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[{Au(NHC)}$_2$(μ-OH)][BF$_4$]: *Silver-Free* and *Acid-Free* Catalysts for Water-Inclusive Gold-Mediated Organic Transformations

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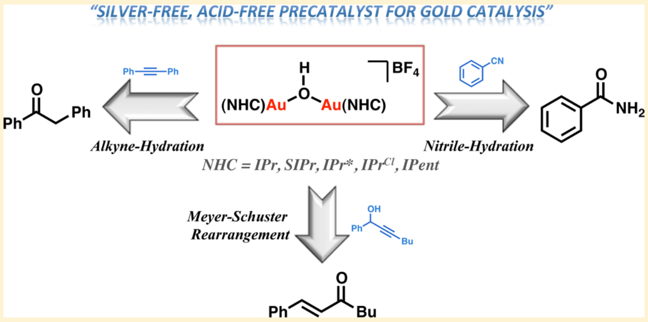
Supporting Information

ABSTRACT: The synthesis of a series of digold hydroxide complexes is reported. These diaurated species, of the formula [{Au(NHC)}$_2$(μ-OH)][BF$_4$] (where NHC = IPr^{Cl}, IPr*, IPent), were easily prepared via the cationic species [Au(NHC)(NCCH$_3$)][BF$_4$] in aqueous media. The catalytic activity of these novel complexes was tested and compared to that of the previously reported IPr and SIPr derivatives. These digold hydroxide species are highly active in water-inclusive organic transformations, such as the alkyne and nitrile hydration reactions, and the Meyer−Schuster rearrangement. One salient feature of these systems is the lack of any additive to induce catalytic activity.

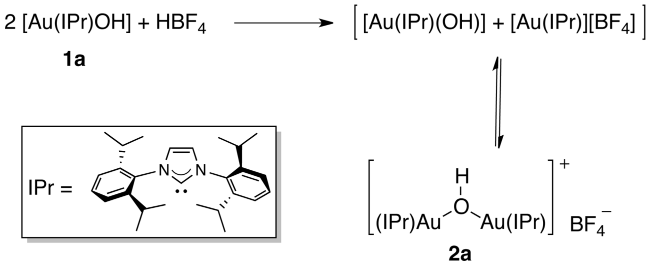


INTRODUCTION

Homogeneous gold catalysis has emerged as one of the most practical and important tools for organic chemists during the last few decades.[1] The success of gold catalysis can be explained by the ability of the gold center to activate C−C multiple bonds, specially alkynes, toward nucleophilic attack.[2] Generally, organogold(I) species are linear, two-coordinate complexes of the formula [Au(L)Cl], where L is a phosphine or *N*-heterocyclic carbene (NHC) ligand.[1] The use of a halide abstractor, usually a silver salt, is necessary in order to generate the active catalyst from Au(I) halide complexes.[1] This procedure has several drawbacks, such as the high price of the silver salt activator, the light sensitivity of these silver salts, and the fact that silver can itself be a catalyst, oftentimes exhibiting a different reactivity profile that can modify the otherwise *gold-only* catalyzed reaction.[3] For these reasons the development of new silver-free protocols has become an important issue in gold catalysis. Our group has recently contributed to this field with the synthesis of the gold hydroxide species [Au(IPr)(OH)] (**1a**), which can be easily activated by an acid, e.g. HBF$_4$ or HSbF$_6$, to generate the active species [Au(IPr)]$^+$.[4] In the course of these studies a diaurated species of the formula [{Au(IPr)}$_2$(μ-OH)][BF$_4$] (**2a**) was discovered (Scheme 1).[4a]

Dinuclear organogold species, such as *gem*-diaurated compounds or σ,π-diaurated acetylide complexes, have recently attracted increased attention as key intermediates in gold-catalyzed reactions.[5] A number of research groups have targeted the study and isolation of such species.[6] We have recently reported that **2a** can be used to gain access to both types of complexes, *gem*-diaurated and σ,π-acetylides, in a straightforward manner from aryl- and vinylboronic acids and terminal alkynes, respectively.[7]

Scheme 1. Reaction Sequence Leading to the Formation of the Diaurated Species 2a



To the best of our knowledge, only a handful of digold hydroxide complexes of the formula [{Au(L)}$_2$(μ-OH)][X] have been reported to date (Figure 1). We have reported the synthesis and characterization of **2a** and [{Au(SIPr)}$_2$(μ-OH)][BF$_4$] (**2b**), while Maier et al. have most recently disclosed the synthesis of two diaurated complexes bearing Buchwald-type phosphine ligands and [{Au(IMes)}$_2$(μ-OH)][BF$_4$].[8] Up until now, only the catalytic activity of the IPr derivative **2a** has been studied.[4a,b,9] This diaurated complex has proven to be highly active in a number of water-inclusive gold-catalyzed transformations, such as alkyne hydration, nitrile hydration, and the Meyer−Schuster rearrangement, all being conducted without any additives to induce catalyst activation.[4a,b,9] With these early results in hand, we now expand the library of diaurated hydroxide complexes and test their catalytic activity in order to illustrate the feasibility of silver-free, acid-free gold-catalyzed methodologies. Herein we report the synthesis of three new [{Au(NHC)}$_2$(μ-OH)][BF$_4$] complexes bearing IPr^{Cl} (**2c**),

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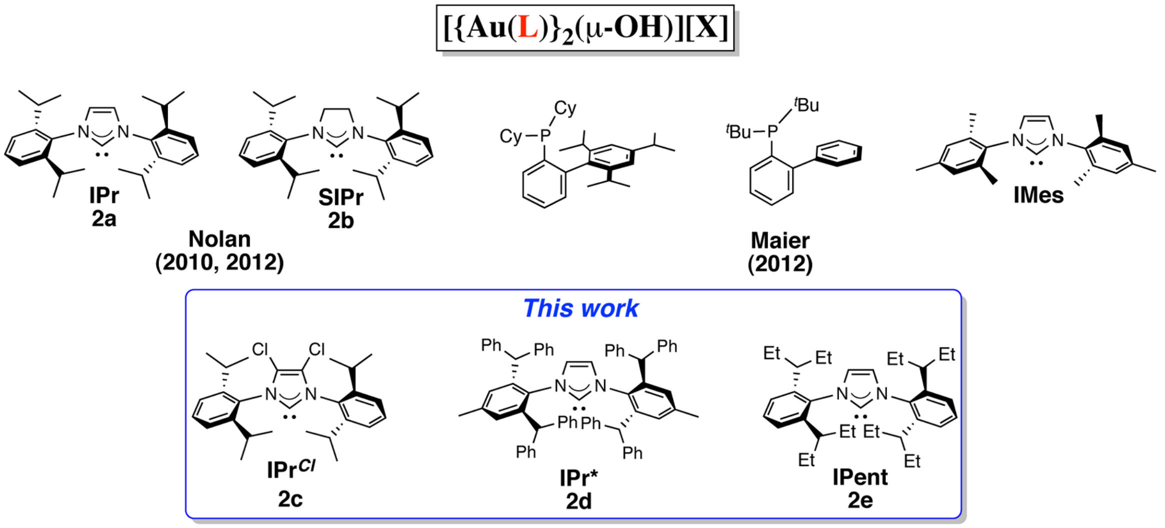
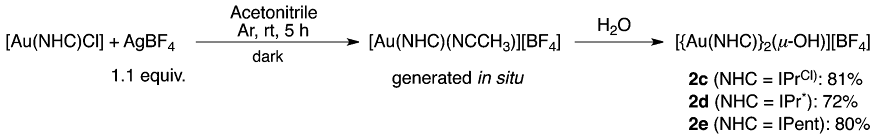


Figure 1. [$\{Au(L)\}_2(\mu\text{-}OH)$][X] (L = NHC, PR_3) complexes reported to date.

Scheme 2. Synthesis of Digold Complexes 2c−e



IPr* (**2d**), and IPent (**2e**) ligands[10] and a study of their respective catalytic activity in several gold-catalyzed transformations which permits a comparison to that of the previously reported IPr (**2a**) and SIPr (**2b**) derivatives.

■ RESULTS AND DISCUSSION

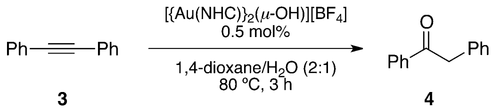
There are two main routes for the synthesis of [$\{Au(NHC)\}_2$(μ-OH)][BF_4] complexes: (a) reaction of [Au(NHC)(OH)] with 0.5 equiv. of a strong acid, such as HBF_4,[4a,9] and (b) chloride abstraction from [Au(NHC)Cl] by a silver salt, e.g. $AgBF_4$, in acetonitrile, forming the corresponding [Au(NHC)($NCCH_3$)][BF_4] complex in situ, and subsequent addition of water.[11] For synthetic purposes the route used in the present study was the latter methodology. According to this procedure the following complexes were obtained in good yields: [$\{Au(IPr^{Cl})\}_2$(μ-OH)][BF_4] (**2c**; 81%), [$\{Au(IPr^*)\}_2$(μ-OH)][BF_4] (**2d**; 72%), and [$\{Au(IPent)\}_2$(μ-OH)][BF_4] (**2e**; 80%) (Scheme 2). The diaurated nature of complexes **2c**−**e** was confirmed by ^1H and ^{13}C NMR spectroscopy as well as by elemental analysis. Compounds **2c**,**e** present the characteristic OH resonance between 0 and 1 ppm in ^1H NMR spectrum, while for the IPr* derivative **2d** a significant shift toward higher fields can be observed (−0.74 ppm). This shift may be due to the high steric hindrance provided by the IPr* ligand.

As [$\{Au(NHC)\}_2$(μ-OH)][BF_4] complexes have been postulated as possible catalytic intermediates for gold-catalyzed water-inclusive transformations, their activity was tested in alkyne and nitrile hydration, as well as in the Meyer−Schuster rearrangement. In order to confirm their utility as a source of [$Au(IPr)]^+$ when activated by an acid, their catalytic activity was also investigated in the rearrangement of allylic acetates.

Alkyne Hydration. The hydration of alkynes to obtain carbonyl derivatives represents one of the most environmentally friendly and atom-economical procedures for the formation of C═O bonds.[12] The importance of this reaction is related to the significant impact of the carbonyl motif in organic synthesis.[13,14] Alkyne hydration can be catalyzed either by Brønsted acids or by a variety of transition-metal complexes.[15] Among the latter, organogold species stand out as some of the most efficient and milder catalysts.[4f,16] In 2002, Tanaka et al. reported the first gold(I)-catalyzed alkyne hydration using [$Au(PPh_3)(Me)$] (0.1−1.0 mol %) and 50% sulfuric acid in methanol as the catalytic system.[16a] Despite the efficiency of this groundbreaking methodology, the use of such large quantities of a strong acid was bothersome. In 2008, we reported the hydration of alkynes at very low catalyst loadings (10−1000 ppm) using [Au(IPr)Cl]/$AgSbF_6$ in a mixture of 1,4-dioxane and H_2O as the catalytic system.[16c] This novel procedure replaced the use of concentrated solutions of strong acids for a stoichiometric amount (relative to the catalyst) of a silver salt to activate the gold complex. In 2009, Corma et al. reported the first acid-free, silver-free gold(I)-catalyzed alkyne hydration using Gagosz-type complexes[17] [$Au(L)(NTf_2)$] (where L = SPhos, PPh_3, P^tBu_3) at room temperature.[16d] Despite the milder reaction conditions, this new methodology required the use of higher catalyst loadings (0.5−5 mol %) and longer reaction times.[16d] With the aim of developing new silver-free protocols, we have recently reported the use of gold hydroxide **1a** activated by an excess of acid (3 equiv. with respect to gold) at low catalyst loadings (100−1000 ppm).[4f]

Digold hydroxide complexes have also been shown to be suitable catalysts for silver-free and acid-free alkyne hydration.[4a] In order to test the catalytic activities of the new complexes and compare them with the previously reported catalytic results, we next performed the hydration of alkynes in a mixture of 1,4-dioxane and H_2O (2/1) at 80 °C for 3 h. Diphenylacetylene (**3**) was chosen as the test substrate, as it is one of the most challenging substrates for this transformation. To challenge our catalysts, relatively low catalyst loadings (0.5 mol %) were employed. As shown in Table 1, IPr* complex **2d** performed

Table 1. Gold-Catalyzed Alkyne Hydration[a]



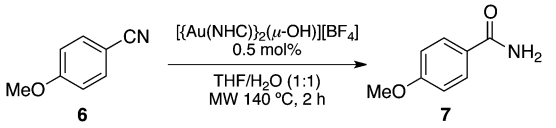
entry	cat. [amt, mol %]	conversion, %[b]
1	$[\{\text{Au(IPr)}\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2a**) [0.5]	92
2	$[\{\text{Au(SIPr)}\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2b**) [0.5]	83
3	$[\{\text{Au(IPr}^{Cl})\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2c**) [0.5]	91
4	$[\{\text{Au(IPr*)}\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2d**) [0.5]	55
5	$[\{\text{Au(IPent)}\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2e**) [0.5]	74
6[c]	$[\{\text{Au(IPr)}\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2a**) [0.1]	57
7[c]	$[\{\text{Au(IPr}^{Cl})\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2c**) [0.1]	95
8[d]	$[\{\text{Au(IPr}^{Cl})\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2c**) [0.05]	95 (90)

[a] Reaction conditions unless stated otherwise: [Au] (2.5 μmol), **3** (0.5 mmol) in a mixture of 1,4-dioxane and H_2O (2/1, 2 mL), 80 °C, 3 h. [b] Conversions determined by GC. Average of at least two runs. The isolated yield is given in parentheses. [c] Reaction conditions: [Au] (1.25 μmol), **3** (1.25 mmol) in a mixture of 1,4-dioxane and H_2O (2/1, 5 mL), 120 °C, 24 h. [d] Reaction conditions: [Au] (1.25 μmol), **3** (2.50 mmol) in a mixture of 1,4-dioxane and H_2O (2/1, 10 mL), 120 °C, 24 h.

poorly in this transformation, with only 55% conversion to the desired ketone (**4**) after 3 h (Table 1, entry 4). The SIPr- and IPent-bearing complexes, **2b**,**e**, furnished similar activities with better conversions (74–83%; Table 1, entries 2 and 5). The IPr derivative **2a** and the newly synthesized IPr^{Cl} complex **2c** were the best catalysts for the hydration of diphenylacetylene, with 92% and 91% conversions, respectively (Table 1, entries 1 and 3). To determine which of the two complexes, **2a** or **2c**, was the most active, experiments at lower catalyst loadings were performed (Table 1, entries 6–8). To the best of our knowledge, in the literature the optimum results for the hydration of diphenylacetylene at low catalyst loadings were obtained using 0.1 mol % of either $[\text{Au(IPr)Cl}]/\text{AgSbF}_6$ or $[\text{Au(IPr)OH}]/\text{HBF}_4$ at 120 °C for 24 h, with conversions between 70 and 77%.[4f,16c] Gratifyingly, 95% conversion (90% isolated yield) to the desired product could be obtained under the same conditions using 0.05 mol % of **2c** (Table 1, entry 8). This result highlights that the digold species $[\{\text{Au(IPr}^{Cl})\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2c**) is the best catalyst reported to date for the hydration of challenging alkynes at low catalyst loadings. Our findings are in direct contrast with the recent contribution by Shi et al. regarding the *"silver effect"* in gold catalysis, where Shi claims that the gold-catalyzed alkyne hydration cannot be catalyzed only by $[\text{Au}]^+$ and that the presence of silver is required for the reaction to proceed.[18] As is the case for the Corma system (2009)[16d] and our previous contribution on silver-free protocols (2010),[4a] here no additive (acid, silver) is required to perform the catalytic reaction.

Nitrile Hydration. The hydration of nitriles represents the most atom-economical synthetic pathway toward the formation of amides.[19] This procedure has been described as catalyzed by all the transition metals of groups 8–11, including gold.[19] However, only two catalytic systems based on gold have been reported.[9,20] We described the first gold-catalyzed nitrile hydration in 2009.[20] Moderate to excellent yields (34–99%) were obtained using the well-defined Gagosz-type complex $[\text{Au(IPr)(NTf}_2)]$ (**5a**)[17b] in reactions conducted in a mixture of THF and H_2O (10/1) at 140 °C for 2 h under microwave irradiation.[20] After this initial study, and once the digold species **2a** had been synthesized, it was postulated as a potential key intermediate in this process.[9] Using 1 mol % of **2a** as catalyst, it was possible to obtain excellent conversions (75–100%) and substantial improvements for two particularly troublesome substrates.[21] Encouraged by these results, the activity of the new catalysts was tested in this transformation. *p*-Methoxybenzonitrile (**6**) was the substrate of choice for this transformation, as a 20% improvement was observed when **2a** was used as catalyst instead of the monomeric **5a**.[9] The experiments were carried out under the conditions mentioned above, but using lower catalyst loadings (0.5 mol %) (Table 2). As in the case of the alkyne hydration, the complex bearing IPr*, **2d**, performed poorly in this reaction with only 53% conversion after 2 h (Table 2, entry 4). On the other hand, the reactions using **2a**–**c**,**e** gave excellent conversions, between 86 and 92% (Table 2, entries 1–3 and 5). In order to determine which was the most active complex, experiments at lower catalyst loadings were performed. Gratifyingly, a difference in reactivity could be observed at 0.25 mol %. While the IPr^{Cl} (**2c**) and IPent derivatives (**2e**) provided moderate conversions, ca. 58% (Table 2, entries 7 and 8), the SIPr derivative (**2b**) was the most active catalyst with 70% conversion (Table 2, entry 6). **2b** is therefore the catalyst of choice for gold-catalyzed nitrile hydration reactions.

Table 2. Gold-Catalyzed Nitrile Hydration[a]



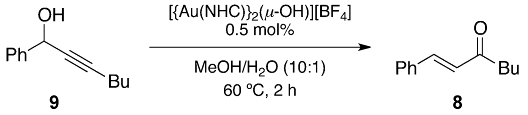
entry	cat. [amt, mol %]	conversion, %[b]
1	$[\{\text{Au(IPr)}\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2a**) [0.5]	86
2	$[\{\text{Au(SIPr)}\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2b**) [0.5]	92 (90)
3	$[\{\text{Au(IPr}^{Cl})\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2c**) [0.5]	91
4	$[\{\text{Au(IPr*)}\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2d**) [0.5]	53
5	$[\{\text{Au(IPent)}\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2e**) [0.5]	90
6[c]	$[\{\text{Au(SIPr)}\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2b**) [0.25]	70
7[c]	$[\{\text{Au(IPr}^{Cl})\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2c**) [0.25]	59
8[c]	$[\{\text{Au(IPent)}\}_2(\mu\text{-OH})][\text{BF}_4]$ (**2e**) [0.25]	57

[a] Reaction conditions unless stated otherwise: [Au] (2.5 μmol), **6** (0.5 mmol) in a mixture of THF and H_2O (1/1, 1 mL), 140 °C, 2 h. [b] Conversions determined by ^1H NMR. Average of at least two runs. The isolated yield is given in parentheses. [c] Reaction conditions: [Au] (1.25 μmol), **6** (0.5 mmol) in a mixture of THF and H_2O (1/1, 1 mL), 140 °C, 2 h.

Meyer–Schuster Rearrangement. An alternative transformation to the classical route for the synthesis of *α*,*β*-unsaturated ketones is the rearrangement of propargylic alcohols, known as the Meyer–Schuster rearrangement.[22] This reaction can be catalyzed by acid or by several metal complexes.[22,23] The case of gold has been widely studied by several groups.[4b,24] In 2009, we reported that *α*,*β*-unsaturated ketone **8** could be obtained in good yield and good *E*/*Z* selectivity by heating propargylic alcohol **9** at 60 °C for 16 h in a 10/1 mixture of MeOH and H_2O in the presence of $[\text{Au(IPr)Cl}]/\text{AgSbF}_6$ (2 mol %).[24d] Further investigations of this reaction allowed us to report, 1 year later, the use of the Meyer–Schuster rearrangement for the synthesis of prostaglandins.[4b] Using 2 mol % of gold hydroxide **1a** (acid activated) or digold complex **2a**, in a 10/1 mixture of MeOH and H_2O, ketone **8** was obtained in excellent yields (93–97%) within 1 h at room temperature.[4b] The catalyst screening was commenced using these conditions. Initial results using 1 and 0.5 mol % of digold complex **2a** allowed us to obtain 99% and 69% conversions, respectively, in

3 h at room temperature. In order to use the lowest amount of catalyst combined with the shortest reaction times possible, experiments were conducted using 0.5 mol % of our diaurated complexes at 60 °C for 2 h (Table 3). Unfortunately, under these conditions complexes **2c**–**e** showed poor reactivity for this transformation, yielding conversions between 3 and 27% (Table 3, entries 3–5). In the case of **2d**, this may be due to its poor solubility in the reaction mixture. On the other hand, the complexes bearing SIPr (**2b**) and IPr ligands (**2a**) showed good reactivity with excellent conversions (85 and 98%, respectively; Table 3, entries 1 and 2). In order to test the limit of the system, a reaction was performed with 0.1 mol % of **2a** over 24 h. Gratifyingly, good conversion (74%) was obtained (Table 3, entry 6). These results place the digold catalyst **2a** among the best for the gold-catalyzed Meyer–Schuster rearrangement. While Shi et al. found that this transformation can only be poorly performed by [Au(IPr)][SbF$_6$] (26% conversion),[25] and that the addition of silver salts greatly enhanced the reactivity (94% conversion), our results, in accordance with those published by Sheppard[24g,i] and Shi himself,[24h] highlight that gold alone can catalyze the Meyer–Schuster rearrangement in high yields. Interestingly, Sheppard also noticed that the presence of silver impurities in his gold catalyst afforded the substitution of the alcohol with methoxide, derived from the MeOH employed during the reaction.[24i,26] An exhaustive study of the reaction revealed that AgNTf$_2$ could catalyze this process.[24i] Further work to explore the role of silver is ongoing in our laboratories.

Table 3. Gold-Catalyzed Meyer–Schuster Rearrangement[a]

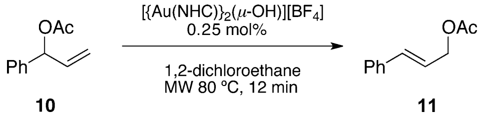


entry	cat. [amt, mol %]	conversion, %[b]
1	[{Au(IPr)}$_2$(μ-OH)][BF$_4$] (**2a**) [0.5]	98 (95)
2	[{Au(SIPr)}$_2$(μ-OH)][BF$_4$] (**2b**) [0.5]	85
3	[{Au(IPr^{Cl})}$_2$(μ-OH)][BF$_4$] (**2c**) [0.5]	18
4	[{Au(IPr*)}$_2$(μ-OH)][BF$_4$] (**2d**) [0.5]	3
5	[{Au(IPent)}$_2$(μ-OH)][BF$_4$] (**2e**) [0.5]	27
6[c]	[{Au(IPr)}$_2$(μ-OH)][BF$_4$] (**2a**) [0.1]	74

[a]Reaction conditions unless stated otherwise: [Au] (1 μmol), **9** (0.2 mmol) in a mixture of methanol and H$_2$O (10/1, 1 mL), 60 °C, 2 h. [b]Conversions determined by GC. Average of at least two runs. The isolated yield is given in parentheses. [c]Reaction conditions: [Au] (1 μmol), **7** (1.0 mmol) in a mixture of methanol and H$_2$O (10/1, 1 mL), 60 °C, 24 h.

Rearrangement of Allylic Acetates. Finally, the rearrangement of allylic acetates was tested in order to study the potential of the new complexes as acid-activated precatalysts. This classical skeletal rearrangement has been catalyzed by several transition metals, including gold.[27] We reported in 2007 the complete conversion of allylic acetate **10** into **11** after 12 min at 80 °C in 1,2-dichloroethane using microwave irradiation and a combination of [Au(IPr)Cl] (3 mol %) and AgBF$_4$ (2 mol %).[27b] More recently, we described the use of 1 mol % of [{Au(IPr)}$_2$(μ-OH)][BF$_4$]/HBF$_4$ under the conditions previously mentioned over 30 min to obtain full conversion of **10** into **11**.[4a] To determine the lowest amount of catalyst combined with shorter reaction times, reactions were carried out using 0.25 mol % of digold hydroxides, at 80 °C in a microwave reactor (Table 4). Under these reaction conditions, diaurated complexes **2a**,**d**,**e** provided moderate conversions (59–67%; Table 4, entries 1, 4, and 5). On the other hand, the use of the SIPr and IPr^{Cl} derivatives **2b**,**c**, gave excellent conversions (94–99%; Table 4, entries 2 and 3). In order to determine the best catalyst, a reaction was performed under the same conditions but at lower catalyst loading (0.1 mol %). We were very pleased to observe that, even at these low loadings, catalyst **2b** provided very high yields (90%).

Table 4. Gold-Catalyzed Allylic Acetate Rearrangement[a]



entry	cat. [amt, mol %]	conversion, %[b]
1	[{Au(IPr)}$_2$(μ-OH)][BF$_4$] (**2a**) [0.25]	63
2	[{Au(SIPr)}$_2$(μ-OH)][BF$_4$] (**2b**) [0.25]	99
3	[{Au(IPr^{Cl})}$_2$(μ-OH)][BF$_4$] (**2c**) [0.25]	94
4	[{Au(IPr*)}$_2$(μ-OH)][BF$_4$] (**2d**) [0.25]	59
5	[{Au(IPent)}$_2$(μ-OH)][BF$_4$] (**2e**) [0.25]	67
6[c]	[{Au(SIPr)}$_2$(μ-OH)][BF$_4$] (**2b**) [0.1]	99 (90)
7[c]	[{Au(IPr^{Cl})}$_2$(μ-OH)][BF$_4$] (**2c**) [0.1]	52

[a]Reaction conditions unless stated otherwise: [Au] (0.75 μmol), HBF$_4$·OEt$_2$ (0.75 μmol), **10** (0.3 mmol), in DCE (3 mL), 80 °C, 12 min. [b]Conversions determined by GC. Average of at least two runs. The isolated yield is given in parentheses. [c]Reaction conditions: [Au] (0.3 μmol), HBF$_4$·OEt$_2$ (0.3 μmol), **8** (0.3 mmol), in DCE (3 mL), 80 °C, 12 min.

■ CONCLUSION

In conclusion, three novel digold complexes have been synthesized and their catalytic activity has been tested in important organic transformations. Gratifyingly, over 90% isolated yields were obtained at low catalyst loadings (0.05–0.5 mol %) in the reactions examined. In addition, these digold catalysts do not require any additive (e.g., acid, silver salts) to promote the reactions. Particularly interesting are the results for the hydration of diphenylacetylene and the Meyer–Schuster rearrangement, as they are in contradiction with some recent literature reports. These results are part of our ongoing investigations to clarify the role of gold in organic transformations and to develop new *silver-free*, *acid-free* gold-catalyzed processes.

■ EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all solvents and reagents were used as purchased and all reactions were performed under air. Deuterated solvents (CD$_2$Cl$_2$, CDCl$_3$) were filtered through basic alumina in order to remove traces of HCl. NMR spectra were recorded on 400 and 300 MHz spectrometers at room temperature in CD$_2$Cl$_2$ or CDCl$_3$. Chemical shifts are given in parts per million (ppm) with respect to TMS. Elemental analyses were performed by the analytical services of London Metropolitan University. [{Au(IPr)}$_2$(μ-OH)][BF$_4$] (**2a**) and [{Au(SIPr)}$_2$(μ-OH)][BF$_4$] (**2b**) were synthesized according to our previous reports.[9,11]

General Procedure for the Synthesis of [{Au(NHC)}$_2$(μ-OH)][BF$_4$] (2c–e). To a solution of the corresponding [Au(NHC)Cl] (1 equiv.) in dry acetonitrile (5 mL), under an argon atmosphere, was added AgBF$_4$ (1.1 equiv.). The reaction mixture was stirred at room temperature, in the absence of light, for 5 h. The reaction mixture was then filtered through a pad of Celite, the solvent removed in vacuo, and the crude reaction product dissolved in ca. 10 mL of CH$_2$Cl$_2$. The organic solution was washed three times with ca. 30 mL of water, dried over anhydrous MgSO$_4$, and concentrated under vacuum.[28] To purify the final product, the resulting solid was dissolved in the minimum amount of CH_2Cl_2 (ca. 2 mL), and the product was precipitated by addition of pentane (ca. 8 mL). If after evaporation of the solvent an oil is obtained, the final product can be triturated by addition of Et_2O (ca. 4 mL). The precipitate was collected by filtration, affording the desired complexes as white solids.

[{Au(IPr^{Cl})}$_2$(μ-OH)][BF$_4$] (**2c**). Following the general procedure 300 mg (0.434 mmol) of [Au(IPr^{Cl})Cl] and 93 mg (0.478 mmol) of $AgBF_4$ were used. The desired complex was obtained as a white solid in 81% isolated yield (497 mg). ^{1}H NMR (CD_2Cl_2; 400 MHz): δ 7.59 (t, J = 7.8 Hz, 4H, $CH_{p\text{-Ar}}$), 7.32 (d, J = 7.8 Hz, 8H, $CH_{m\text{-Ar}}$), 2.29 (sept, J = 6.9 Hz, 8H, CH_{iPr}), 1.23 (d, J = 6.9 Hz, 24H, CH_3), 1.13 (d, J = 6.8 Hz, 24H, CH_3), 0.77 (s, 1H, OH). ^{13}C NMR (CD_2Cl_2; 101 MHz): δ 163.0 (C_{carb}), 146.4 ($C_{o\text{-Ar}}$), 132.2 ($CH_{p\text{-Ar}}$), 131.1 (C_{N-Ar}), 125.1 ($CH_{m\text{-Ar}}$), 120.1 (C_{Cl}), 29.4 (CH_{iPr}), 24.8 (CH_3), 23.5 (CH_3). ^{19}F NMR (CD_2Cl_2; 376 MHz): δ −153.89, −153.94. Anal. Calcd for $C_{54}H_{69}Au_2BCl_4F_4N_4O$ (1412.70): C, 45.91; H, 4.92; N, 3.97. Found: C, 45.86; H4.83; N, 3.87.

[{Au(IPr)}$_2$(μ-OH)][BF$_4$]* (**2d**). Following the general procedure 300 mg (0.262 mmol) of [Au(IPr*)Cl] and 56 mg (0.288 mmol) of $AgBF_4$ were used. The desired complex was obtained as a white solid in 72% isolated yield (438 mg). ^{1}H NMR (300 MHz; CD_2Cl_2): δ 7.28−7.24 (m, 24H, CH_{Ar}), 7.06 (s, 8H, $CH_{m\text{-Ar}}$), 7.00−6.87 (m, 56H, CH_{Ar}), 5.98 (s, 4H, $CH_{imidazole}$), 5.24 (s, 8H, $CHPh_2$), 2.36 (s, 12H, CH_3), −0.76 (s, 1H, OH). ^{13}C NMR (75 MHz; CD_2Cl_2): δ 164.2 (C_{carb}), 142.85 (C_{Ar}), 142.68 (C_{Ar}), 141.3 ($C_{o\text{-Ar}}$), 140.9 (C_{N-Ar}), 134.0 ($C_{p\text{-Ar}}$), 131.0 ($CH_{m\text{-Ar}}$), 130.0 (CH_{Ar}), 129.6 (CH_{Ar}), 129.1 (CH_{Ar}), 128.8 (CH_{Ar}), 127.6 (CH_{Ar}), 127.1 (CH_{Ar}), 124.4 ($CH_{imidazole}$), 51.9 ($CHPh_2$), 22.1 (CH_3). ^{19}F NMR (282 MHz; CD_2Cl_2): δ −153.96, −154.02. Anal. Calcd for $C_{138}H_{113}Au_2BF_4N_4O$ (2324.14): C, 71.32; H, 4.90; N, 2.41. Found: C, 71.17; H, 4.77; N, 2.33.

[{Au(IPent)}$_2$(μ-OH)][BF$_4$] (**2e**). Following the general procedure 300 mg (0.409 mmol) of [Au(IPr^{Cl})Cl] and 87.6 mg (0.450 mmol) of $AgBF_4$ were used. The desired complex was obtained as a white solid in 80% isolated yield (491 mg). ^{1}H NMR (CD_2Cl_2; 300 MHz): δ 7.53 (t, J = 7.8 Hz, 4H, $CH_{p\text{-Ar}}$), 7.20 (d, J = 7.8 Hz, 8H, $CH_{m\text{-Ar}}$), 7.07 (s, 4H, $CH_{imidazole}$), 1.97 (quintet, J = 7.1 Hz, 8H, CH), 1.66−1.37 (m, 32H, CH_2), 0.72 (dt, J = 12.9, 7.3 Hz, 48H, CH_3), 0.20 (s, 1H, OH). ^{13}C NMR (CD_2Cl_2; 75 MHz): δ 163.4 (C_{carb}), 143.7 ($C_{o\text{-Ar}}$), 136.8 (C_{N-Ar}), 130.8 ($CH_{p\text{-Ar}}$), 125.1 ($CH_{m\text{-Ar}}$), 124.8 ($CH_{imidazole}$), 43.2 (CH), 29.5 (CH_2), 28.6 (CH_2), 13.2 (CH_3), 12.6 (CH_3). ^{19}F NMR (CD_2Cl_2; 282 MHz): δ −153.94, −154.00. Anal. Calcd for $C_{70}H_{105}Au_2BF_4N_4O$ (1499.35): C, 56.07; H, 7.06; N, 3.74. Found: C, 55.89; H 7.12; N, 3.84.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving additional experimental details and figures giving NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) Abbreviations: IPr^{Cl}, 4,5-dichloro-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene;, IPent , 1,3-bis(2,6-bis(1-ethylpropyl)phenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene; IPr*, 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene.

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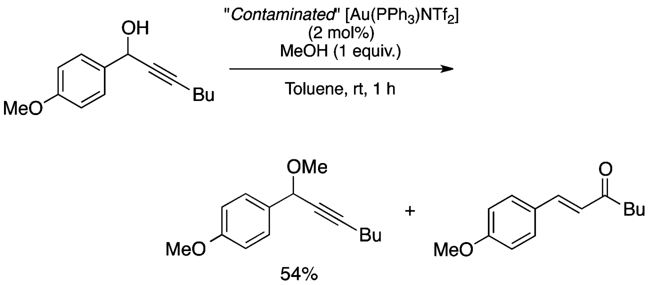
(25) Reaction conditions: [Au(IPr)][SbF$_6$] (2 mol%, filtered through Celite), MeOH/H$_2$O (10/1), 60 °C, 4 h.

(26)



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