# **ORGANOMETALLICS**

# Oxidative Access via Aqua Regia to an Electrophilic, Mesoionic Dicobaltoceniumyltriazolylidene Gold(III) Catalyst

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**S** Supporting Information

**ABSTRACT:** A gold(III) complex with the hitherto most electron poor mesoionic carbene ligand is presented. Aqua regia was the oxidizing agent of choice for the synthesis of this unusual organometallic compound. The Au<sup>III</sup> complex is redox-rich and also acts as a catalyst for oxazole formation, delivering selectively a completely different isomer in comparison to its Au<sup>I</sup> congener.



The use of gold complexes in homogeneous catalysis has L been a dormant field of research for decades. However, gold catalysis has emerged from a mere curiosity to one of the most powerful means for the activation of C-C multiple bonds toward a variety of complexity-oriented transformation reactions.<sup>1-6</sup> Whereas the expertise in gold(I) catalysts has attained a progressive level to date,<sup>7,8</sup> comparatively less information is available regarding gold(III) catalysts.<sup>9,10</sup> However, gold(III) catalysts have an advantage over their gold(I) congeners, as they are usually relatively cheap materials and, more importantly, they are in general insensitive to air, moisture, and light with the exclusion of AuCl<sub>3</sub>, AuBr<sub>3</sub>, and HAuCl<sub>4</sub> $\cdot n$ H<sub>2</sub>O.<sup>1,9,11</sup> For this reason gold(III) catalysts have a broad spectrum of applications in organic syntheses under mild conditions. Square-planar gold(III) complexes are diamagnetic 16-electron systems frequently used in regio- and stereoselective intra- and intermolecular addition reactions as well as in multicomponent reactions (MCRs), with their established areas still expanding.<sup>12,13</sup> A prerequisite to using well-defined gold(III) complexes as catalysts is the development of facile synthetic routes to gain access to these materials.

Au(I) complexes of mesoionic carbenes (MICs) of the 1,2,3triazol-4-ylidene type have been used in homogeneous catalysis in the past few years, and a few examples of Au(III) complexes with these ligands were reported as well.<sup>14–22</sup> Within this communication, we would like to address the question whether the Au(III) complex of the hitherto electron poorest NHC ligand, represented by 1,4-dicobaltoceniumyl-3-methyl-1,2,3-

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triazol-4-ylidene (MIC),<sup>23</sup> can be synthesized. Furthermore, we wish to compare and contrast the catalytic activity of the resulting Au(III) complex with that of its Au(I) congener, which we reported recently. The preparation of the corresponding tricationic triazolium salt (1) of its MIC<sup>24,25</sup> gold(I) complex, and the catalytic activity thereof were reported in our previous work.<sup>23</sup> Taking these investigations further toward the envisaged MIC gold(III) complex (3), a straightforward approach would be deprotonation of the triazolium precursor with Ag<sub>2</sub>O<sup>26</sup> followed by transmetalation to K[AuCl<sub>4</sub>]. However, all our attempts via this synthetic route led to the target compound persistently accompanied by its homoleptic gold(III) congener, with the dimeric silver(I) intermediate and the substrate as byproducts, each embodying multicationic species that proved impossible to separate. For this reason, an alternative oxidative route was pursued (Scheme 1), starting from the readily accessible gold(I) complex  $2^{23}$  as a precursor of the desired MIC gold(III) complex (3). Interestingly, the use of various standard oxidizing agents, e.g. Br<sub>2</sub>, CsBr<sub>3</sub>, etc,. failed<sup>27,28</sup> or, in the case of iodobenzene dichloride, 29,30 lead again to inseparable mixtures. Finally and remarkably, aqua regia—a very uncommon oxidant in organometallic chemistry-proved to be the reagent of choice.

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## Scheme 1. Synthetic Route toward MIC Gold(III) Complexes 3a,b



In detail, 2 was stirred in 5 mL of freshly prepared agua regia at room temperature overnight. After evaporation of excess of aqua regia in vacuo, the product was washed with water to remove the remaining amounts of acid, dissolved in acetone, and precipitated by addition of Et<sub>2</sub>O, thereby affording airstable, yellow 3a in 68% isolated yield. The clean chemoselectivity of this reaction-no formation of undesired homoleptic complexes-is most likely due to the very high concentration of available chlorido ligands that form intermediate chlorido-aurate complexes, which are less prone to further substitution. Quite remarkably, the carbene-gold bond remains intact under these harsh conditions. Synthetically, from an organometallic chemist's point of view, aqua regia is a very convenient new oxidizing agent in gold coordination chemistry, potentially simplifying the synthesis of new trichlorido(NHC)gold(III) catalysts in future work.

Complex 3a was fully characterized by <sup>1</sup>H/<sup>13</sup>C/<sup>19</sup>F NMR, IR, and HRMS (see the Supporting Information). The <sup>13</sup>C NMR signal of the carbene carbon was observed at 137.5 ppm, significantly shifted upfield in comparison to its Au(I) precursor 2 ( $\delta_{carbene}$  162.2 ppm).<sup>23</sup> Interestingly, the weakly coordinating triflates remain as the present counterions under these harsh conditions, as could be corroborated by  ${}^{13}C/{}^{19}F$ NMR, IR, and PXRD (see the Supporting Information). A single-crystal X-ray analysis of 3a provided a data set of poor quality; therefore the counterions were changed to hexafluoridophosphates (compare the Supporting Information) and good-quality single crystals of 3b suitable for X-ray analysis (R1 = 3.64%, Supporting Information) were obtained. Figure 1 shows the molecular structure of 3b. Overall, the dication has a regular square-planar gold center with a perpendicular triazolylidene ligand containing regular, undistorted cobaltoceniumyl substituents that are positioned in an anti conformation, clearly due to electrostatic repulsion. Furthermore, complex 3b shows a strong trans effect with a Au-Cl<sub>trans</sub> bond length of 2.307(2) Å, slightly elongated in comparison to its gold(I) congener, evincing a bond length of 2.284(1) Å.<sup>23</sup> This trans effect was also palpable in the HRMS (ESI positive)



Figure 1. Molecular structure of 3b with key atoms labeled. Selected bond lengths (Å): Au(1)-C(12) = 2.019(5), Au(1)-Cl(1) = 2.307(2), Au(1)-Cl(2) = 2.286(2), Au(1)-Cl(3) = 2.267(2). Selected angles (deg): C(12)-Au(1)-Cl(1) = 178.68(14), Cl(3)-Au(1)-Cl(2) = 174.69(7).

spectrum of **3a**, wherein one chlorido ligand was readily replaced by a methoxide, formed by the solvent. When the aforementioned elongated bond length is taken into account, it is only reasonable to attribute this reactivity to the loss of the *trans*-chlorido ligand.

As reported by us earlier, the triazolium salt 1 displays two close-lying one-electron-reduction steps that can be assigned to the successive reduction of the formally Co<sup>III</sup> centers to Co<sup>II</sup>. Those reduction steps are followed by two further close-lying one-electron-reduction processes that are assigned to the reduction of the  $Co^{II}$  centers to  $Co^{I.23}$  We have now performed UV-vis-NIR spectroelectrochemistry on 1, and the measurements prove that the four aforementioned reduction steps are also reversible on the spectroelectrochemistry time scale (Figures S9 and S10 and Tables S7 and S8). A further one-electron-reduction step assignable to the triazolium ring was also observed for 1. This process is also reversible in the spectroelectrochemical measurements. Similar redox events were also observed for the Au<sup>I</sup> complex 2.<sup>23</sup> The Au<sup>III</sup> complex **3a** displays reduction steps at -0.24, -0.98, -1.08, -1.93, -2.02, and -2.25 V in CH<sub>3</sub>CN/0.1 M Bu<sub>4</sub>NPF<sub>6</sub> (Figure 2). Except for the redox wave at -0.24 V, all other redox events observed for 3a are very similar to those observed for 1 and 2. The position of the reduction peak at -0.24 V was found to be dependent on the experimental conditions. Additionally, as can



**Figure 2.** Cyclic voltammogram of **3a** in  $CH_3CN$  and 0.1 M  $NBu_4PF_6$  at 100 mV/s with a glassy-carbon working electrode.

be seen from Figure 2, this wave is irreversible, and a comparison of the current height of this wave with those of the following waves indicates that this redox wave is likely a twoelectron-transfer event. We thus assign the redox wave at -0.24 V to the reduction of the Au<sup>III</sup> center to Au<sup>I</sup>. This step will certainly be accompanied by the dissociation of two chloride ions from the Au center, making this process irreversible. It has been previously reported that the redox potential of such Au-centered processes are very sensitive to the experimental conditions.<sup>31</sup> The waves at higher negative potentials are thus assigned to the reduction of both the Co<sup>III</sup> centers first to  $Co^{II}$  and then to  $Co^{I}$ . The peak at -2.25 V is assigned to the reduction of the triazolylidene ring. The oxidation wave observed at 0.73 V is a follow-up of the reduction peak at -0.24 V. Even though the irreversible nature of the redox events on the spectroelectrochemical time scale prohibits a direct assignment of the redox events, the comparison of the redox processes and their potentials with 1 and 2 does lend credibility to the assignments made above.

We recently reported that the  $Au^{I}$  complex 2 selectively catalyzes the conversion of substrate A to the corresponding oxazoline B (Scheme 2) without the need of any additional

Scheme 2. Catalytic Activity of the Electron-Poor Gold(III) Carbene Complex 3 in Comparison to the Reactivity of the Previously Investigated Corresponding Gold(I) Complex 2<sup>23</sup>



additives.<sup>23</sup> Unfortunately, under identical conditions no conversion was observed with the Au<sup>III</sup> complex 3. We then decided to use AgSbF<sub>6</sub> as an additional additive in the catalytic reaction. The use of the additive delivered only about 5% B in 2 h when 1 mol % of 3 was used. During these experiments we observed that the catalytic mixture was not well soluble in CD<sub>2</sub>Cl<sub>2</sub>. We thus decided to change to CD<sub>3</sub>CN and increased both the catalyst and the additive loading to 3 mol % each. Under those conditions in CD<sub>3</sub>CN at room temperature we observed a conversion of 4% after 3 h and 17% after 24 h. Furthermore, during this reaction, we started observing the formation of a different product, the other isomer, 5-methyl-2phenyloxazole (C). To investigate whether the addition of the additive was necessary for the conversion, we decided to perform the catalytic reaction with 3 mol % of 3 in CD<sub>3</sub>CN at 70 °C without any additional silver salts. Gratifyingly, under these conditions more than 90% conversion was observed after 24 h, and we also observed the exclusive formation of the isomer C (Figures S11 and S12). Thus, it is seen that, through optimization of the reaction conditions, it is possible to

selectively form the isomer **B** by using the Au<sup>I</sup> complex **2** as a catalyst or the isomer **C** by using the Au<sup>III</sup> complex **3** as a catalyst. However, it should be borne in mind that the mechanisms of action of Au(I) and Au(III) catalysts are usually different. The formation of isomer **C** through Au<sup>III</sup> catalysis has also been reported previously.<sup>32</sup>

Summarizing, we have presented here the first example of a Au<sup>III</sup> complex with the hitherto most electron-poor carbene ligand. This complex is redox-rich and displays gold-, cobaltoceniumyl-, and triazolylidene-based reductions. The Au<sup>III</sup> complex is an active catalyst, delivering selectively a different isomer as a product in comparison to its Au<sup>I</sup> congener.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.9b00616.

Experimental procedures, analytical, electrochemical, and catalytic data, and spectra (PDF)

Cartesian coordinates for the calculated structure (XYZ)

## Accession Codes

CCDC 1938205 contains 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.

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# Notes

The authors declare no competing financial interest.

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