) Hratchian, H. P.; Schlegel, H. B. in *Theory and Applications of Computational Chemistry: The First 40 Years*, Ed. Dykstra, C. E.; Frenking, G.; Kim, K. S.; Scuseria, G. Elsevier, Amsterdam, **2005**, 195.
25. (a) Reed, E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899; (b) Foster J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211; (c) Reed A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736.
26. Glendening, E. D.; Badenhoop, J, K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. Theoretical Chemistry Institute, University of Wisconsin, Madison, **2001**.
27. MOLEKEL 4.3, Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. Swiss Center for Scientific Computing, Manno (Switzerland), **2000-2002**.
28. GaussView, Version 5, Dennington, R.; Keith, T.; Millam, J. *Semichem Inc.*, Shawnee Mission, KS, **2009**.
29. Langseth, E.; Görbitz, C. H.; Heyn, R. H.; Tilset, M. *Organometallics* **2012**, *31*, 6567.
30. See supporting information for details.
31. *Cis* configuration is indicated by the dd signal observed for the C_{naphthyl}Au atom, with $^{2}J_{\mathrm{PC}}$ coupling constants of 114.0 and 5.1 Hz.
32. Given their low boiling points, only part of the formed propylene and propane remains in solution (~ 25–30% yield for each based on the *n*-Pr chain and according to the integration of

the respective ^{1}H NMR signals, using the naphthyl backbone of the (P,C) ligand as internal standard).

33. (a) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139; (b) Xu, H.; Diccianni, J. B.; Katigbak, J.; Hu, C.; Zhang, Y.; Diao, T. *J. Am. Chem. Soc.* **2016**, *138*, 4779.
34. (a) Rünzi, T.; Tritschler, U.; Roesle, P.; Göttker-Schnetmann, I.; Möller, H. M.; Caporaso, L.; Poater, A.; Cavallo, L.; Mecking, S. *Organometallics* **2012**, *31*, 8388; (b) Berkefeld, A.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 1565.
35. Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.
36. For a rare example of characterized gold(III) hydride complex, see reference 10f.
37. The Au−N distance is longer than those found in the NHC gold(III) triflimidate complex (d = 2.165(8) Å: Jacques, B.; Kirsch, J.; de Frémont, P.; Braunstein, P. *Organometallics* **2012**, *31*, 4654) and in $(Ph_3P)AuNTf_2$ (d = 2.102(3) Å: Mezailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133); but very similar to that found in the *o*-carboranyl diphosphine gold(I) species (d = 2.221(2) Å: ref 17b).
38. For a recent study of alkene coordination and insertion with Au(III) complexes, see: Balcells, D.; Eisenstein, O.; Tilset, M.; Nova, A. *Dalton Trans.* **2016**, *45*, 5504.
39. *Cis*/*trans* isomerization of palladium complexes play an important role in the coordination/insertion of olefins and β–hydride elimination. For detailed studies on Pd complexes bearing bidentate phosphine-sulfonate ligands, see: (a) Nozaki, K.; Kusumoto, S.; Noda, S.; Kochi, T.; Chung, L. W.; Morokuma, K. *J. Am. Chem. Soc.* **2010**, *132*, 16030; (b) Guironnet, D.; Caporaso, L.; Neuwald, B.; Göttker-Schnetmann, I.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 4418.
40. For a recent review on the energetic span model, see: Kozuch, S.; Shaik, S. *Acc. Chem. Res.* **2011**, *44*, 101.
41. See Wang, W.; Hammond, G. B.; Xu, B. *J. Am. Chem. Soc.* **2012**, *134*, 5697 and references therein.

TOC Graphic


X
H
P
Au
R
Ag$^+$
P
Au
Me
H
P
Au
R
R = Me, Et
propylene
1-butene
2-butenes
• β-hydride elimination
• terminal/internal olefin formation (chain walking)
• olefin exchange (chain transfer)