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Visible Light Promoted Au(I) to Au(III) Oxidation in Triazol-5-ylidene Complexes

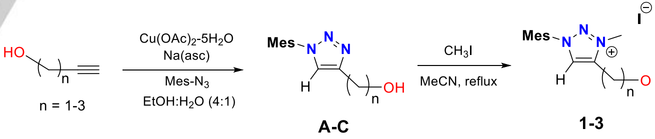
Daniel Mendoza-Espinosa,*[a] David Rendón-Nava,[a] Alejandro Alvarez-Hernández,[b] Deyanira Angeles-Beltrán,[a] Guillermo E. Negron-Silva,*[a] and Oscar R. Suárez-Castillo[b]

Dedicated to Emma Espinosa García

Abstract: Reaction of triazolium precursors [MIC$(CH_2)_n$-H^+]I^- (n = 1-3) with potassium hexamethyldisilazane (KHMDS) and AuCl(SMe_2) generates the gold(I) complexes of the type MIC$(CH_2)_n$·AuI. Visible light exposure of the latter complexes promotes a spontaneous disproportionation process rendering gold(III) complexes of the type $[\{MIC(CH_2)_n\}_2 \cdot AuI_2]^+I^-$. Both the Au(I) and Au(III) complex series were tested in the catalytic hydrohydrazination of terminal alkynes using hydrazine as nitrogen source.

Gold-based chemistry is recently finding great utility in a variety of catalytic, synthetic, and biomedical applications.[1] Most of the catalytic systems employed range from commercial inorganic salts, such as Au(I) and Au(III) halides,[2] to more versatile complexes stabilized with soft σ-donor ligands, usually phosphines[3] or *N*-heterocyclic carbenes (NHCs).[4] The Au complexes supported by NHCs, in particular, have been widely studied for their abilities to catalyse C−C, C−O, and C−N bond-forming reactions.[5] While the majority of literature reports describing the chemistry of Au−NHC complexes involve gold ions in the +1 oxidation state, recent attention has been directed toward Au(III)−NHC complexes.[6] However, due to the high redox potential of the Au(I)/Au(III) couple (E_0 = +1.41 V),[7] the organometallic chemistry of gold(III) with NHCs appears less developed than for gold(I) species and is mainly restricted to neutral halide Au(III) complexes, and there is strong evidence for an in situ reduction of simple gold(III) catalysts by oxidative C-C coupling in the intermediates.[8] A common methodology to attain the oxidation of NHC-Au(I) species relies on the addition of strong oxidants such as fluorinating or hypervalent iodine reagents,[6h] or treatment with molecular Cl_2, Br_2, or I_2.[6e,g] More recently a few outstanding examples of oxidative addition to C-Br/I and C-C- bonds onto Au(I) have been reported by Bourissou and Toste.[9] Applying this concept, a range of oxidative homo- and heterocoupling reactions have been developed giving access to a variety of functionalized products using non activated arenes and alkynes as starting materials.[10] Despite the success of these methods, the use of large excess of strong external oxidants, unavoidably reduces their appeal with respects to functional group tolerance and cost, while most examples are also conducted at high reaction temperatures. Late in the last decade, a new subclass of NHCs namely 1,2,3-triazol-5-ylidenes was discovered and even isolated in their free form.[11] This new generation of NHCs termed as “mesoionic carbenes” (MICs) have shown stronger donor capabilities than classical NHCs,[12] opening a new alternative of ligands for highly stable gold (I-III) complexes. With the goal of developing milder gold-catalysed coupling reactions excluding external oxidants, we describe herein the one-pot synthesis of Au(I)-MIC complexes and their facile visible light conversion to cationic gold(III) complexes. This unprecedented mild one step redox transformation will be discussed along with the structural diversity in solution and solid state. Preliminary catalytic activities of the Au(I)-MIC and Au(III)-MIC complexes in hydrohydrazination of terminal alkynes using parent hydrazine will be discussed.

The preparation of the MIC precursors **1-3** was performed according to Scheme 1. The first step involves the copper catalyzed cycloaddition of the proper alkyne with mesityl azide in ethanol/water to provide triazoles **A-C**.[12d,e] Further treatment of the latter precursors with excess methyl iodide in acetonitrile, delivers the expected triazolium salts **1-3** obtained after recrystallization of the crude materials with acetonitrile/diethyl ether (87-92% yields). All compounds were characterized by NMR spectroscopy, FT-IR, and elemental analysis.



Scheme 1. Synthesis of triazoliums **1-3**.

Formation of the triazoliums was easily monitored by the appearance of a new signal in the ^{1}H NMR spectrum at ca. δ = 4.5 ppm, indicating methylation of the triazolyl moiety (at *N*-3). Most of the other resonances in the ^{1}H NMR spectrum shifted only slightly, with the exception of the now acidic triazolium proton, which moves to higher frequency (δ = 8.6-9.0 ppm). Unambiguous characterization of the salts **1** and **2** was also achieved by X-Ray crystallography with the molecular structures displayed in Figure 1.

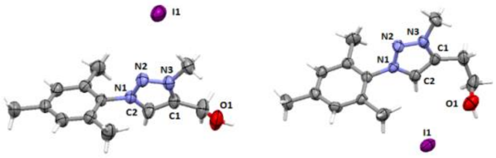


Figure 1. Molecular structures of salts **1** (left) and **2** (right). Ellipsoids shown at 50% of probability.

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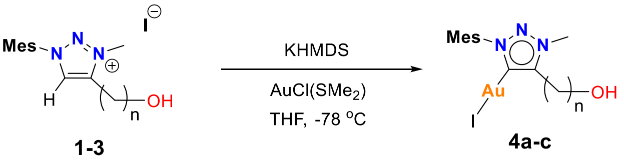
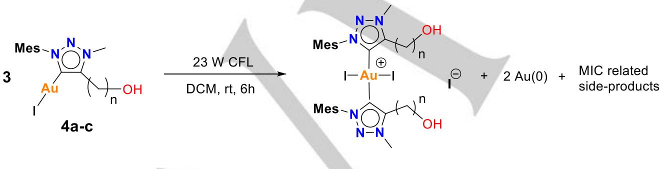
Our interest on the preparation of precursors **1-3** was due the fact that besides the possible formation of the MIC ligands after deprotonation, the remaining hydroxyl group could also be available for further functionalization. The initial exploration on the coordination capabilities of salts **1-3** was carried out by its one-pot reaction with potassium hexamethyldisilazane and $AuCl(SMe_2)$ under strict exclusion of light (Scheme 2). After work up and purification, the products were obtained in good yields (83-91%) as white crystalline powders. NMR spectroscopy studies and elemental analyses confirmed the formation of the expected Au(I)-MIC complexes **4a-c** by the disappearance of the acidic CH^+ proton in the ^1H NMR, and the observation of a low field signal around 171 ppm in ^{13}C NMR which is similar to previously reported mononuclear MIC-gold(I) complexes.[13]



1-3 **4a-c**

Scheme 2. Synthesis of Au(I) complexes **4a-c**.

Interestingly, after the preparation of the NMR samples in $CDCl_3$ and exposure of the solutions to visible light (from a 23W fluorescent light bulb), we observed that complexes **4a-c** underwent a colour change from colourless to deep-red along with the formation of a small amount of precipitate. After filtration, the solid was identified as gold(0), which was reused subsequently for the preparation of $AuCl(SMe_2)$. NMR spectroscopy analysis of the supernatants showed similar ^1H NMR patterns as for those observed in **4a-c**, however, the presence of new carbene peaks at ca. 160 ppm in ^{13}C NMR suggested a major structural transformation. Purification of the new species was performed by column chromatography rendering dark-red solids in moderate yields. Surprisingly, elemental analysis of the purified complexes indicated a carbene-gold 2:1 ratio and lower carbon content than the expected for a gold center with a single iodine atom. To gain further insight into the structural features of the type-**5** complexes, single crystals of **5a** were grown by cooling down a THF/DCM solution at -35°C. The crystals characterization by X-ray diffraction unveiled the formation of Au(III) species with a general formula of $[\{MIC(CH_2)n\}_2{\cdot}AuI_2]^+I^-$ (Scheme 3).



4a-c **5a-c**

Scheme 3. Synthesis of Au(III) complexes **4a-c**.

The molecular structure of **5a** depicted in Figure 2, shows a cationic gold(III) center coordinated to two MIC ligands and two iodine atoms in an overall square planar geometry. The C(5)-Au(1)-C(10) (178.9 °) and I(1)-Au(1)-I(2) (172.9 °) angles are almost linear, while the Au-C and Au-I bond distances of 2.024(8) and 2.617(9) Å, respectively, are both similar to analogue gold(I) complexes supported by MIC ligands.[13] Complex **5a** features a *trans*-disposition with the MIC ligands pointing out to the same direction, and the overall charge is compensated by the presence of the non-coordinated I(3) atom.

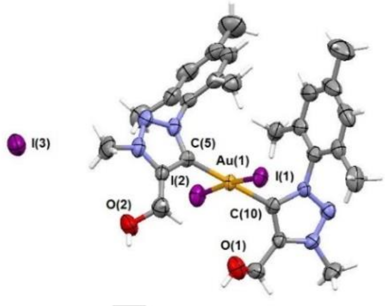


Figure 2. Molecular structure of **5a**. Ellipsoids shown at 50% of probability.

With the free hydroxyl groups and the presence of sp^2-nitrogen atoms, the possibility of hydrogen bonds in the solid state structure of **5a** was investigated. Figure 3 depicts the constructed hydrogen-bonded model showing the different interactions of the the hydroxyl groups on the MIC ligands. For instance, the O(1)-H(1A) moiety present short contacts with a vicinal molecule through the O(1)···H(6C) and H(1A)···N(3) interactions with distances of 2.543 and 3.045 Å, respectively. In case of the O(2)-H(2B) fragment, there is only a weak interaction with a neighboring *N*-Me group though the O(2)···H(19C) contact with a distance of 2.694 Å.

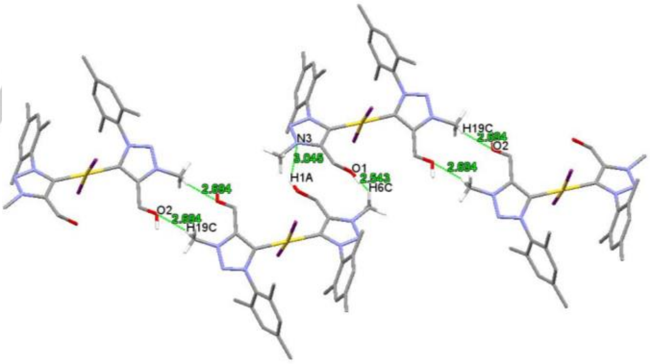


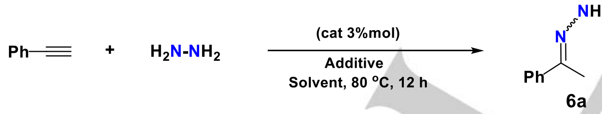
Figure 3. Hydrogen bonding in the solid state structure of **5a**.

Notably, the synthesis of complexes **5a-c** relies on a light induced disproportionation reaction in which the $MIC(CH_2)n{\cdot}$**AuI** complexes undergo oxidation, followed by stabilization with the coordination of a second triazol-5-ylidene (process which is probably favored by the small size of the ligand), and finally accompanied by reduction to Au(0) to complete the redox process. Is noteworthy mentioning that the disproportionation of Au(I) is known to be very slow for Au(I) halides,[14] because it requires formation of a bimolecular species involving a gold-gold bond and takes place only at high temperature in acidic media. Therefore, examples of visible light promoted self-disproportionation process have not been reported to date. Only a related example of disproportionation to generate a biscarbenic cationic gold(III) complex was reported by Bielawski where the oxidation process required of a biscarbenic gold(I) precursor and stoichiometric amounts of $AuCl(SMe_2)$ to proceed.[15]

The development efficient routes for the generation of carbon–nitrogen containing products using accessible bulk materials such as parent hydrazine is of great appeal. Nevertheless, hydrazine is a strong reducing agent, which can promote the formation of inactive metal(0), or lead to the formation of catalytic inactive Werner-like complexes. Therefore, very few examples of catalytic reactions involving this reagent have been reported. For instance, it has been demonstrated that Pd- and Cu-catalysed cross-coupling of hydrazine with aryl chlorides and tosylates was successful with the usage of an electron rich bulky P-ligand.[16] Bertrand and Hashmi have shown that the hydrohydrazination of unactivated allynes and allenes can be efficiently accomplished by cationic (L)Au(I) complexes supported by several non-classical NHC ligands.[17] Based on the positive results observed in the hydrohydrazination of unactivated alkynes promoted by cationic gold complexes, we decided to test our Au(I) and Au(III) MIC series in the hydrohydrazination of terminal akynes.

As initial screening tests, we carried out the stoichiometric reaction of parent hydrazine and phenylacetylene, at 80 °C for 12 h with 3 mol% of complexes **4a-c** and 5**a-c**. In case of complexes type-**4,** $AgSbF_6$ was included as initial additive to render the cationic metal center (entries 1-3), whilst due to the cationic nature of complexes type-**5** no addition was tested at first (entries 3-6). As observed in Table 1, the initial results showed that complexes **4c** and **5c** achieved the best yields under the standard reaction conditions. Further investigation of the weakly coordinating anions effect was accomplished by the mixing of complex **4c** with several potassium and silver salts (entries 7-9), showing that the usage of $KB(C_6F_5)_4$ improves the overall catalytic efficiency.

Table 1. Catalytic screening of **4a-c** and **5a-c** in the synthesis of **6a**.



Entry	Catalyst	Additive	Solvent	Yield(%)
1	**4a**	$AgSbF_6$	THF	57
2	**4b**	$AgSbF_6$	THF	52
3	**4c**	$AgSbF_6$	THF	74
4	**5a**	---------	THF	41
5	**5b**	---------	THF	38
6	**5c**	---------	THF	49
7	**4c**	AgOTf	THF	69
8	**4c**	$AgSbF_6$	THF	62
9	**4c**	$KB(C_6F_5)_4$	THF	85

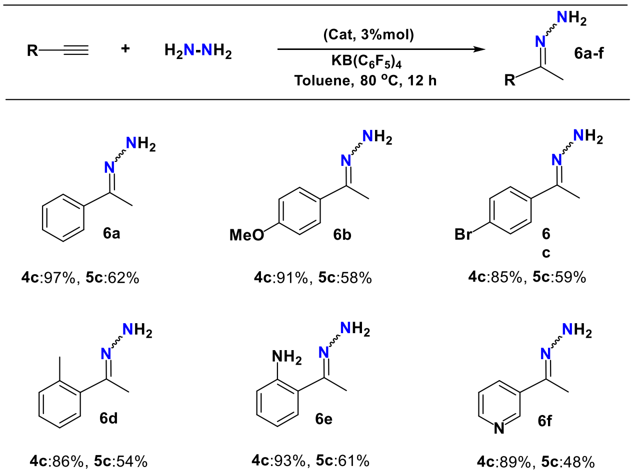
Remarkably, the product formation is highly beneficiated by the replacement of THF for non-polar solvents (Table 2, entries 1-4) with toluene as the best choice. Additionally, in an attempt to improve the catalytic efficiency complex **5c**, we carried out the iodine exchange reaction with several salts (Table 2, entries 5-8) achieving a maximum yield of 62%.

Table 2. Optimization of the catalytic reaction conditions.

Entry	Catalyst	Additive	Solvent	Yield(%)
1	**4c**	$KB(C_6F_5)_4$	Toluene	97
2	**5c**	---------	Toluene	55
3	**4c**	$KB(C_6F_5)_4$	Benzene	91
4	**5c**	---------	Benzene	52
5	**5c**	$AgSbF_6$	Toluene	34
6	**5c**	AgOTf	Toluene	37
7	**5c**	$AgBF_4$	Toluene	49
8	**5c**	$KB(C_6F_5)_4$	Toluene	62
9	**4c**	--------	Benzene	<5

Having identified precatalysts **4c** and **5c** (3 mol%) in mixture with $KB(C_6F_5)_4$ (3 mol%) as the best of the series, we evaluated the scope of the reaction with several terminal aryl alkynes and parent hydrazine to yield the hydrazones **6a–f**. According to Table 3, is easily observable that **4c** is more proficient in the catalytic conversions to hidrazones **6** than the Au(III) complex **5c** The lower conversions obtained with **5c** may be related to the instability of Au(III) complexes under highly reducing conditions (given the use of hydrazine) resulting in a reduced lifetime of such catalytic species.

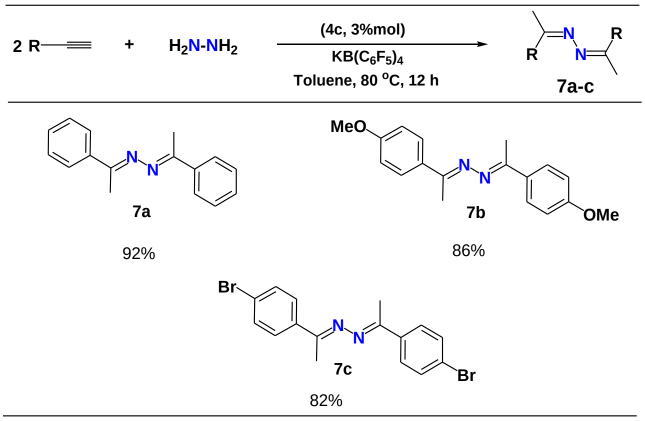
Table 3. Scope of the hydrohydrazination of terminal alkynes with hydrazine.



Reaction conditions: Alkyne (1.0 mmol), hydrazine (1.2 mmol), toluene 3 mL. Isolated yields.

During the course of studies, we noted the formation of trace amounts of products resulting from a bis-hydrohydrazination reaction. Under the standard conditions with **4c**, but using half equivalent of parent hydrazine, we were able to obtain the corresponding azines **7a–c** in good yields (Table 4) after a simple purification by means of chromatographic column.

Table 4. (Bis)hydrohydrazination of terminal alkynes with hydrazine.



Reaction conditions: Alkyne (1.0 mmol), hydrazine (0.49 mmol), toluene 3 mL. Isolated yields.

The possibility of formation of heterogeneous gold as the active catalyst, prompted us to perform mercury poisoning tests in the formation **6a** (ESI-Figure S1).[18] Hence, the formation process of **6a** was disturbed by the addition of excess of elemental mercury to the reaction mixture using the precatalysts **4c** and **5c**. According to GC monitoring during reaction time, no significant changes in the product yields were noticed (Fig S1-ESI). These results suggest that at 80°C the catalytic conversions are performed essentially by molecular species. Further analysis of the gold catalysts nature were tested by following Crabtree´s test for the selective homogeneous catalysts poisoning by the addition of slight excess of dibenzo[*a*,*e*]cyclooctatriene (DCT).[19] In this case the activity for the pre-catalysts **4c** and **5c** remains similar until the fourth hour of reaction, however as the time progresses and the DCT start the inhibition process, the conversion to products decreases drastically to 46% (for **4c**) and 27% (for **5c**) (Fig S2-ESI). These conversion data complements well the mercury poisoning tests, suggesting the homogeneous nature of the gold catalysts at the process reaction condition.

In summary, we report the facile preparation of a series of MIC$(CH_2)_n$·**Au**I complexes by the one-pot reaction of the triazolium precursors $[MIC(CH_2)_n\text{-}H^+]I^-$ (n = **1-3**) with potassium hydride (KHMDS) and AuCl(SMe_2). Visible light exposure of chloroform solutions of the latter gold(I) complexes results in a spontaneous disproportionation process rendering gold(III) complexes of the type $[\{MIC(CH_2)_n\}_2$·**Au**$I_2]^+I^-$. All complexes have been characterized in solution and solid state and both the **Au**(I) and **Au**(III) complex series were tested in the catalytic hydrohydrazination of terminal alkynes using hydrazine as nitrogen source. From the catalytic conversions, we can observe that although both the **Au**(I) and **Au**(III) complexes series are successful to generate the hydrohydrazination products under mild conditions, the combination of complexes **4c** with $KB(C_6F_5)_4$ as additive, display the best performance of the series. Further exploration of the catalytic potential of complexes **4** and **5** is currently being explored in our laboratory.

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Keywords: Mesoionic carbenes •gold(I) •gold(III) • hydrohydrazination • oxidation

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Layout 2:

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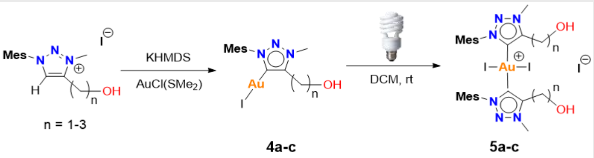

We report the visible light promoted disproportionation of Au^{I} complexes (**4**) which produces Au^{III} complexes of type **5**. Both the Au^{I} and Au^{III} series were tested in the hydrohydrazination of terminal alkynes using hydrazine as nitrogen source.

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Visible Light Promoted Au(I) to Au(III) Oxidation in Triazol-5-ylidene Complexes