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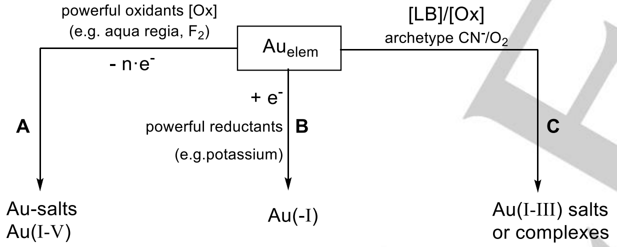
# Noble Metal Corrosion: Halogen Bonded Iodocarbenium Iodides Dissolve Elemental Gold – A Direct Access to Gold-Carbene Complexes

Jana M. Holthoff, Elric Engelage, Alexander B. Kowsari, Stefan M. Huber* and Robert Weiss*

**Abstract:** A common method to dissolve elemental gold involves the combination of an oxidant with a Lewis base, coordinating to the gold surface and thus lowering the metal's redox potential. Herein we report the usage of organic iodide salts providing both oxidative power and coordinating ligand, to dissolve gold under formation of organo-gold complexes. The obtained products were identified as $Au^{III}$ complexes, all featuring Au-C bonds, as shown by X-Ray single crystal analysis, and can be isolated in good yields. Additionally, our method is providing a direct access to NHC(-type) complexes and avoids costly organometallic precursors. The investigated complexes show dynamic behavior in acetonitrile and in case of the NHC(-type) complexes, the involved species could be identified as a mono-$[AuI_3(carbene)]$ and bis-carbene complex $[AuI_2(carbene)_2]^+$.

Gold, the noblest of all metals, is notoriously inert to all but the strongest redox reagents. Dissolution of elemental gold, thus, requires either powerful oxidants like *aqua regia* (category **A** in Scheme 1) or strong reductants like elemental potassium (category **B**). Most commonly the activation of elemental gold is achieved by a combination of an oxidant with a Lewis base (category **C**), as in the industrial process involving cyanide and oxygen. Category **C** is commonly referred to as corrosion.

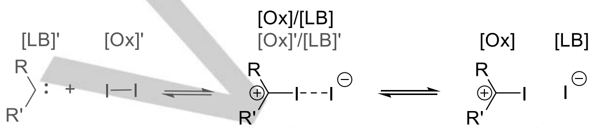


**Scheme 1.** Conceptionally different approaches towards the dissolution of elemental gold (Ox = oxidant, LB = Lewis base).

In recent years, a growing number of type **C** methods have been developed, involving oxidants such as iodine,[1–6] hydrogen peroxide,[7] oxygen,[8] or thionyl chloride[9] and coordinating Lewis bases like halides,[2–4,10] phosphines[8] or sulfur-bearing organic ligands.[1,5,11] Almost all of these examples, though, require the use of two distinct reagents and provide products which need further modification towards organo-gold products, like e.g. carbene complexes.

Herein, we report the first synthesis of gold(III) carbene complexes directly from $Au_{elem}$ using organic reagents which provide both oxidative power and the coordinating ligand. More generally this procedure also represents the first generation of Au-C bonds from elemental gold as a stoichiometric reagent, a novel entry into organo-gold chemistry.

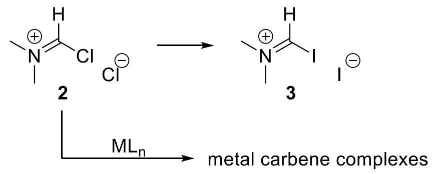
As such reagents, iodocarbenium iodides **1** were chosen (Scheme 2), which are salt-like if one of R/R' is a donor group.[12]



**1a** **1b** **1c**

**Scheme 2.** Two ways of liberation of oxidant and Lewis Base from the hypervalent adduct [Ox]/[LB] ([Ox]'/[LB]'). Both, **1a** and **1c** are dissociation products of [Ox]/[LB].

Their structures may be considered as being in-between two limiting cases of halogen-bonded adducts: either – as the name implies – as complexes between an iodocarbenium cation and iodide (**1b**), or as the adduct of a carbene to elemental iodine (**1a**). Both cases represent the combination of an oxidant with a LB and thus constitute an ideal combination for the oxidative addition to elemental gold.



**Scheme 3.** *N,N*-dimethyliodomethyleneiminium iodide **3** as simplest iodocarbenium iodide, which can be derived from DMF via Vilsmeier reagent **2**.

Arguably the simplest such iodocarbenium iodide is *N,N*-dimethyliodomethyleneiminium iodide **3**, which is accessible by iodination of Vilsmeier reagent **2**.[12,13] The latter is known to oxidize metal precursors leading to so-called *secondary carbene ((mono)dimethylamino carbene*) complexes, but only with starting materials like $Pd(PPh_3)_4$[14,15] and other metals less noble than gold (see scheme 3).[14–20] To the best of our knowledge, such carbene complexes have not yet been prepared from elemental metals[21] and in case of gold not even by more conventional methods.

Salt **3** has been known for decades[22] but its crystal structure has remained elusive until now (Figure 1 left). It features a halogen bond between the cation and the anion, and thus its structure is best represented by **1b** (Scheme 2), as had already been shown by one of us for a related compound.[12]

When to a suspension of **3** in dichloromethane (DCM) at room temperature gold powder was added, the metal powder was dissolved in less than 30 min. $^1H$-NMR spectroscopy indicated the formation of several species including an organogold complex, with the latter being finally confirmed by X-Ray analysis of a single crystal (Figure 1 right).

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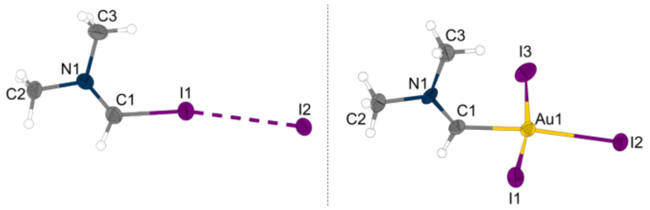
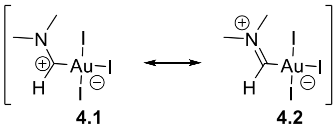


**Figure 1.** Solid state molecular structure of *N*,*N*-dimethyliodomethyleneiminium iodide **3** (left, $d_{I\text{-}I}$ = 3.4198(8) Å, ∡ (C1-I1-I2) = 168.580(91) °) and triiodo-(dimethylamino)methylene-gold(III) **4** (right, ∡(N1-C1-Au-I2) = 91.951(595) °). Thermal ellipsoids at 50% probability level.

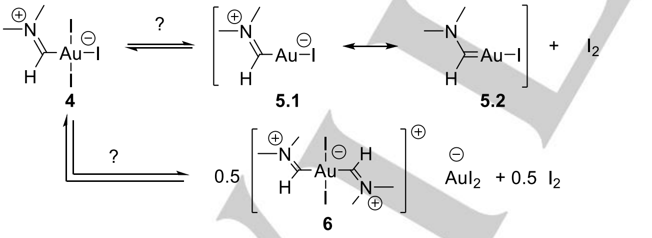
Although classical gold catalysis does not feature oxidative addition steps, this kind of reaction step has attracted more interest in recent years. It was shown by Toste, Russel, Hashmi and others that oxidative additions of e.g. organic halides to Au(I) species are possible under certain conditions.[23] To the best of our knowledge an oxidative addition process was not yet employed for the synthesis of gold carbene complexes.



**Scheme 4.** Resonance structures of triiodo-((dimethylamino)methylene)-gold(III) 4.

The crystal structure of triiodo-((dimethylamino)methylene)-gold(III) **4** indicates that the electronic structure of gold dimethylamino carbene complexes is best described by the iminium-like resonance structure **4.2**: The C-N-double bond in iodocarbenium iodide ($d_{C\text{-}N}$ = 1.272(5) Å) is identical in length to the corresponding bond in complex **4** ($d_{C\text{-}N}$ = 1.272(8) Å). This is also confirmed by $^1$H-NMR-spectroscopy, which indicates hindered rotation around the C1-N bond, and is in agreement to data presented for the corresponding carbene complexes with other metal centers.[18–20]

$^1$H-NMR spectroscopy also indicates that an equilibrium exists in some solvents: while the spectrum of dissolved crystals of **4** in DCM showed only one set of signals, a second species is apparently formed in acetonitrile. When the solvent is changed back to DCM, the signals of **4** are found again together with those of the newly formed species.

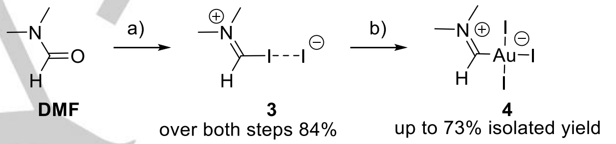


**Scheme 5.** The gold(I) carbene complex **5** and the bis-carbene complex **6** are possible species triiodo-((dimethylamino)methylene)-gold(III) 4 is in equilibrium with.

Since it is described in the literature that $AuI_3(L)$ complexes tend to be in equilibrium with their corresponding gold(I) species,[24] it is possible that complex **4** undergoes a similar reaction. High-field shifts in the proton spectra of open-chain aminocarbene complexes when changing the oxidation state of gold from $Au^{III}$ to $Au^{I}$ are reported in the literature.[25] This is in accordance with the observed high-field shift of C1-H, which is also expected due to the more electron-rich gold center in iodo-(dimethylamino)methylene-gold(I) **5** (see scheme 5). Alternatively, ligand scrambling and formation of ionic species like $[AuI_2(CHNMe_2)_2]^+[AuI_2]^-$ **6** would also explain the spectra (and would be in line with the findings for the NHC(-type) complexes described below).

Heating a solution of the crystals in dry acetonitrile to 80 °C leads to the formation of gold particles. Although dimethylamino carbene complexes of palladium and platinum are described to be stable against water,[17,19,26] addition of water to the solution of **4** in acetonitrile immediately leads to the formation of DMF. This seems to indicate that the gold(III) carbene complexes described herein feature a more electrophilic carbon centre compared to other complexes of these ligands, e.g. with Pt(IV) (which are stable against water).[19]

As the synthesis of **4** suffered from poor yields (18%) and poor reproducibility, further optimization was required. A possible mechanism involves formation of the Au(II) complex $[AuI_2(CHNMe_2)]$ **7** (see Scheme 7 below) after oxidative addition. This species is likely unstable with regard to disproportionation (yielding **4** and the corresponding Au(I) carbene **5**) and other possible decomposition products, which would explain the observed problems. A potential remedy to this issue could be the addition of a further oxidant which converts the unstable Au(II) complex **6** to the stable Au(III) complex **4**, and to this end elemental iodine (in 0.5 equivalents) was chosen (Scheme 6).



**Scheme 6.** Synthesis of the secondary carbene complex triiodo-((dimethylamino)methylene)-gold(III) **4**. a) DCM, r.t., 1. $(COCl)_2$, 1 h, 2. $Me_3SiI$ (2 eq), 2h, b) Au, $I_2$ (0.5 eq), r.t. DCM or acetonitrile, overnight.

$^1$H-NMR spectroscopy in $CD_2Cl_2$ of the crude product mixture indicated complete conversion under formation of complex **4** and a second species (e.g. **5** or **6**, see above) with a ratio of $AuI_3(CHNMe_2)$ **4**:second species of ≈ 5:4 (reaction in acetonitrile) and of 5:1 (performed in DCM) respectively. The crude product mixture containing **4** in about 55% yield, according to NMR, was dissolved in acetonitrile and stored at -30 °C for several days to crystallize complex **4**. The product was isolated in up to 73% yield, confirming the existence of an equilibrium between **4** and the second species.

Since triiodide has been reported to dissolve elemental gold,[2–4] additional mechanistic pathways are feasible beside the one indicated above, the direct reaction between gold particles (or $AuI^-$, which is only a formal particle, representing the iodide coordinated to the gold surface, see below) and the carbenium ion to form Au(II) species **7** with subsequent oxidation. Gold could also be first oxidized to Au(I) species like AuI or $AuI_2^-$, which would then undergo oxidative addition with the organic cation to form the targeted Au(III) complex **4** (Scheme 7).

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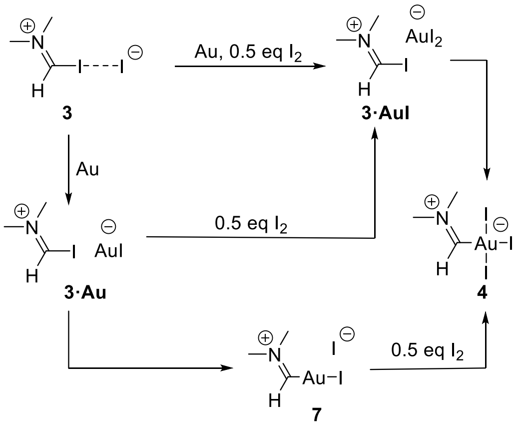


**Scheme 7.** Possible pathways for the reaction between the iodocarbenium iodide **3**, gold and elemental iodine.

While it is outside the scope of this report to fully elucidate the mechanism, comparison experiments were performed to illustrate the role of the individual reaction partners. Firstly, Vilsmeier reagent **2** does not dissolve gold under identical conditions, demonstrating the superior reactivity of the iodo iodide. Secondly, coordination of a LB to the gold surface seems to be crucial for the oxidation process (as also shown *in silico* by Repo et al.[7]): the analogous triflate salt of **3**, obtained by anion exchange with silver triflate, does not undergo any reaction with gold (even after addition of elemental iodine). This clearly illustrates that coordination of iodide to the gold (surface) is a prerequisite for the dissolution process. Thirdly, the organic cation is not decisive for the oxidation of gold (but of course for the formation of the carbene complex): replacing it with tetrabutylammonium still lead to complete dissolution at room temperature in both acetonitrile (as reported by Nakao)[2–4] and DCM, demonstrating that the formation of AuI or $AuI_2^-$ salts could also play a role in the mechanism. To further investigate this, AuI was treated with **3**, which lead to precipitation of gold (~19%) but also to the formation of complex **4** (isolated yield 20%). Obviously, though, our initial experiments had also shown that direct oxidation of Au(0) (or $AuI^-$) by the iodocarbenium iodide is a viable competing pathway.

Finally, the scope of the method was extended towards less electrophilic carbene precursors, which are expected to be more challenging substrates. Indeed, no reaction was observed for the bis-donor-substituted iodocarbenium iodide **8a** and **9** (see Figure 3) at room temperature under our established conditions.

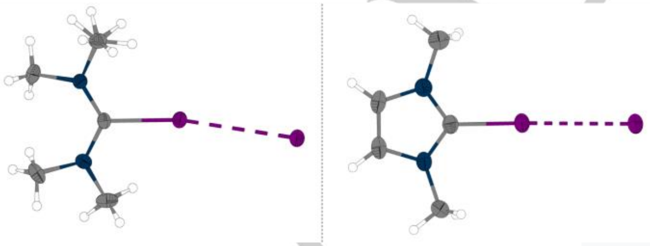


**Figure 3.** Crystal structure of urea-derived bis-(*N,N'*-dimethylamino)iodomethylene iodide **8a** (left, $d_{I\text{-}I}$ = 3.3897(4) Å, ∡(C-I-I) = 170.231(71) °) and 2-iodo-1,3-dimethylimidazolium iodide **9** (right, $d_{I\text{-}I}$ = 3.3298(4) and 3.3096(4) Å, ∡(C-I-I) = 178.018(101) and 176.689(109) °). Thermal ellipsoids at 50% probability.

Therefore, the reaction mixture was stirred in refluxing acetonitrile for 3-4 days, resulting in incomplete dissolution of the gold powder. Nevertheless, in case of the urea-derived salt **8a**, the expected Au(III)-complex **10-mono** (see Figure 4) could be isolated in 37% yield.[27] The mother liquor also yielded crystals of $[(Me_2N)_2CI][AuI_2]$ **8b**, a possible reaction intermediate (see SI). For the NHC-compound, the simultaneous formation of two products could be observed, which were identified by single crystal analyses as mono- and bis-NHC-Au(III) complexes **11-mono** and **11-bis** (see Figure 4). The latter is in an equilibrium with the former, in which the more prevalent **11-bis** is formed by partial reduction of **11-mono** under release of elemental iodine (see SI).

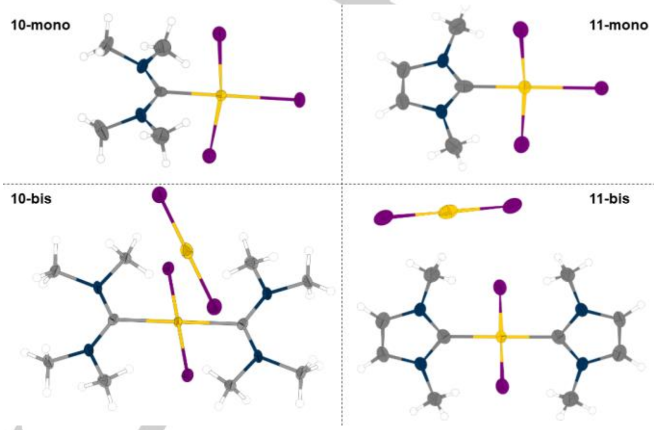
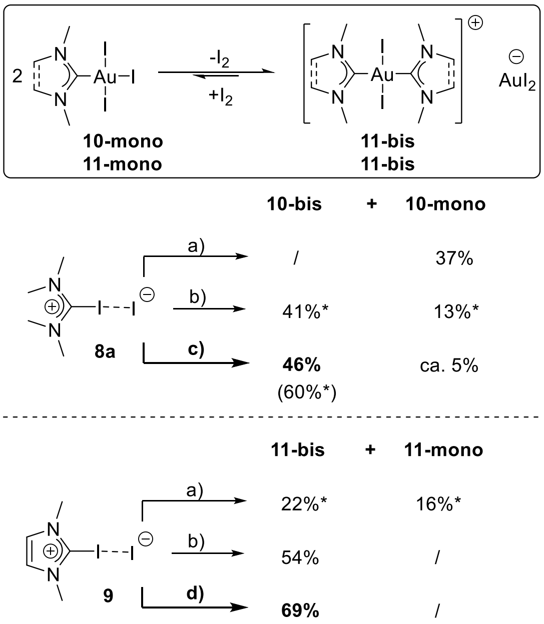


**Figure 4.** Crystal structures of NHC(-like) carbene complexes: the urea-derived complexes **10-mono** (top, left, $d_{Au\text{-}C}$ = 2.041(7) Å) and **10-bis** (bottom, left, $d_{Au\text{-}C}$ = 2.085(4) Å) and the corresponding NHC-complexes **11-mono** (top, right, $d_{Au\text{-}C}$ = 2.074(15) Å) and **11-bis** (bottom, right, $d_{Au\text{-}C}$ = 2.021(7) Å). Thermal ellipsoids at 50% probability.

The crystal structures of the iodocarbenium iodides **8a** and **9** and the mono-carbene complexes **10-mono** and **11-mono** show similar features to the ones of **3** and **4**, respectively (Figure 1). The trans arrangement of the two carbene ligands in **10-bis** and **11-bis** is in agreement with other gold bis-carbene complexes found in literature.[28] In $^1$H-NMR spectroscopy, only one set of signals is obtained for the methyl groups in both systems.

The formation of the bis-carbene complexes, which could be the product of a disproportion reaction of the corresponding Au(II)-species [AuI(carbene)]I, suggests that the reactions of the bis-donor substituted salts **8a** and **9** with gold do not require any additive at all. Indeed, the best yields for **10-bis** and **11-bis** could be achieved when refluxing the starting materials with gold powder only. Notably, under these reaction conditions, the formation of the bis-carbene complexes is preferred over the mono-carbene complexes (see Scheme 9), and in case of **11-bis**, the yield could be increased significantly to 69%.

Obviously, the conversion of gold towards the carbene complexes using additional iodine is somewhat disappointing, which is puzzling since a combination of *tetraalkylammonium* iodide and iodine (0.5 eq) is sufficient to completely dissolve the metal. In contrast to this noncoordinating cation, however, both **8** and **9** are halogen bond donors (halogen-based Lewis acids), and their interaction with iodide would weaken the crucial coordination of iodide to the gold surface. As a counterpoise, we added 0.5 equivalents of tris(dimethylamino)cyclopropenium iodide (TDAI), a source of “naked” iodide,[29] resulting in a significant acceleration of the reaction and a complete consumption of the starting material. In this case **11-mono** is not formed and **11-bis** can be isolated in 54% yield (for more details see SI).[30]



**Scheme 9.** Reaction of imidazolium species **9** or iodocarbenium iodide **8a** with gold (and additives) including isolated yields (*NMR-yields). a) Au, $I_2$ (0.5 eq), MeCN, reflux, 3-4 days, b) Au, $I_2$ (0.5 eq), TDAI, MeCN, reflux, 3-4 days, c) Au, MeCN, reflux, 3-4 days, d) Au, MeCN, reflux, overnight.

In summary, the reaction of iodocarbenium iodides (and iodine) with elemental gold represents the first route for the preparation of carbene complexes directly from the noblest of metals. This simple method thus allows to avoid the use of expensive Au(I) or Au(III) precursors. The reaction of the iodo analogue of Vilsmeier's reagent (**3**) with gold constitutes the first synthesis of a dimethylamino carbene complex from a pure metal and also the first preparation of such a gold complex in general. Also less electrophilic iodocarbenium iodides can be successfully employed in this synthesis protocol, thus providing direct access to NHC(-type) complexes. For the synthesis of these bis-donor substituted carbene complexes, no further additives are required. This finding provides further evidence that the reaction (without addition of $I_2$) likely proceeds via a Au(II)-species, which disproportionates to Au(I)-anion $AuI_2^-$ and the Au(III) product. All investigated carbene complexes showed dynamic behaviour in acetonitrile and in case of the NHC(-like) complexes (**10** and **11**), the involved species could be identified as mono- and bis-carbene complexes.

Examples for oxidative additions to gold are still limited although this kind of reaction attracted much interest lately.[23] Herein, the scope of such reactions could be extended towards carbene complexes of $Au^{III}$. Further investigations in our lab have shown that our type **C** protocol can be successfully transferred to other noble metals, like palladium and platinum. It seems that "Noble Metal Corrosion" could be considered an emerging research field.

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**Keywords:** oxidative addition • gold complexes • carbenes • noble metal • transition metal • halogen bonding

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[27] In the NMR experiments, an equilibrium between **10-mono** and **10-bis** can be observed, even though the bis-carbene complex was not found as a reaction product (see SI). Currently, we cannot explain these findings.

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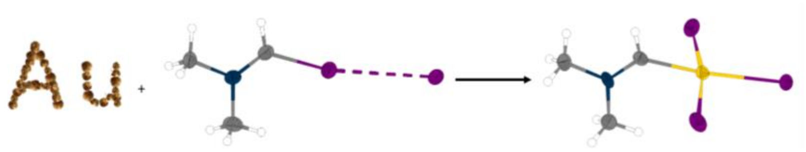
[30] A second species in ca. 19% yield was observed via NMR, but its structure is currently unknown.

## Entry for the Table of Contents

COMMUNICATION



Organic iodide salts, providing both oxidative power and coordinating ligand, dissolve elemental gold under formation of organo-gold complexes. The obtained products were identified as Au$^{III}$ complexes, all featuring Au-C bonds, as shown by X-ray single crystal analyses. This method also provides a direct access to NHC(-type) complexes and avoids costly organometallic precursors.

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**Noble Metal Corrosion: Halogen Bonded Iodocarbenium Iodides Dissolve Elemental Gold – A Direct Access to Gold-Carbene Complexes**