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Gold- *N*-Heterocyclic Carbene Complexes of Mineral Acids

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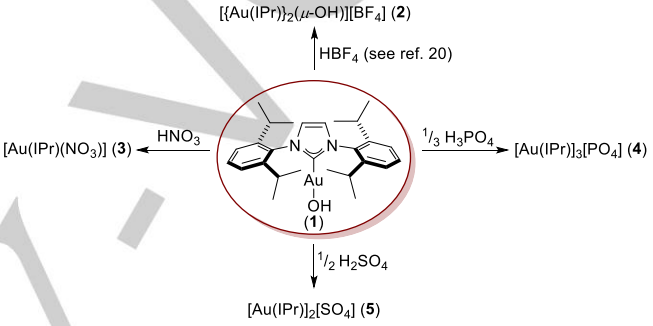
Abstract: We have synthesized and characterized new gold-NHC complexes derived from the deprotonation of mineral acids. The use of sulfuric acid was a particularly interesting case. These complexes were tested in known gold-catalyzed reactions, such as the hydration of alkynes and the Meyer-Schuster rearrangement. They proved to be highly efficient in both reactions.

The design, synthesis and exploration of new motifs in organometallic chemistry are of great importance in the discovery of new and useful complexes for catalysis, medicines, and materials. Developments in the use of gold complexes have been highlighted by numerous applications, particularly as anticancer agents,[1] luminescent materials[2] and as homogenous catalysts enabling various transformations.[3-5] Recent reports have focused on the development of well-defined Au(I) and Au(III) complexes with diverse ancillary ligands to examine the influence of ligand effects on catalytic activity[6] and in an attempt to better understand reaction mechanisms.[5-11] In-depth knowledge of the latter allows for the design of better performing processes. The use of NHC ligands in gold chemistry has allowed for the synthesis of a plethora of organogold complexes.[4] Highly reactive species, such as Au(I)–*tert*-butoxide,[12] Au(I)–fluoride,[12] Au(I)–bifluoride,[13] Au(I)–hydride,[14] Au(I)–hydroxide,[15] Au(I)–alkylperoxo[16a] and Au(I)-phenolate[16b-c] species, have all been isolated because of the unique properties of these ligands. More recently, reports examining the counterion effect in the hydration and alkoxylation of alkynes have drawn much attention and, consequently, have permitted a better understanding of mechanisms implicated in such reactions.[17-19] In this context and in the pursuit of developing new Au(I)-NHC complexes and testing their efficiency in catalysis, we report the synthesis of new Au(I)-NHC complexes based on the deprotonation of various mineral acids using our previously described golden synthon [Au(IPr)(OH)][15] (**1**) (IPr = *N*,*N*'-bis-[2,6-(di-*iso*-propyl)phenyl]imidazol-2-ylidene). **1** has emerged as a highly versatile synthon, allowing easy access to a wide range of complexes; for example, [{Au(IPr)}$_2$(μ-OH)][BF$_4$] (**2**).[20] Our interest in the mineral-acid-derived gold(I) complexes as potential catalysts is mainly due to the known low oxophilicity of gold(I). We believe that these new complexes should provide efficient and simple access to highly electrophilic gold catalysts (Scheme 1).



Scheme 1. Reactions of [Au(IPr)(OH)] (**1**) with mineral acids.

The reaction of **1** with 1 equiv. of HNO_3 affords cleanly the desired complex [Au(IPr)(NO_3)] (**3**) in 98% yield. Similarly, the reaction of **1** with H_3PO_4 (in a 3:1 ratio) forms the expected trigold phosphate, [Au(IPr)]$_3$[PO_4] (**4**), in 94% yield (Scheme 1). Both complexes were fully characterized by NMR spectroscopy and elemental analysis, and were shown to be highly stable compounds. Although complex **3** has been previously reported,[19] its X-ray structure has never been disclosed until now.

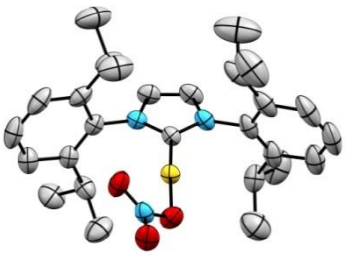


Figure 1. X-Ray crystal structure of [Au(IPr)(NO_3)] (**3**).[21] All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Next, we attempted the reaction of **1** with H_2SO_4. Recent studies have shown that sulfonyl-based Au-NHC compounds were the most efficient catalysts in nucleophilic additions to alkynes.[19,22] For this reason, we hypothesized that a sulfate-based Au-NHC compound could be of interest in such reactions. The formation of the digold sulfate, [Au(IPr)]$_2$[SO_4] (**5**), proved to be more

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difficult than expected, starting from 1 equiv. of **1** and ½ equiv. of H_2SO_4, at room temperature. A mixture of two species was repeatedly obtained (Mixture A); the ^{1}H NMR spectrum indicated a probable exchange between two species, highlighted by the observed broad resonances. Upon addition of an excess of sulfuric acid, *in situ* NMR spectroscopy showed the conversion to one species, tentatively assigned as [Au(IPr)(HSO_4)] (**6**). However, attempts to isolate the latter species, *via* removal of excess H_2SO_4 and filtration, led to the previously observed spectrum exhibiting broad features (Mixture A, Figure 2). We postulated that the [Au(IPr)(HSO_4)] (**6**) species was unstable at room temperature and that it was in equilibrium with the targeted complex, [Au(IPr)]$_2$[SO_4] (**5**). In an attempt to convert all of intermediate **6** into the digold sulfate (**5**), the mixture obtained after removal of excess H_2SO_4 and filtration was titrated with **1** until full conversion was achieved. Based on the total added amounts of **1** and Mixture A, we determined the initial mixture to be composed of [Au(IPr)(HSO_4)] (**6**)/[Au(IPr)]$_2$[SO_4] (**5**) in a 67:33 ratio. This titration process proved highly reproducible, affording the same ratio, repeatedly.[23]

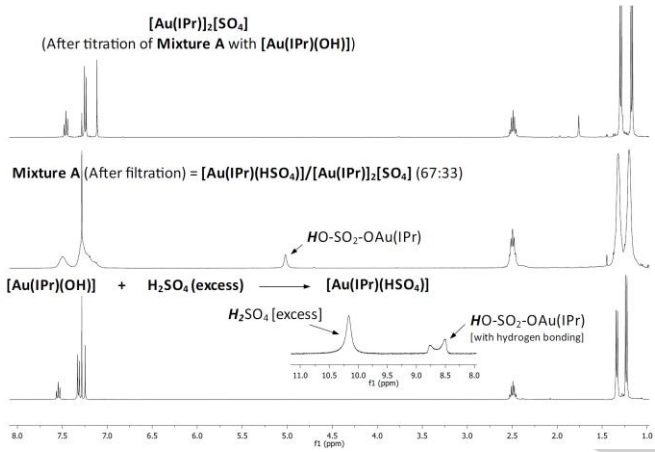


Figure 2. ^{1}H NMR spectra of *in situ* formed [Au(IPr)(HSO_4)] (**6**, with excess H_2SO_4, bottom spectrum), isolated [Au(IPr)(HSO_4)] (**Mixture A:** mixture of **5/6** in a 33:67 ratio, middle spectrum) and isolated [Au(IPr)]$_2$[SO_4] (**5**, after titration with complex **1**, top spectrum)

To our delight and after much frustration dealing with this equilibrium, complex **5** was successfully isolated using this procedure in 92% yield. Complex **5** was fully characterized by NMR spectroscopy and elemental analysis. X-Ray diffraction analysis of **5** confirmed the expected structure of the dinuclear gold complex. It should be mentioned that **5** proved highly air- and moisture-stable.

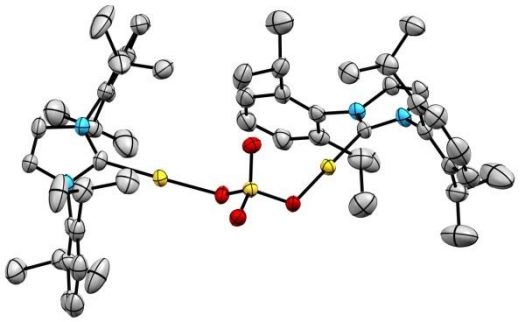
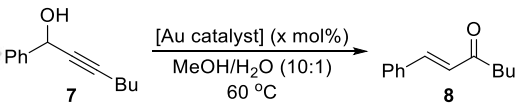


Figure 3. X-Ray crystal structure of [Au(IPr)]$_2$[SO_4] (**5**).[21] All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 25% probability level.

We next tested the newly-formed bench-stable complexes (**3**, **4** and **5**) in known Au-NHC-catalyzed reactions; the Meyer-Schuster rearrangement[24] and alkyne hydration.[19,20] In the rearrangement of propargylic alcohol **7** to α,β-unsaturated ketone **8** (Table 1, entries 1-3), complex **5** showed better activity than the previously reported state-of-the-art catalyst at the same catalyst loading (complex **2**, Table 1, comparing entries 1 and 3) When the catalyst loading is lowered (0.1 mol% in [Au] loading), only complex **3** afforded full conversion (Table 1, entry 6). This remarkable activity constitutes a 10-fold gain in catalytic efficiency compared to previously reported conditions.

Table 1. The Au-NHC-catalysed Meyer-Schuster rearrangement.[a]



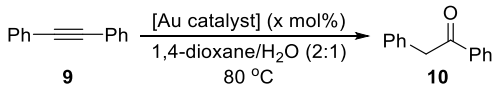
Entry	[Au cat] (mol%)	Time (h)	Conv.[b,c] (%)
1	**[Au(IPr)]$_2$[SO_4] (5) (0.25)**	**1**	**99 (24:1)**
2	**[Au(IPr)]$_2$[SO_4] (5) (0.1)**	**6**	**99 (22:1)**
3	[{Au(IPr)}$_2$(μ-OH)][BF_4] (**2**) (0.25)	3	61
4	[Au(IPr)]$_2$[SO_4] (**5**) (0.05)	24	17
5	**[Au(IPr)(NO_3)] (3) (0.1)**	**24**	**81**
6	**[Au(IPr)(NO_3)] (3) (0.1)**	**72**	**>99 (25:1)**
7	[Au(IPr)]$_3$[PO_4] (**4**) (0.033)	24	7

[a] Reaction conditions: [Au] (x mol%) was added to a solution of 1-phenylhept-2-yn-1-ol (188 mg, 1 mmol, 1 equiv.) in a mixture of MeOH/water (10:1, 2.5 mL). The reaction was stirred at 60 °C for 6 h. [b] Conversion determined by ^{1}H NMR. [c] *E*/*Z* ratio in parenthesis is determined for entries with full conversion by ^{1}H NMR.

Although recent reports have described highly efficient methods to perform alkyne hydration, these procedures still make use of silver (or other halide abstractors) or/and acid to afford high conversion rates at very low catalyst loadings.[19c,25] Silver- and acid-free protocols have emerged as a suitable alternative;[19b,d-20] however, they either still suffer from relatively high catalyst

loadings compared to the aforementioned methods or they haven't yet been applied to internal aromatic alkynes. In this context, we tested the new complexes in the hydration of diphenylacetylene (**9**) under the previously reported conditions using digold hydroxide **2**.[20] We began our investigation using catalyst **5** which, again, proved to be significantly more active than the state-of-the-art catalyst, [{Au(IPr)}$_2$(μ-OH)][BF$_4$] (**2**, Table 2, comparing entries 1 and 3). It should be mentioned that lowering the catalyst loading to 0.1 mol% resulted in significant loss of efficiency (Table 2, entry 3). At the same loading in gold, the mono- and tri-nuclear complexes **3** and **4** did not perform as effectively (Table 2, entries 4-5). We suspect the higher activity of the multinuclear complexes **4** and **5**, compared to the mononuclear gold nitrate **3**, is possibly due to a dual activation mode of catalysis, which has been shown to be relevant in the addition of nucleophiles to triple bonds using digold-type catalysts.[19,20,26]

Table 2. The Au-NHC-catalysed alkyne hydration.[a]



9 **10**

Entry	[Au cat] (mol%)	Time (h)	Conv.[b] (%)
1	**[Au(IPr)]$_2$[SO$_4$] (5) (0.25)**	**6**	**>99**
2	[Au(IPr)]$_2$[SO$_4$] (**5**) (0.1)	6	29
3	[{Au(IPr)}$_2$(μ-OH)][BF$_4$] (**2**) (0.25)	6	57
4	[Au(IPr)(NO$_3$)] (**3**) (0.5)	6	15
5	[Au(IPr)]$_3$[PO$_4$] (**4**) (0.167)	6	70

[a] Reaction conditions: [Au] (x mol%) in a 2:1 mixture of 1,4-dioxane/water was added to solid diphenylacetylene (89.2 mg, 0.5 mmol, 1 equiv.). The mixture was stirred at 80 °C for 6 h. [b] Conversion determined by GC analysis.

In order to gain insights into the dynamic behavior of the digold sulfate **5**, we investigated its reactivity towards neutral donor ligands in *in situ* NMR experiments. We were intrigued by the possible formation of a mixed digold species of the type [Au(IPr)(L)][Au(IPr)(SO$_4$)] as this would reveal a new type of counterion in gold catalysis – one in which a gold atom is part of the cation and anion of a catalytically active gold complex. While the reaction involving one equivalent of diphenylacetylene with **5** did not lead to cleavage of the digold complex at room temperature, the addition of PPh$_3$ to **5** gave rise to two signal sets of gold species (IPr signals sets to be more precise), indicating the formation of the desired complex since one signal set matched those of the literature reported cation [Au(IPr)PPh$_3$]$^+$.[27] Multiple attempts to grow crystals of this species resulted in the crystallization of either [Au(IPr)(PPh$_3$)][HSO$_4$] (**11a**) or a mixture of [Au(IPr)(PPh$_3$)][HSO$_4$] (**11a**) and the desired [Au(IPr)(PPh$_3$)][Au(IPr)(SO$_4$)] (**11b**). The sulfate anion appears to readily bind protons from the solution, even under strictly anhydrous conditions. Nevertheless, the crystal structure of **11b** suggests that mixed anionic and cationic gold species might be relevant intermediates in this type of catalysis.[28]

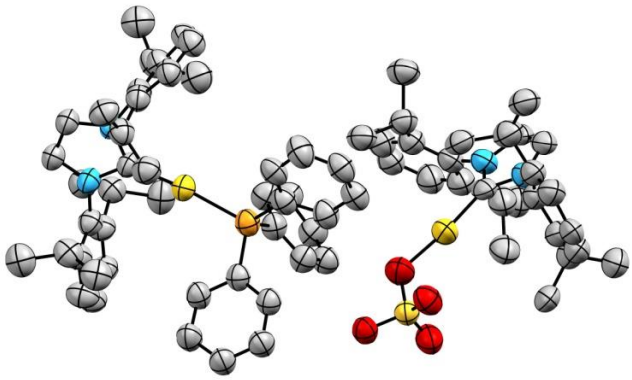


Figure 4. X-Ray crystal structure showing the product (**11b**) obtained from the reaction of [Au(IPr)]$_2$[SO$_4$] (**5**) with one equivalent of PPh$_3$.[21] All hydrogen atoms and [Au(IPr)PPh$_3$][HSO$_4$] (**11a**) also found within the unit cell are omitted for clarity. Thermal ellipsoids are shown at the 25% probability level.

In conclusion, we have synthesized and fully characterized gold-(IPr) complexes derived from nitric, sulfuric and phosphoric acids. The digold sulfate (**5**) case exhibits some peculiarities as it displyed interesting solution behavior. The formation of the digold sufate was thus investigated in more details and a reliable method to access this species was developed. In light of recent investigations into the nature of the counterion of gold complexes and their effect on catalysis,[19] the dissociation of digold sulfate using PPh$_3$ was investigated and an unusual reaction intermediate containing cationic and anionic gold fragments was observed and characterized. Finally, these novel products from mineral acids were tested in the Meyer-Schuster rearrangement of propargylic alcohols and in the hydration of alkynes; in both cases, one of these complexes, the gold sulfate, showed high efficiency and selectivity, surpassing that of the state-of-the-art catalysts for these particular reactions. In an effort to push the boundaries of catalytic efficiency and mechanistic understanding in gold-NHC-catalyzed reactions, studies addressing the development of even more practical and cost-effective catalysts are ongoing.

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Keywords: gold • *N*-heterocyclic carbene • sulfate • catalysis • mineral acids

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[28] This work only addresses the possibility of dissociating the digold sulfate into cationic and anionic fragments. This was shown to be possible, or at least plausible, as indicated by the formation of species **11b**. Possibly, the gold anion moiety, $[Au(IPr)(SO_4)]^-$, can undergo deprotonation of the nucleophile during catalysis leading to a dual activation mode (based on our crystallization attempts we suspect the anion to be quite basic). It should be noted that we have shown that the formation of two cationic gold complexes upon addition of two equivalents of the strong donor ligand PPh_3 is also possible (see Supporting Information for more details). At this point, we do not know if only one catalytically-active cationic gold is formed in the reaction mixture or if a second dissociation is occurring to liberate two catalytically-active cationic gold.

Entry for the Table of Contents (Please choose one layout)

Layout 2:

COMMUNICATION

*Marcel Brill, Fady Nahra, Alberto Gómez-Herrera, Caroline Zinser, David B. Cordes, Alexandra M. Z. Slawin and Steven P. Nolan**

1 – 4

Gold- N-Heterocyclic Carbene Complexes of Mineral Acids

We have synthesized and characterized new gold-NHC complexes derived from the deprotonation of mineral acids. The use of sulfuric acid was a particularly interesting case that exhibited a unique behavior. These complexes were tested in known gold-catalyzed reactions and proved to be highly efficient.