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

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S *Supporting Information*

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 cyclometalated gold(III) alkyl complexes [(P,C)gold(III)(R)]-[NTf₂] [(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/reinsertion into the Au—H bond. The reaction of the cationic gold(III) methyl complex **3c** with ethylene was also explored. According to ¹H and ¹³C 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).
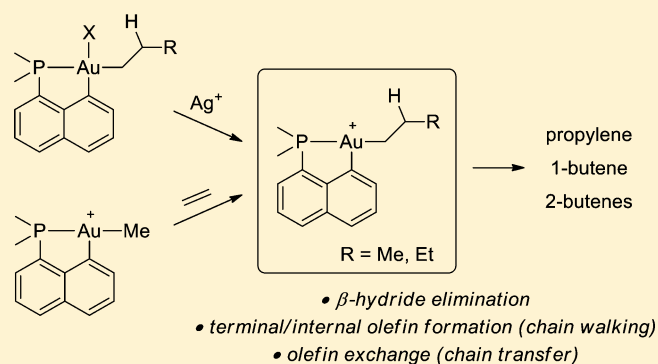
INTRODUCTION

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

Chart 1. Schematic Representation of β-Hydride Elimination
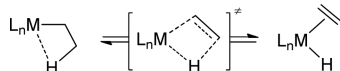
insertion into a M—H bond. β-Hydride elimination plays a major role in the stability/reactivity of metal alkyl complexes. It is also one of the preparative routes to metal hydride species. In catalytic cycles, β-hydride elimination may be a key step or a side reaction. For example, products of Mizoroki—Heck 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 toward β-hydride elimination if highly efficient and selective transformations involving alkyl complexes are to be developed.

In contrast with the other transition metals, very little is known about β-hydride elimination 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 (ΔG‡: 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.
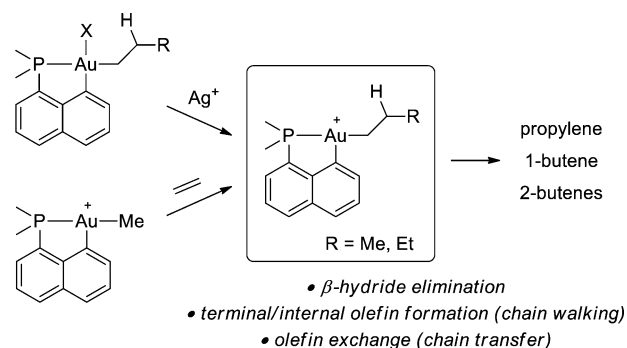
Over the last 15 years, homogeneous gold catalysis has developed tremendously.[6] The field has been largely dominated by gold(I) catalysis, but recent contributions have highlighted the catalytic interest and potential of gold(III) complexes.[7,8] These landmark achievements have sparked renewed interest in gold(III) complexes, and our knowledge of gold(III) organometallic chemistry has significantly progressed over the past few years.[9,10] The reactivity of gold(III) species toward reductive elimination,[11] transmetalation,[12] and migratory insertion[13,14] reactions has been documented and thoroughly investigated. Yet comparatively, β-hydride elimination reactions at gold(III) remain very seldom. In a seminal study, Kochi et al. reported in the 1970s a spontaneous *tert*-butyl → iso-butyl isomerization at gold(III) [upon attempts to purify $(t\text{-Bu})\text{AuMe}_2(\text{PPh}_3)$] that was proposed to proceed via β-hydride elimination, but no olefin, free or coordinated, could be detected.[15] More recently, Toste investigated C_{sp^3}–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 cyclometalated (P,C) gold(III) complexes, which are stable toward 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 cyclometalated (P,C) gold(III) complexes to thoroughly investigate the stability/reactivity of gold(III) alkyl species toward 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, olefin isomerization and olefin exchange, have also been evidenced with gold and are discussed hereafter.

■ 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]

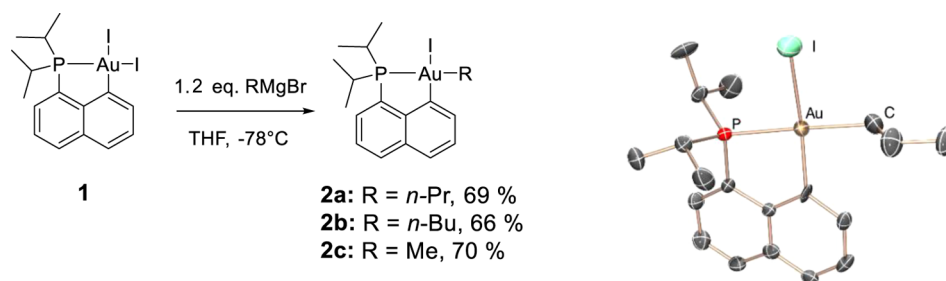**Chart 2. Formation of Cationic Gold(III) Alkyl Complexes and β-Hydride Elimination**

- β-hydride elimination
- *terminal/internal olefin formation (chain walking)*
- *olefin exchange (chain transfer)*

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 counteranion NTf$_2$ and solvent effect (DCM: CH$_2$Cl$_2$) 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) was plotted with Molekel 4.3,[27] and all of 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 cyclometalated [(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 (≥ 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).

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 −90 °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 ($J_{PC} = 88.7$ 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).

Scheme 1. Preparation of the Mono-alkylated [(P,C)Au(III)] Complexes 2a–c, and Molecular View of 2a with Thermal Ellipsoids Drawn at the 50% Probability Level

Scheme 2. β-Hydride Elimination from the Cationic Gold(III) n-Propyl Complex 3a
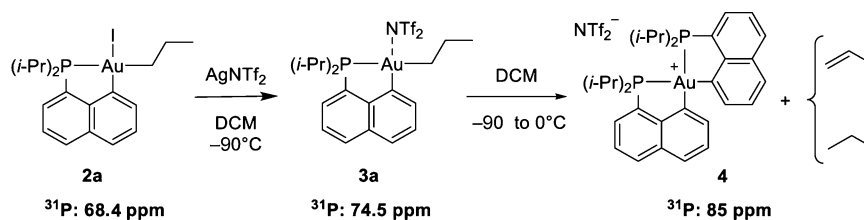
Scheme 3. β-Hydride Elimination from the Cationic Gold(III)–Butyl Complex 3b with Formation of Complex 4, 2-Butenes (cis and trans Isomers), and Butane
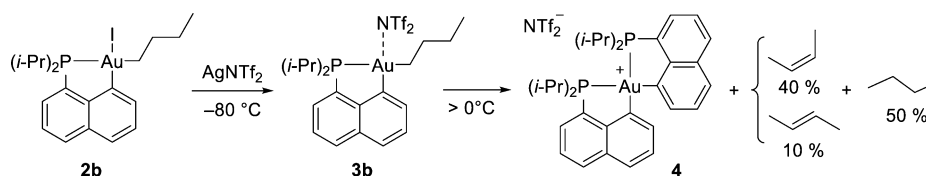
However, no sign of such an interaction was found for **3a**, in contrast with what we recently observed in a related gold(III) bis(norbornyl) complex.[18] For all of the CH_2 and CH_3 groups of the n-propyl chain, the $^1J_{CH}$ coupling constant is of about 130 Hz, in the normal range for C_{sp^3}–H bonds.

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-cyclometalated gold(III) complex based on NMR spectroscopy and mass spectrometry.[31] In addition, ^1H 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 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 one to investigate possible reinsertion 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 AgNTf₂ 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-(cyclometalated) complex **4** as indicated by ^{31}P NMR spectroscopy. In addition, GC–MS analyses and $^1H/^{13}C$ NMR spectroscopy reveal concomitant formation of 2-butene (cis and trans isomers) and butane. The relative integration of the ^1H NMR signals for the organic products versus 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]

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/reinsertion reactions.[35] This suggests that the highly reactive gold(III) hydride intermediate[36] rapidly reinserts 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 AgNTf₂. The resulting complex [(P,C)gold(III) (methyl)][NTf₂] **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
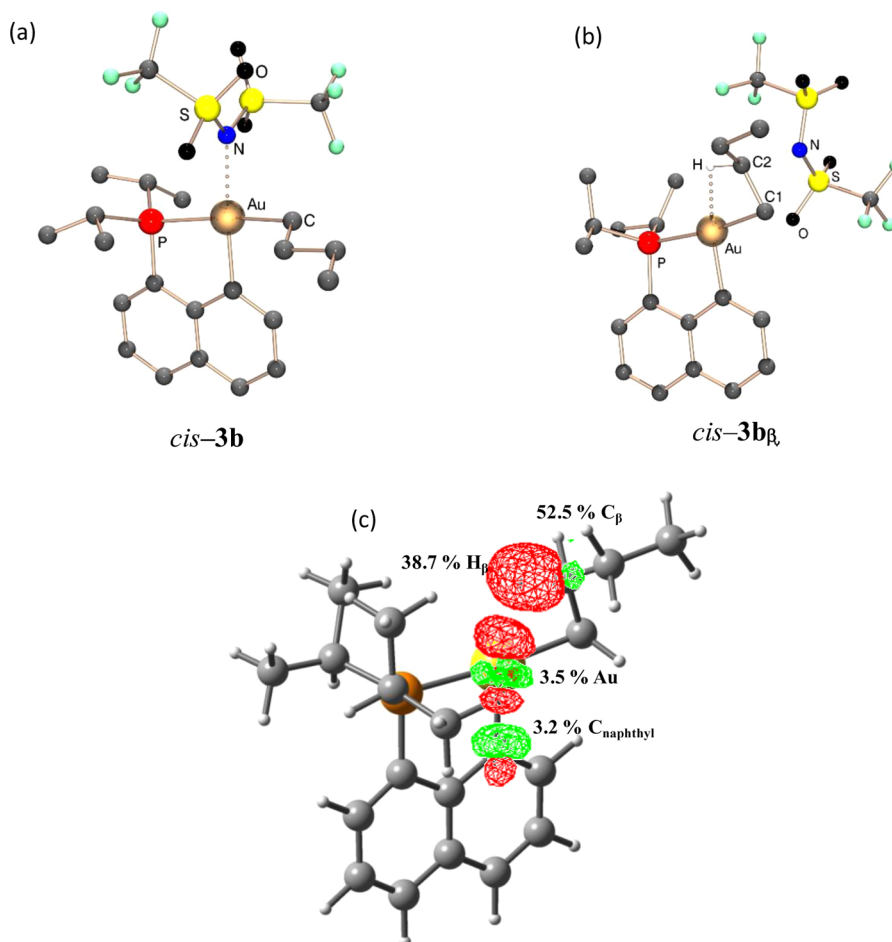
Figure 1. DFT-optimized structures of the $[(P,C)gold(III)(n\text{-}butyl)][NTf_2]$ complex *cis*-**3b** (a) and *cis*-**3b**$_\beta$ (b) [B3PW91(SMD-CH$_2$Cl$_2$)/SDD +f(Au)/6-31G**(other atoms)]: Au···NTf$_2$ (2.228 Å) versus Au···H$_\beta$ (1.954 Å) contact. (c) NBO/NLMO analysis. Superposition of the donor $\sigma_{C-H\beta}$ and acceptor σ^*_{C-Au} (chicken-wire) NBOs (cutoff: 0.07 au) associated with the β-agostic interaction in complex *cis*-**3b**$_\beta$.
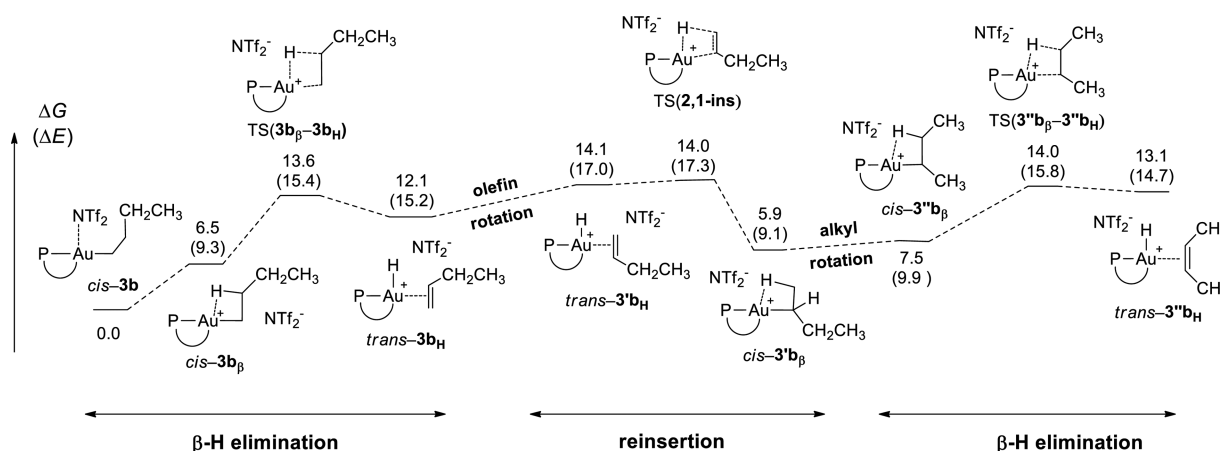

Figure 2. Energy profile (ΔG and ΔE values in kcal mol^{-1}) computed at the B3PW91(SMD-CH$_2$Cl$_2$)/SDD+f(Au)/6-31G**(other atoms) level of theory for β-hydride elimination from the $[(P,C)gold(III)(n\text{-}butyl)][NTf_2]$ complex *cis*-**3b**, as well as subsequent olefin rotation and 2,1-insertion of 1-butene into the Au–H bond.

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$_2$] counteranion. The ground-state structure corresponds to a tight ion pair with a Au···N contact of 2.228 Å (Figure 1a).[37] The [NTf$_2$] counteranion can be readily displaced from the coordination sphere by the *n*-butyl chain to give structures such as *cis*-**3b**$_\beta$ (Figure 1b), which is only slightly uphill in energy (ΔG = +6.5 kcal mol^{-1}). Detailed examination of the optimized geometry of *cis*-**3b**$_\beta$ indicates the presence of a short contact between gold and one of the

Scheme 4. Reaction of the Gold(III) Methyl Complex 3c with Ethylene, and Formation of the Bis(phosphine) Gold(I) Complex 5, Propylene, and 1- and 2-Butenes
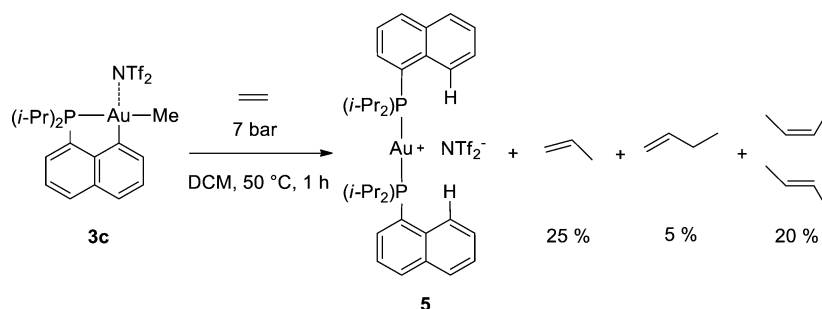
hydrogen atoms in a β-position (Au···H_β = 1.954 Å; AuH$_\beta$C$_\beta$ = 99.0°), which is located in the coordination plane of the gold center, in a *trans* position to C$_{naphthyl}$ (Figure 1, right). The corresponding C$_\beta$−H bond is significantly elongated as compared to the other C−H bonds 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*-**3b**$_\beta$ was confirmed by NBO analyses. A $\sigma_{C−H}$ → $\sigma^*_{AuCnaphthyl}$ donor−acceptor interaction was found at the second-order perturbation level with a stabilizing energy $\Delta E(2)$ of 29.1 kcal 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$_\gamma$/H$_\delta$ 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.

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 ($\Delta G^\ddagger$ = 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 ($\Delta G^\ddagger$ = 1.5 kcal mol^{-1} from *trans*-**3b**$_H$). However, the formation of internal olefins (*cis* and *trans* 2-butene) suggests that reinsertion 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, $\Delta G^\ddagger$ = 1.9 kcal mol^{-1}) to give the corresponding gold(III) *sec*-butyl complex *cis*-**3′b**$_\beta$, which is downhill in energy (ΔG = −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 kca mol^{-1}) afford 2-butene gold(III) hydride species. For the 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 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(cyclometalated) complex **4**.

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$_{naphthyl}$ versus 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 ($\Delta G \approx$ 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** toward 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$_2$Cl$_2$ solution of the methyl complex

Scheme 5. Mechanism Proposed To Account for the Formation of Propylene and 1- and 2-Butenes
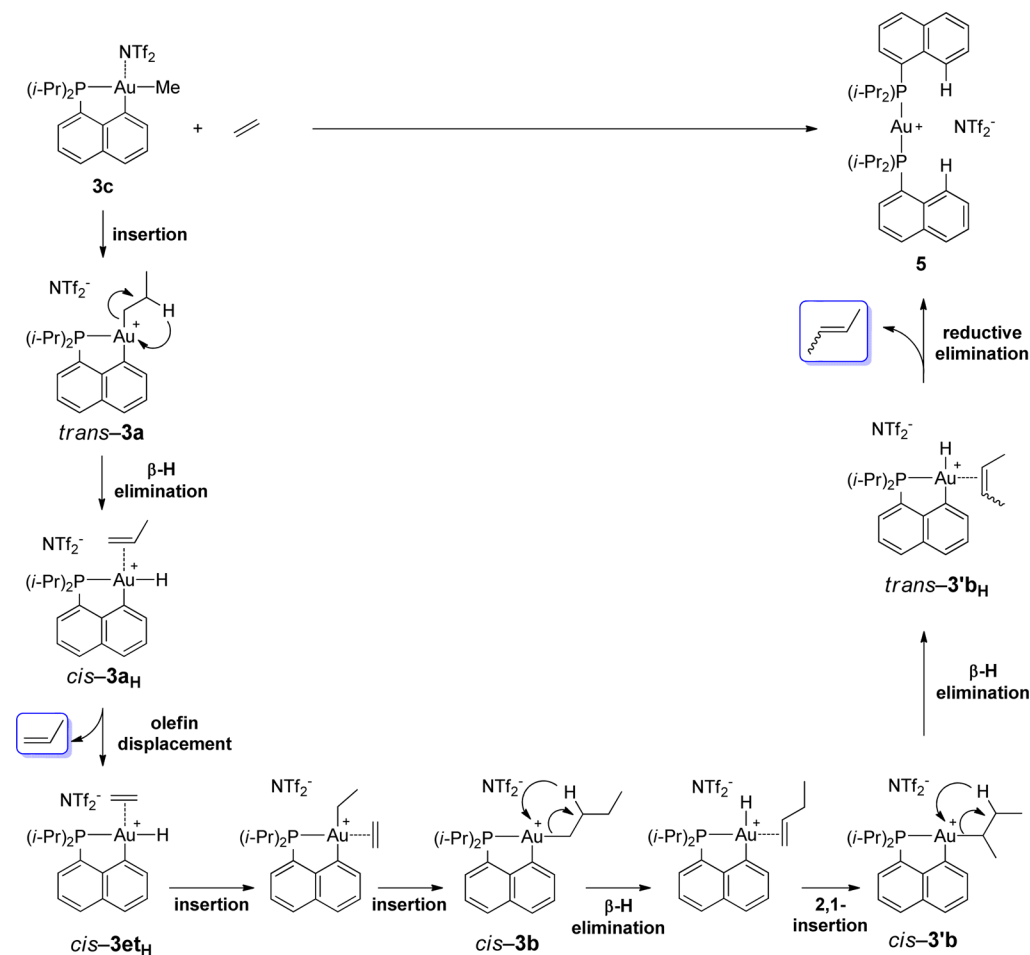
3c was reacted with ethylene at room temperature in a J. Young NMR tube. ^{1}H NMR spectroscopy indicates slow formation of a mixture of alkenes (complete conversion after 12 h at 7 bar). ^{31}P NMR monitoring shows concomitant conversion of 3c into a new species (δ 60 ppm), which was unequivocally identified as the cationic 2-coordinate bis(phosphine) gold(I) complex 5 based on multinuclear 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 of 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.

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. Yet 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 C_{sp}^2–H bond reductive elimination from the unstable (P,C)gold(III) hydride species followed by ligand redistribution, as was commonly observed with cationic LAu$^+$ fragments.[41]

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_{sp}^2–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 counteranion and solvent effects.

1. Coordination–Insertion of Ethylene. 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}) (Figure 3). Migratory insertion of ethylene into the Au−Me bond then proceeds through an in-
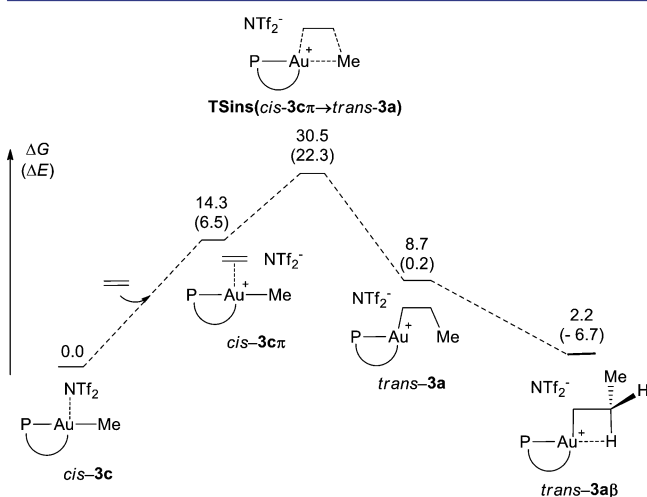
Figure 3. Energy profile (ΔG and ΔE values in kcal mol^{-1}) computed at the B3PW91(SMD-CH$_2$Cl$_2$)/SDD+f(Au)/6-31G**(other atoms) level of theory for the insertion of ethylene into the Au−Me bond of complex *cis*-**3c**.

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 ($\Delta G^\ddagger$ = 30.5 kcal mol^{-1}, $\Delta E^\ddagger$ = 22.3 kcal mol^{-1}) is significant but accessible under the experimental conditions (50 °C, 7 bar).

2. β-Hydride Elimination of Complex trans-3a$_\beta$ and Subsequent Propylene → Ethylene Displacement. The *β*-agostic intermediate *trans*-**3a$_\beta$** readily undergoes *β*-hydride elimination (Figure 4). The associated activation barrier is much lower than that predicted for the Au(III) *n*-butyl complex *cis*-**3b$_\beta$** ($\Delta G^\ddagger$ = 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 versus phosphorus. In the case of *trans*-**3a$_\beta$**, the *β*-hydride elimination
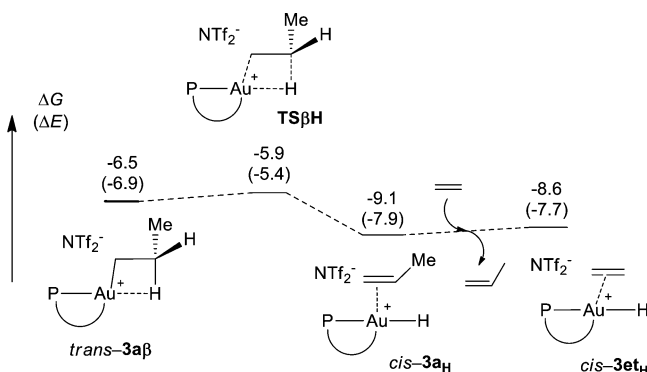
Figure 4. Energy profile (ΔG and ΔE values in kcal mol^{-1}) computed at the B3PW91(SMD-CH$_2$Cl$_2$)/SDD+f(Au)/6-31G**(other atoms) level of theory for the *β*-hydride elimination reaction from complex *trans*-**3a$_\beta$** and subsequent olefin displacement.

reaction is slightly exergonic (by 2.6 kcal mol^{-1}). The ensuing propylene hydride complex *cis*-**3a$_H$** then undergoes olefin exchange in the presence of the large excess of ethylene (chain transfer). The formed ethylene adduct *cis*-**3et$_H$** is quasi isoenergetic with the propylene complex *cis*-**3a$_H$** (ΔG = 0.5 kcal mol^{-1}, ΔE = 0.2 kcal mol^{-1}).

3. Double Insertion of Ethylene. Starting from *cis*-**3et$_H$**, insertion of ethylene into the Au−H bond is predicted to be very facile (with a low activation barrier of $\Delta G^\ddagger$ = 1.8 kcal mol^{-1}) giving the *trans* gold ethyl complex *trans*-**3d$_\beta$**, which is stabilized by *β*-agostic interaction (Figure 5). A second molecule of ethylene then 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* influence of the naphthyl carbon enhances the migrating ability of the ethyl group and facilitates the insertion of ethylene as compared to that observed for complex *cis*-**3c$_\pi$** ($\Delta G^\ddagger$ = 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 reinsertion 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.

4. C$_{sp}^2$−H Bond Forming Reductive Elimination. Finally, the formation of the naphthylphosphine gold(I) complex (C$_{sp}^2$−H coupling) was investigated computationally (Scheme 6). The reaction most likely involves reductive elimination from unstable gold(III) hydride species. From the 3-coordinated cationic complex *cis*-**3$_H$** (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 ($\Delta G^\ddagger$ = 17.3 kcal mol^{-1}; $\Delta E^\ddagger$ = 17.1 kcal mol^{-1}). The ensuing phosphine gold(I) complex then evolves into **5** by ligand redistribution, following the classical decomposition pathway of monocoordinate cationic gold(I) species.[41]

■ CONCLUSION

This experimental/theoretical study 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 multinuclear 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; and (iii) although 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-
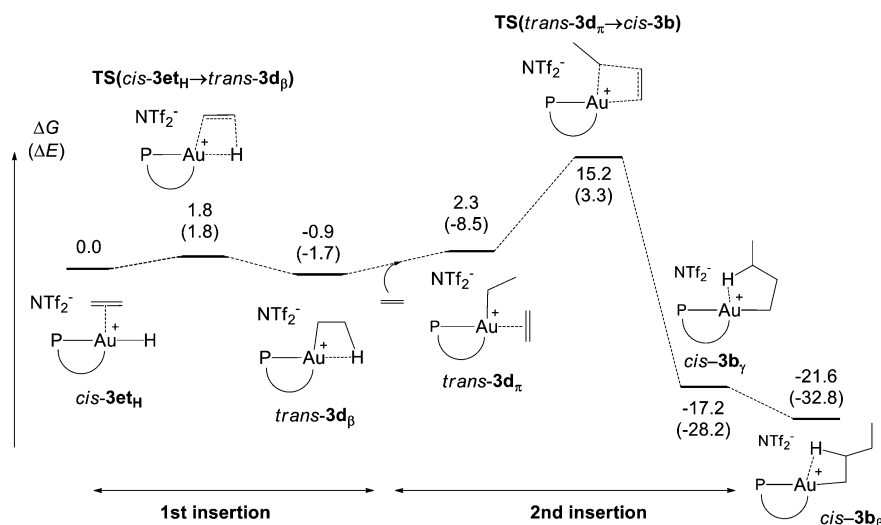
Figure 5. Energy profile (ΔG and ΔE values in kcal mol^{-1}) computed at the B3PW91(SMD-CH$_2$Cl$_2$)/SDD+f(Au)/6-31G**(other atoms) level of theory for the double insertion of ethylene leading to the gold(III) n-butyl complex cis-$3b_\beta$.

Scheme 6. Reductive Elimination (C$_{sp}^2$–H Coupling) of the Gold(III) Hydride Complex cis-3_H
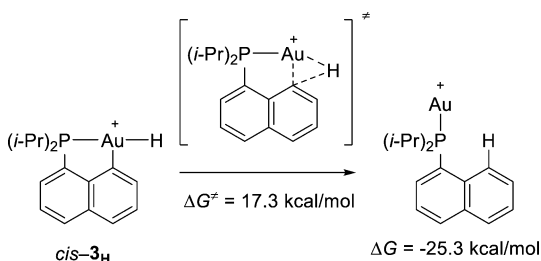
walking) and olefin exchange (chain-transfer), have been evidenced with gold(III) complexes.

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.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07035.

> Detailed experimental conditions and procedures, theoretical details, and analytical data (PDF)
> X-ray data for compound **2a** (CIF)
> X-ray data for compound **2c** (CIF)
> CCDC numbers, optimized structures (XYZ)

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