Inorganic Chemistry

Featured Article

P,N-Chelated Gold(III) Complexes: Structure and Reactivity

Ann Christin Reiersølmoen, Stefano Battaglia, Andreas Orthaber, Roland Lindh, Máté Erdélyi,* and Anne Fiksdahl*

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ABSTRACT: Gold(III) complexes are versatile catalysts offering a growing number of new synthetic transformations. Our current understanding of the mechanism of homogeneous gold(III) catalysis is, however, limited, with that of phosphorus-containing complexes being hitherto underexplored. The ease of phosphorus oxidation by gold(III) has so far hindered the use of phosphorus ligands in the context of gold(III) catalysis. We present a method for the generation of *P,N*-chelated gold(III) complexes that circumvents ligand oxidation and offers full counterion control, avoiding the unwanted formation of AuCl$_4^-$. On the basis of NMR spectroscopic, X-ray crystallographic, and density functional theory analyses, we assess the mechanism of formation of the active catalyst and of gold(III)-mediated styrene cyclopropanation with propargyl ester and intramolecular alkoxycyclization of 1,6-enyne. *P,N*-chelated gold(III) complexes are demonstrated to be straightforward to generate and be catalytically active in synthetically useful transformations of complex molecules.
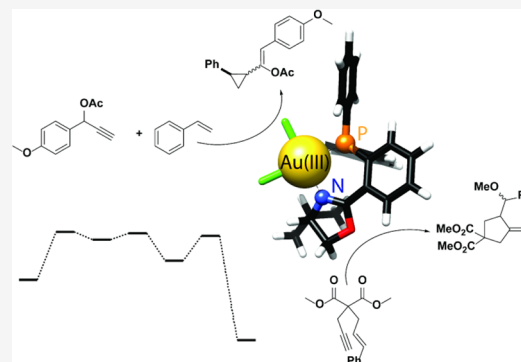
INTRODUCTION

Whereas gold had barely been applied in organic synthesis before the 21st century, over the past 2 decades, gold catalysis has grown into a distinct subfield, with its wide applicability having already been demonstrated.[1−8] In spite of its young age, gold catalysis has provided new organic transformations and has been shown to offer chemoselectivity under mild conditions,[9,10] often with higher tolerance toward moisture and oxygen than the more established transitions metals, such as palladium, platinum, rhodium, cobalt, and nickel. Homogeneous gold(I) catalysts are comparably well-developed and understood,[11] as evidenced by the number of ligated gold(I) complexes in use and by the variety of gold(I)-catalyzed transformations and mechanistic studies available in the literature.[12−18] In contrast, gold(III) catalysis mainly uses the initially developed inorganic gold(III) salts, without a stabilizing ligand.[19,20] The successful development of widely applicable synthetic techniques and access to complex structures has hitherto been demonstrated, yet without a detailed mechanistic understanding.[21−23] A few examples of ligated gold(III) complexes used as catalysts are known and have revealed that ligation provides increased catalyst lifetime and tuneability.[24] These have enabled mechanistic studies that were previously impossible because of the instability of gold chlorides.[25−35] Ligands encompassing phosphorus donor(s) are common in gold(I) catalysis,[6,36−38] which also include *P,N*-chelated gold(I) complexes.[39] However, conventional phosphine ligands have so far scarcely been explored in gold(III) chemistry because phosphorus easily gets oxidized in the presence of gold(III). Indeed, gold(III) salts have been proposed to be "activated" by being reduced to gold(I),

"the catalytically active species", by phosphorus ligands.[40] Phosphorus-based ligands forming more stable gold(III) complexes typically contain one or more phosphines coordinating to a chelated and cyclometalated gold(III), as shown in Figure 1.

Gold(III)-complexing ligands offering a phosphine coordination site along with an additional heteroatomic electron donor
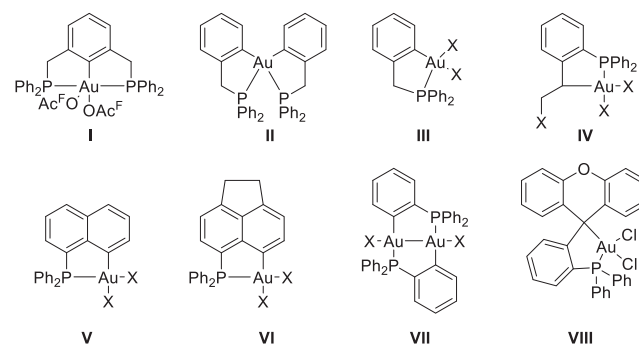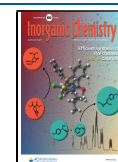

Figure 1. Representative gold(III) phosphine complexes **I**,[41] **II**,[42] **III**,[42] **IV**,[43,44] **V**,[41,45,46] **VI**,[47] **VII**,[48,49] and **VIII**.[50]

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are rare,[51] although the use of *P,N* ligands for gold(III) have allowed the synthesis of organogold(III) complexes and mechanistic studies.[52,53] The mechanism of catalysis with phosphorus-containing gold(III) complexes remains virtually unexplored. Herein, we assess the structure and reactivity of gold(III) complexes of *P,N*-donor ligands with solution NMR spectroscopic, X-ray crystallographic, and computational (density functional theory, DFT) techniques. Capitalizing on the known high affinity of oxazoline nitrogen to gold(III),[34,54,55] the novel *P,N* ligands **1−4** (Figure 2) studied here were designed to possess an alkylated oxazoline linked to an arylphosphine moiety.
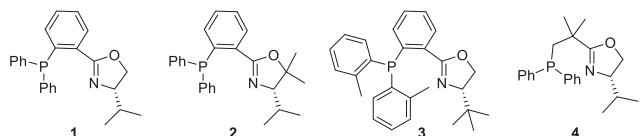

Figure 2. *P,N* ligands for gold(III) coordination studies.

RESULTS AND DISCUSSION

Ligand **1**, (*S*)-2-[2-(diphenylphosphanyl)phenyl]-4-isopropyl-4,5-dihydrooxazole, was used for optimization of gold(III) coordination. Its direct coordination to gold(III) upon mixing with $AuCl_3$ and $AgSbF_6$ in acetonitrile yielded two species (Scheme 1a), as judged from ^1H and ^{31}P NMR. The oxidized phosphine derivative of ligand **1**, (*S*)-[2-(4-isopropyl-4,5-dihydrooxazol-2-yl)phenyl]diphenylphosphine oxide (**1′**; ^{31}P NMR δ 40.5), was identified as the main product using ^{31}P NMR, whereas [**1**-Au(III)]SbF_6 (^{31}P NMR δ 34.7), the target gold(III) complex, is the minor one. Altering the order of $AuCl_3$ and $AgSbF_6$ addition to the ligand, the ratio of **1′** and [**1**-Au(III)]SbF_6 was modulated (2.5:1 to 4:1); see Table S1 for details. Simultaneous addition of the gold and silver salts facilitated phosphorus oxidation to a larger extent than the initial addition of $AuCl_3$, before the addition of $AgSbF_6$. Coordinating under an inert atmosphere, using dry acetonitrile, changing the gold(III) source to $KAuCl_4$, or using dichloromethane as the solvent instead of acetonitrile did not improve the product/byproduct ratio in noteworthy manner. Attempts at gold(III)

Scheme 1. Preparation of Complexes 1−4-Au(III)]SbF$_6$ (a) Directly from Ligands 1−4, AuCl$_3$, and AgSbF$_6$ and (b−d) via Oxidation of 1−4-Au(I) Complexes
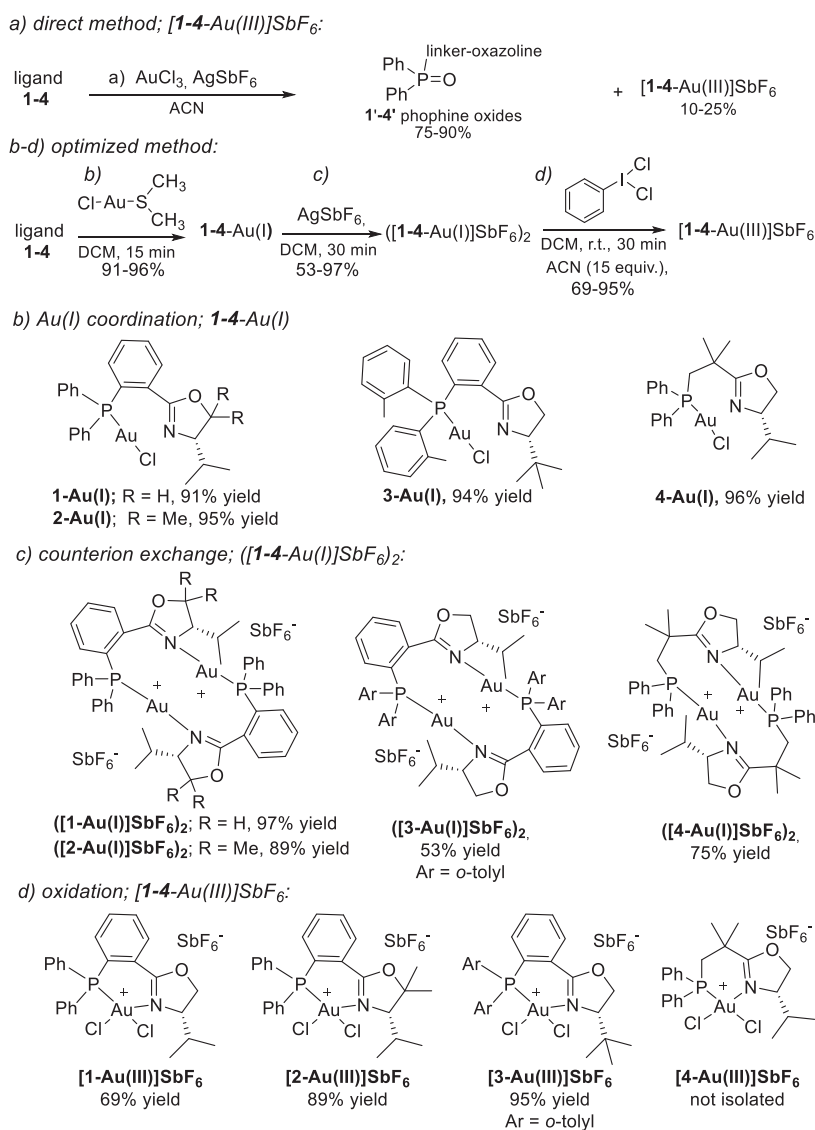
Table 1. Experimental $\delta^{15}N$, $\Delta\delta^{15}N_{coord}$, $\delta^{31}P$, and $\Delta\delta^{31}P_{coord}$ NMR Chemical Shifts (ppm) in CD_2Cl_2[a]

complex	$\delta^{15}N_{complex}$	$\delta^{15}N_{ligand}$	$\Delta\delta^{15}N_{coord}$	$\delta^{31}P_{complex}$	$\delta^{31}P_{ligand}$	$\Delta\delta^{31}P_{coord}$
1-Au(I)	−129.9	−141.3	11.4	33.6	−5.5	39.1
	−140.7	*−149.1*	*8.4*	*7.3*	*−14.6*	*21.9*
2-Au(I)	−127.0	−138.6	11.6	33.4	−5.4	38.8
	−133.6	*−141.8*	*8.2*	*5.8*	*−15.6*	*21.4*
3-Au(I)	−126.7	−141.4	14.7	13.0	−22.0	35.0
	−140.0	*−148.5*	*8.5*	*−14.8*	*−27.6*	*12.8*
4-Au(I)	−149.2	−154.9	5.7	21.4	−23.2	44.6
	−161.8	*−166.3*	*4.5*	*−9.6*	*−34.2*	*24.6*
([**1**-Au(I)]SbF$_6$)$_2$	−161.7	−141.3	−20.4	27.9	−5.5	33.5
	−190.8	*−149.1*	*−41.7*	*7.9*	*−14.6*	*22.5*
([**2**-Au(I)]SbF$_6$)$_2$	−171.1	−138.6	−32.5	21.3	−5.4	26.7
	−190.1[b]	*−141.8*	*−48.3[b]*	*6.6[b]*	*−15.6*	*22.3[b]*
([**3**-Au(I)]SbF$_6$)$_2$	−171.1	−141.4	−29.7	16.7	−22.0	38.7
	−201.2[b]	*−148.5*	*−52.7[b]*	*−19.0[b]*	*−27.6*	*8.6[b]*
([**4**-Au(I)]SbF$_6$)$_2$	*c*	−154.9	*c*	21.5	−23.2	44.7
	−211.1[d]	*−166.3*	*−44.8[d]*	*−10.4[d]*	*−34.2*	*23.7[d]*
[**1**-Au(III)]SbF$_6$	−222.9	−141.3	−81.6	34.7	−5.5	40.2
	−230.2	*−149.1*	*−81.1*	*37.6*	*−14.6*	*52.2*
[**2**-Au(III)]SbF$_6$	−228.4	−138.6	−89.8	33.8	−5.4	39.2
	−229.2	*−141.8*	*−87.4*	*37.3*	*−15.6*	*53.0*
[**3**-Au(III)]SbF$_6$	−228.3	−141.4	−86.9	29.3	−22.0	51.2
	−235.1	*−148.5*	*−86.6*	*31.4*	*−27.6*	*59.0*
[**4**-Au(III)]SbF$_6$	−213.8	−154.9	−58.9	27.0	−23.2	60.2
	−223.5	*−166.3*	*−57.2*	*40.2*	*−34.2*	*74.4*

[a]Corresponding computed quantities are shown in italic. [b]Values obtained with structures optimized without solvent effects; see the Supporting Information for more information. [c]Not available because of poor solubility. [d]Values corresponding to the antarafacial conformer, averaging the two distinct nitrogen signals. See the Supporting Information for more information.

coordination to ligands **2**−**4** in an analogous manner afforded the phosphine oxides **2′**−**4′** as the main products.

We developed a protocol that exploits the lesser tendency of gold(I) to oxidize phosphorus, thereby avoiding competing phosphorus oxidation by gold(III) when generating [**1**-Au-(III)]SbF$_6$. Hence, we initially prepared the **1**-Au(I) phosphine complex and subsequently oxidized it to [**1**-Au(III)]SbF$_6$ (Scheme 1b−d). The preparation of ligated gold(III) complexes by the oxidation of gold(I) complexes with dichloro(phenyl)-λ^3-iodane[56−58] or Br$_2$[59−62] was previously proven to be efficient. The **1**-Au(I) complex was prepared in quantitative yields by mixing chloro(dimethyl sulfide)-Au(I) and ligand **1** in dichloromethane (Scheme 1b). The preference of gold(I) to coordinate to phosphine instead of the oxazoline nitrogen was suggested by the $\Delta\delta^{31}P_{coord}$ = 39.1 ppm and $\Delta\delta^{15}N_{coord}$ = 11.4 ppm, observed by ^{31}P and ^{15}N NMR, respectively (Table 1). Gold(III) coordination of oxazolines causes $\Delta\delta^{15}N_{coord}$ = −40 to −76 ppm.[34,54] The observed small and positive $\Delta\delta^{15}N_{coord}$ = 11.4 ppm upon coordination is hence most likely an indirect effect and not a consequence of the formation of a gold(I)−nitrogen secondary bond. This hypothesis is corroborated by DFT, predicting a 8.4 ppm coordination shift for **1**-Au(I) (Scheme 1b). Counterion exchange from Cl$^-$ to the weakly coordinating SbF$_6^-$ was performed by the addition of AgSbF$_6$ to **1**-Au(I) in dichloromethane (Scheme 1c). The anion exchange was successful in both the absence and presence of acetonitrile (3 equiv), with the latter having been explored to evaluate whether a Lewis basic solvent may facilitate the process by charge stabilization (for details, see Figure S2). The lack of acetonitrile coordination to gold(I) throughout the process was confirmed by the observation of $\Delta\delta^{15}N$ = 0 ppm on the acetonitrile nitrogen.

For the oxazoline of **1**-Au(I) after anion exchange, a moderate $\Delta\delta^{15}N_{coord}$ = −20.4 ppm (Table 1) was observed. This is ∼20 ppm smaller than that reported for the oxazoline nitrogen of a bidentate gold(III) complex[34] and accordingly may reflect weak gold(I) coordination. Following anion exchange, the charge of gold(I) is, hence, rather stabilized by oxazoline coordination through dimerization to ([**1**-Au(I)]SbF$_6$)$_2$ (Scheme 1c), instead of acetonitrile coordination yielding [**1**-Au(I)-ACN]SbF$_6$. Coordination to the nearby oxazoline nitrogen intramolecularly is unfeasible: the ([**1**-Au(I)]SbF$_6$)$_2$ dimer is 105.7 kcal/mol lower in energy, according to DFT, than the corresponding monomer possessing an intramolecular gold(I)−oxazoline nitrogen coordinative bond (2 × [**1**-Au(I)]SbF$_6$).

The gold(I) complexes of ligands **2**−**4** were prepared following the procedure described for ligand **1**, yielding **2**-Au(I)−**4**-Au(I) in comparable yields (94−96%; Scheme 1b). The ([**2**-Au(I)]SbF$_6$)$_2$ and ([**3**-Au(I)]SbF$_6$)$_2$ complexes were subsequently obtained by anion exchange of **2**-Au(I) and **3**-Au(I) with AgSbF$_6$, as confirmed by the observation of $\Delta\delta^{31}P_{coord}$ and $\Delta\delta^{15}N_{coord}$ comparable to those of ([**1**-Au(I)]-SbF$_6$)$_2$ (Table 1). Similar to that observed for the anion exchange of **1**-Au(I), the addition of acetonitrile had no effect, as judged by ^1H and ^{15}N NMR, not even for the more sterically hindered complex **3**-Au(I). Anion exchange of the most flexible **4**-Au(I) complex, lacking an aromatic bridge between the phosphine and oxazoline units, was more difficult in terms of poorer solubility and slightly more unstable after anion exchange.

The plausible structures of the monomeric and dimeric complexes were assessed by DFT and are discussed here for the complexes of ligand **1**. The monomeric complex may have three possible geometries, as shown in Figure 3a−c, of which two, a
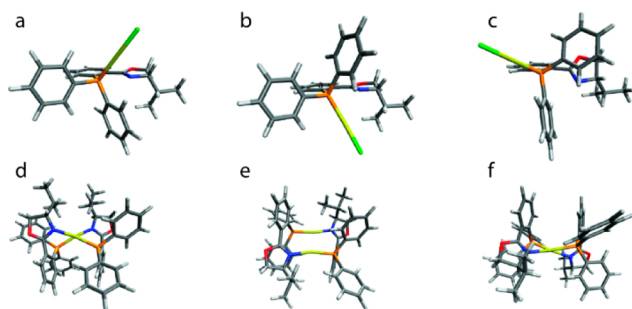
Figure 3. DFT-computed low-energy geometries of (a−c) **1**-Au(I) and (d−f) ([**1**-Au(I)]$^+$)$_2$.

Figure 4. Solid-state geometries of (a) ([**4**-Au(I)]SbF$_6$)$_2$, (b) [**1**-Au(III)]SbF$_6$, (c) [**2**-Au(III)]SbF$_6$, and (d) [**3**-Au(III)]SbF$_6$ obtained by X-ray crystallographic analyses. Counterion and hydrogens are omitted for clarity.

and b, are isoenergetic, whereas the third, c, is slightly higher in energy (3.8 kcal/mol). Upon dimerization, the two low-energy monomers may combine into three possible geometries, as shown in Figure 3d−f, in which the isopropyl functionalities are either suprafacial (d and f) or antarafacial (e). Because of their symmetry, dimers d and f are expected to give a single set of NMR signals, compatible with our experimental observations, whereas geometry e is anticipated to provide two sets of signals and can therefore be excluded. Because of the high energy of the nitrogen−gold(I) and phosphorus−gold(I) bonds, rapid interconversion between various dimeric forms is unlikely. The DFT-predicted ^{31}P and ^{15}N NMR chemical shifts of these geometries (d-f) are in agreement with those obtained experimentally (Table 1; for details, see the Supporting Information). The accurate prediction of the NMR chemical shifts of heteroatoms, such as ^{15}N, remains a challenge, and dozens of parts per million deviations are common.[63,64] DFT systematically underestimates the nitrogen shifts, in a consistent manner. There is a systematic error for ^{31}P NMR estimation as well, with the only difference being that the calculated chemical shifts of the products, [**1**−**3**-Au(III)]SbF$_6$, are slightly over-estimated. The accuracy of the chemical shift prediction was not improved significantly upon the introduction of a correction factor using a reference.[65] Importantly, all coordination shifts for both ^{15}N and ^{31}P NMR follow the same trend for all four ligands.

We attempted to grow single crystals for X-ray analysis for all of the Au(I) complexes of ligands **1**−**4** by slow diffusion of *n*-pentane into a dichloromethane solution of the complexes, which gave suitable crystals for ([**4**-Au(I)]SbF$_6$)$_2$ (Figure 4a). Its X-ray analysis confirmed the preference of formation of a dimeric gold(I) complex, after anion exchange (Figure 4a), corroborating the NMR- and DFT-based structural proposals. The positive charge of each of the two phosphorus−gold(I) units is stabilized in this complex by the oxazoline nitrogen of the opposite unit. The observed $\Delta\delta^{15}$N$_{coord}$ values for the oxazoline nitrogen of the ([**1**−**3**-Au(I)]SbF$_6$)$_2$ complexes (Table 1) are in agreement with those back-calculated for the X-ray structure.

The oxidation of [**1**−**4**-Au(I)]SbF$_6$ with dichloro(phenyl)-λ^3-iodane in dichloromethane (Scheme 1d) took place directly, as indicated by an immediate change of the solution from colorless to strong yellow. The oxidation was confirmed by ^{1}H and ^{31}P NMR monitoring of the reaction mixture of ([**1**-Au(I)]SbF$_6$)$_2$ following the addition of dichloro(phenyl)-λ^3-iodane. This reaction yielded two complexes, as indicated by ^{31}P NMR (Figure S1). The complex with the lowest δ^{31}P = 24.3 ppm was assigned to an intermediate that slowly converted into [**1**-Au(III)]SbF$_6$. The latter gold(III) complex possessed δ^{31}P = 34.7 ppm, comparable to the calculated δ^{31}P = 37.7 ppm for the [**1**-Au(III)]SbF$_6$ complex. The interconversion of the inter-
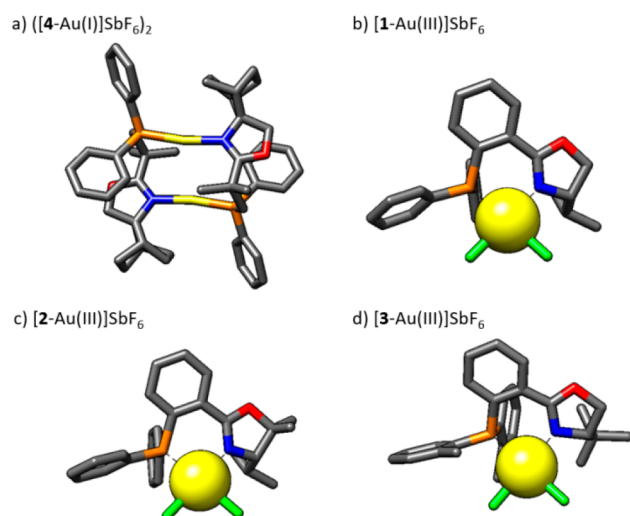
mediate is slow, and approximately 40% remained even after 2 days of reaction. We propose the intermediate to be the oxidized square-planar dimeric gold(III) complex ([**1**-Au(III)]SbF$_6$)$_2$ (Figure 5b), with two chlorides, generated by dichloro-

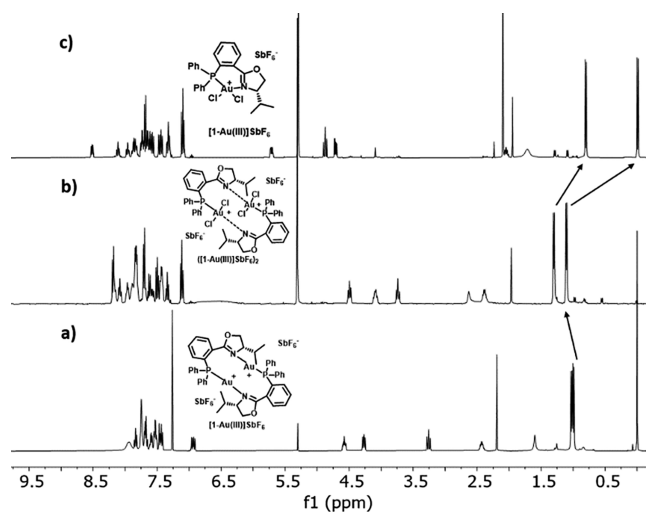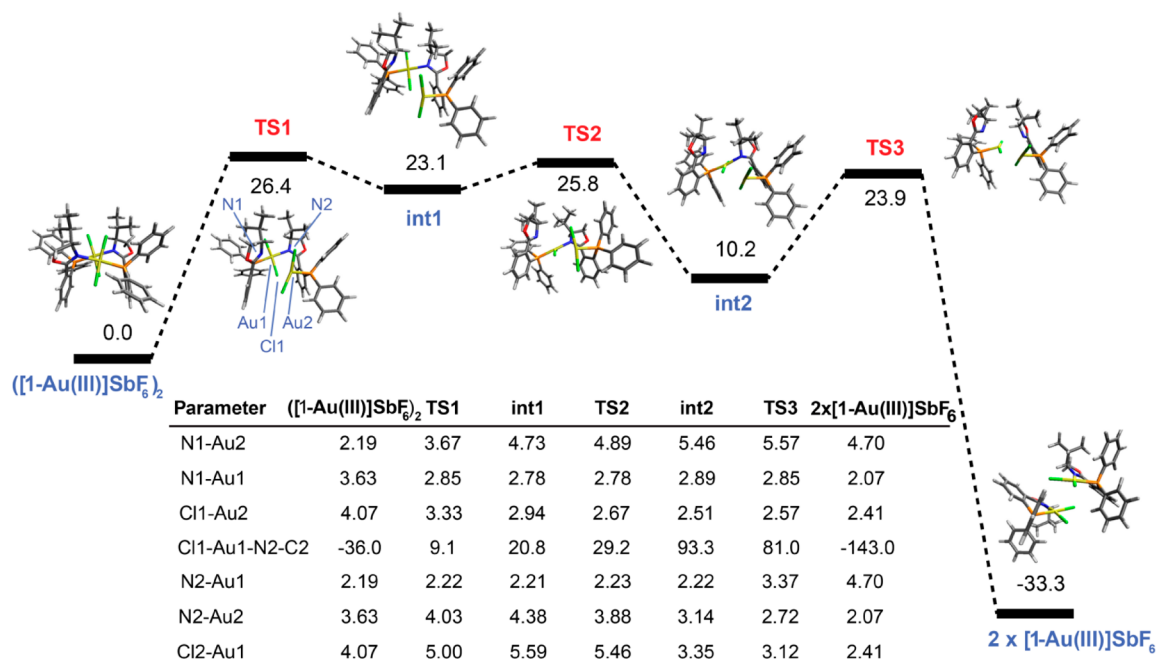**Figure 5.** ^{1}H NMR monitoring of the oxidation of ([**1**-Au(I)]SbF$_6$)$_2$ to [**1**-Au(III)]SbF$_6$ in dichloromethane-d_2: (a) ([**1**-Au(I)]SbF$_6$)$_2$; (b) intermediate ([**1**-Au(III)]SbF$_6$)$_2$, formed directly after the addition of dichloro(phenyl)-λ^3-iodane; (c) following full conversion into complex [**1**-Au(III)]SbF$_6$.

(phenyl)-λ^3-iodane oxidation, added in a *trans* manner. This geometry is energetically feasible, as predicted by DFT. Analogous stability differences of the *cis* and *trans* orientations of chlorides, favoring the *trans* orientation, have previously been reported for the gold(III)[56] and palladium(II)[66] complexes. The dynamic nature of the complex ([**1**-Au(III)]SbF$_6$)$_2$ was indicated by the inability to observe the δ^{15}N of this complex, even at high concentration and with prolonged experiments. The smaller $\Delta\delta^1$H of the oxazoline protons of ([**1**-Au(III)]-SbF$_6$)$_2$ than those of [**1**-Au(III)]SbF$_6$ (Figure 5a−c) suggests,

Scheme 2. Computed Gibbs Free Energy Profile (ΔG in kcal/mol) of the Proposed Mechanism for Formation of $[1\text{-Au(III)}]SbF_6$ from $([1\text{-Au(III)}]SbF_6)_2$[a]

Parameter	$([1\text{-Au(III)}]SbF_6)_2$	TS1	int1	TS2	int2	TS3	$2\times[1\text{-Au(III)}]SbF_6$
N1-Au2	2.19	3.67	4.73	4.89	5.46	5.57	4.70
N1-Au1	3.63	2.85	2.78	2.78	2.89	2.85	2.07
Cl1-Au2	4.07	3.33	2.94	2.67	2.51	2.57	2.41
Cl1-Au1-N2-C2	-36.0	9.1	20.8	29.2	93.3	81.0	-143.0
N2-Au1	2.19	2.22	2.21	2.23	2.22	3.37	4.70
N2-Au2	3.63	4.03	4.38	3.88	3.14	2.72	2.07
Cl2-Au1	4.07	5.00	5.59	5.46	3.35	3.12	2.41

[a]The rate-determining step is proposed to be the first gold(III)−nitrogen bond dissociation from $([1\text{-Au(III)}]SbF_{6)2}$ to **int1**. Relevant structural parameters are reported as a table within the scheme (bond lengths are given in angstroms, and angles are given in degrees), with the labels shown only on the **TS1** structure for clarity. Details of the DFT calculations as well as the Gibbs free energy profile obtained with the M06 functional for comparison are given in the Supporting Information.

however, that the oxazoline of the intermediate coordinates more weakly to gold(III).

On the basis of the above observations, the first step toward the generation of $[1\text{-Au(III)}]SbF_6$ is formation of the dimeric $([1\text{-Au(I)}]SbF_6)_2$ from **1-Au(I)**. DFT predicts $([1\text{-Au(I)}]\text{-}SbF_6)_2$ to be 105.7 kcal/mol lower in energy than the corresponding monomers, explaining the exclusive existence of the dimeric form in solution. Whereas this complex could not be crystallized, the analogous dimeric form was observed by X-ray diffraction for the corresponding $([4\text{-Au(I)}]SbF_6)_2$. Upon oxidation, $([1\text{-Au(I)}]SbF_6)_2$ is converted into the dimeric gold(III) complex, $([1\text{-Au(III)}]SbF_6)_2$, which we conceivably detected by NMR (Figure 5b). Direct dissociation of the $([1\text{-Au(III)}]SbF_6)_2$ dimer into $trans\text{-}[1\text{-Au(III)}]SbF_6$ is unfeasible, requiring ∼60 kcal/mol activation energy according to DFT, because it would involve the simultaneous breaking of two gold(III)−nitrogen coordinative bonds. This can only be feasible if it happens in a stepwise fashion, accompanied by transformations that compensate for the energy loss. A feasible route for this transformation, as shown in Scheme 2, is initiated with the breakage of one nitrogen−gold(III) coordinative bond (going from 2.19 to 3.67 Å in **TS1**), which, according to DFT, necessitates 26.4 kcal/mol activation energy. Following a slight rotation of the oxazoline group, the "free" nitrogen weakly coordinates to the second gold(III), with a nitrogen−gold(III) bond distance of 2.78 Å, such that a local energy minimum is reached upon formation of the intermediate **int1**. The latter possesses one tetracoordinated and another tricoordinated gold(III). Because of the unfavorable tricoordination of one of the two gold(III) centers, **int1** is fairly unstable and is thus at 23.1 kcal/mol higher energy compared to $([1\text{-Au(III)}]SbF_6)_2$. The reaction continues, with the latter gold(III) getting

stabilized by coordination to one of the chlorides of the other gold(III), requiring a bond rotation that passes a 2.7 kcal/mol energy barrier (**TS2**), and that provides an overall 13.1 kcal/mol energetic gain. This step can be appreciated by the corresponding gold(III)−chlorine bond shortening from 2.94 Å in **int1** to 2.51 Å in **int2** and the torsional angle centered on the second nitrogen−gold(III) bond going from 20.8° to 93.3°. This second intermediate is converted into $[1\text{-Au(III)}]SbF_6$ upon breakage of the remaining nitrogen−gold(III) bond, which necessitates 13.7 kcal/mol activation energy (**TS3**) and is followed by a series of events providing an overall 57.2 kcal/mol energy gain. This transformation is thus irreversible. The lower barrier (13.7 kcal/mol) compared to the first nitrogen−gold(III) bond breaking (26.4 kcal/mol) is due to the simultaneous formation of a gold(III)−chlorine bond with the chloride anion of the other gold(III), triggering a barrierless chlorine exchange between the monomers and terminating in the product. The table included in Scheme 2 illustrates the chloride exchange, where the Cl1−Au2 and Cl2−Au1 distances change from 4.07 Å (hence, part of the different monomers) to 2.41 Å. The large energetic gain of 57.2 kcal/mol originates mainly from the *trans*-to-*cis* isomerization of the chlorides bound to each gold(III) and from the formation of two new gold(III)−nitrogen bonds (see the N1−Au1 and N2−Au2 bond distances in Scheme 2). The energetic gain for the $([1\text{-Au(III)}]SbF_6)_2$-to-$[1\text{-Au(III)}]SbF_6$ transformation, through a route that, following the first activation barrier, lacks high-laying transition states, is overall −33.3 kcal/mol. The rate-determining step is dissociation of the intermediate $([1\text{-Au(III)}]SbF_6)_2$ dimer into a half-opened dimer, a step that is predicted by DFT to require 26.4 kcal/mol energy. This is in agreement with the long time required (12 h) to obtain the products following gold oxidation

as well as by 40% of the intermediate complex remaining even 2 days of reaction. It should be noted that the continuously altering environment of the oxazoline nitrogen atoms throughout the transformation explains the difficulty to detect an $^1H-^{15}N$ HMBC cross-peak for any intermediate(s).

The addition of small amounts of acetonitrile accelerates the oxidation, facilitating the formation of the target $[\mathbf{1}\text{-Au(III)}]$-$SbF_6$. Accordingly, full conversion to $[\mathbf{1}\text{-Au(III)}]SbF_6$ was reached within 12 h in the presence of 0.5 equiv of acetonitrile but in less than 30 min in the presence of 15 equiv. Acetonitrile complexation to $\mathbf{1}$-Au(I) offers 43.2 kcal/mol energetic gain, according to DFT, likely providing a feasible low-energy route toward $([\mathbf{1}\text{-Au(I)}]SbF_6)_2$. The latter dimer is 19.4 kcal/mol lower in energy compared to 2 equiv of $[\mathbf{1}\text{-Au(I)-ACN}]^+$, and the acetonitrile complex of $\mathbf{1}$-Au(I) formed upon chloride abstraction. Acetonitrile may also facilitate dissociation of the gold(III)−nitrogen bonds of the dimeric $([\mathbf{1}\text{-Au(III)}]SbF_6)_2$. Metal−halogens may participate in halogen bonding,[67] which is capable of activating the metal−halogen bond, for example, in gold(I) complexes.[68] Motivated by this observation, we prepared $[\mathbf{1}\text{-Au(III)}]SbF_6-[\mathbf{3}\text{-Au(III)}]SbF_6$ by dichloro-(phenyl)-λ^3-iodane oxidation of the corresponding $\mathbf{1}-\mathbf{3}$-Au(I) complexes also in the presence of acetonitrile (Scheme 1d; 69−95% yield). We observed comparable $\Delta\delta^{31}P_{coord}$ for the phosphorus-containing gold(I) and P,N-chelated gold(III) complexes (Table 1). Stronger nitrogen coordination of gold(III) than of gold(I) was seen, as indicated for ligands $\mathbf{1}-\mathbf{3}$ by $\Delta\delta^{15}N_{coord} = -81.6$ to -89.8 ppm of the former complexes compared to $\Delta\delta^{15}N_{coord} = -20.4$ to -32.5 ppm of the latter complexes. These coordination shifts are in line with those predicted by DFT (Table 1).

The oxidation of $([\mathbf{4}\text{-Au(I)}]SbF_6)_2$ gave the unstable $[\mathbf{4}\text{-Au(III)}]SbF_6$ complex along with 30% byproducts. This complex, in contrast to the analogous complexes of $\mathbf{1}-\mathbf{3}$, decomposed within 1 day in solution. Counterion exchange of $\mathbf{4}$-Au(I) was also difficult and is likely due to the lack of a rigid aromatic linker in this ligand (Scheme 1c). The $[\mathbf{4}\text{-Au(III)}]SbF_6$ complex was therefore not isolated but used directly in catalytic activity studies.

Slow diffusion of n-pentane into dichloromethane solutions of the $\mathbf{1}-\mathbf{4}$-Au(III)SbF$_6$ complexes provided single crystals for all but the $[\mathbf{4}\text{-Au(III)}]SbF_6$ complex. X-ray analyses confirmed the bidentate P,N-coordination of the phosphine oxazoline ligands $\mathbf{1}-\mathbf{3}$, yielding P,N-chelated gold(III) complexes (Figure 4b−d). We observed a notable *trans* effect on the chloride anions of $\mathbf{1}-\mathbf{3}$-Au(III)SbF$_6$ complexes, 2.2619(12) and 2.3408(12) Å *trans* to nitrogen and phosphorus, respectively.

We evaluated the catalytic ability of the gold(I) and gold(III) complexes using the established model reactions cyclopropanation of styrene with propargyl ester[55,68−70] and intramolecular alkoxycyclization of 1,6-enyne[34,40,69−74] (Table 2). All gold(I) and gold(III) complexes showed catalytic activity in both transformations. The gold(III) complexes showed a generally higher reactivity in cyclopropanation than in alkoxycyclization. Whereas the gold(III) complexes gave faster conversion compared to the gold(I) complexes in cyclopropanation, we observed the opposite trend for alkoxycyclization. When the reactions for both gold(I) and gold(III) complexes of ligand $\mathbf{1}$ were monitored with ^1H, ^{31}P, and ^{15}N NMR, similar routes of catalyst activation were detected. Hence, the dimer $([\mathbf{1}\text{-Au(I)}]SbF_6)_2$ is activated by gold(I)−nitrogen bond cleavage, with the resulting complex being stable throughout the reaction. Whereas the reaction could be followed by ^{31}P NMR, the ^{15}N

Table 2. Reactivity of Gold(I) and Gold(III) Complexes Evaluated in Alkoxycyclization Reaction of a 1,6-Enyne and Cyclopropanation of Styrene with Propargyl Ester

a)

b)
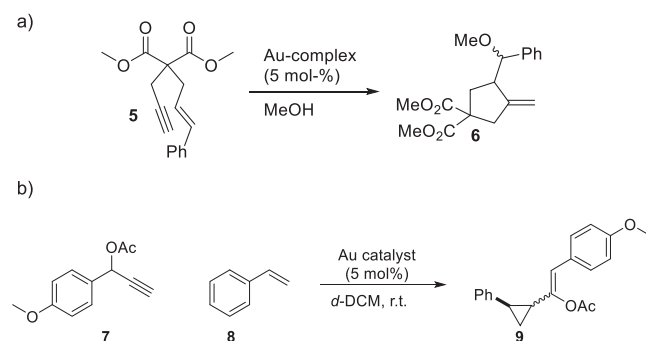
entry	complex	reaction time	yield of **6** (%)
(a) Alkoxycyclization of a 1,6-Enyne			
1	$([\mathbf{1}\text{-Au(I)}]SbF_6)_2$	<2.5 h	70
2	$[\mathbf{1}\text{-Au(III)}]SbF_6$	overnight	20
3	$([\mathbf{2}\text{-Au(I)}]SbF_6)_2$	overnight	72
4	$[\mathbf{2}\text{-Au(III)}]SbF_6$	overnight	16
5	$([\mathbf{3}\text{-Au(I)}]SbF_6)_2$	3 h	52
6	$[\mathbf{3}\text{-Au(III)}]SbF_6$	overnight	14
7	$([\mathbf{4}\text{-Au(I)}]SbF_6)_2$	overnight	78
8	$[\mathbf{4}\text{-Au(III)}]SbF_6$	overnight	34

entry	complex	reaction time	yield (%) of **9** (*cis:trans*)
(b) Cyclopropanation			
9	$([\mathbf{1}\text{-Au(I)}]SbF_6)_2$	3 h	95 (37:63)
10	$[\mathbf{1}\text{-Au(III)}]SbF_6$	30 min	88 (25:75)
11	$([\mathbf{2}\text{-Au(I)}]SbF_6)_2$	overnight	51 (16:84)
12	$[\mathbf{2}\text{-Au(III)}]SbF_6$	1 h	79 (23:77)
13	$([\mathbf{3}\text{-Au(I)}]SbF_6)_2$	overnight	54 (15:85)
14	$[\mathbf{3}\text{-Au(III)}]SbF_6$	1.5 h	93 (75:25)
15	$([\mathbf{4}\text{-Au(I)}]SbF_6)_2$	overnight	61 (11:89)
16	$[\mathbf{4}\text{-Au(III)}]SbF_6$	15 min	79 (48:52)

NMR chemical shifts could not be detected using $^1H-^{15}N$ HMBC, for neither the gold(I)- nor gold(III)-mediated reactions. The ^1H NMR chemical shift changes of the i-Pr group of $[\mathbf{1}\text{-Au(III)}]SbF_6$ throughout the reaction suggest that the oxazoline nitrogen gets decoordinated. Hence, deshielding of up to 1 ppm of the i-Pr methyl, which has been observed for this system upon coordination of the oxazoline to gold(III) and consequent orientation of a phenyl ring, is absent for this complex. ^{31}P NMR monitoring revealed gold−phosphorus bond cleavage during the reaction progress, leading to oxidized phosphorus. This indicates a higher affinity of both gold(I) and gold(III) to phosphorus than to nitrogen. However, differences in the relative reaction rates suggest that the catalytically active species are different when starting from $([\mathbf{1}\text{-Au(I)}]SbF_6)_2$ and $[\mathbf{1}\text{-Au(III)}]SbF_6$. None of the complexes provide enantioselectivity despite the chiral nature of the ligand.

■ CONCLUSION

P,N-chelated gold(III) complexes are introduced as homogeneous catalysts. We show that these can be generated via a new method, based on the oxidation of gold(I) to gold(III) complexes. This, in contrast to their direct synthesis by ligand coordination to AuCl$_3$, circumvents the critical phosphine ligand oxidation that has hitherto hindered their use and investigation. Our method offers counterion control and, hence, avoids the unwanted formation of AuCl$_4^-$ that is unavoidable upon direct

coordination, further hindering the investigation of phosphorus-containing gold(III) complexes.

By systematic NMR spectroscopic, X-ray crystallographic, and computational assessment of the synthesis of a series of structurally closely related *P,N*-chelated gold(III) complexes, we describe the mechanism of their formation and show it to involve dimeric gold(I) and gold(III) intermediates. The addition of small amounts of acetonitrile was demonstrated to accelerate the formation of catalytically active species. Both the *P,N*-ligated gold(I) and gold(III) complexes are catalytically active in cyclopropanation and in intramolecular alkoxycyclization, with the latter complexes being more efficient in cyclopropanation in terms of the conversion rate and the gold(I) complexes more efficient than the gold(III) complexes in alkoxycyclization. Both gold(I) and gold(III) were observed to have a higher phosphorus than nitrogen affinity, making gold−nitrogen bond cleavage the critical step of the reaction.

Ligated gold(III) complexes, and especially those providing a phosphorus coordination site, are scarce. Having been challenging to obtain, their structures, catalytic activity, and mechanisms of their transformations remain to be explored. This work clears a pathway for the efficient generation and application of phosphorus-containing ligated gold(III) complexes by providing the first fragments of understanding based on spectroscopic, crystallographic, and computational data.

■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02720.

> Details on the synthesis and spectroscopic data for compound identification and on the NMR, computational, and X-ray diffractometric investigations (PDF)

> All calculated DFT structures provided in xyz format (ZIP)

Accession Codes

CCDC 2006132−2006135 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Máté Erdélyi − *Department of Chemistry☒BMC, Uppsala University, 75237 Uppsala, Sweden;* ⓞ orcid.org/0000-0003-0359-5970; Email: mate.erdelyi@kemi.uu.se

Anne Fiksdahl − *Department of Chemistry, Norwegian University of Science and Technology, 7491 Trondheim, Norway;* Email: anne.fiksdahl@ntnu.no

Authors

Ann Christin Reiersølmoen − *Department of Chemistry, Norwegian University of Science and Technology, 7491 Trondheim, Norway;* ⓞ orcid.org/0000-0001-9840-2769

Stefano Battaglia − *Department of Chemistry☒BMC, Uppsala University, 75237 Uppsala, Sweden;* ⓞ orcid.org/0000-0002-5082-2681

Andreas Orthaber − *Ångström Laboratory, Department of Organic Chemistry, Uppsala University, 75120 Uppsala, Sweden;* ⓞ orcid.org/0000-0001-5403-9902

Roland Lindh − *Department of Chemistry☒BMC, Uppsala University, 75237 Uppsala, Sweden;* ⓞ orcid.org/0000-0001-7567-8295

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.inorgchem.0c02720

Notes

The authors declare no competing financial interest.

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