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Gold(III) Diazonium Complexes for Electrochemical Reductive Grafting

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S *Supporting Information*

ABSTRACT: Gold(III) diazonium complexes were synthesized for the first time and studied for electrochemical reductive grafting. The diazonium complex $[CN\text{-}4\text{-}C_6H_4N{\equiv}N]AuCl_4$ was synthesized by protonating $CN\text{-}4\text{-}C_6H_4NH_2$ with chloroauric acid $H[AuCl_4]\cdot 3H_2O$ to form the ammonium salt $[CN\text{-}4\text{-}C_6H_4NH_3]AuCl_4$, which was then oxidized by the one-electron oxidizing agent $[NO]PF_6$ in CH_3CN. The highly irreversible reduction potential of 0.1 mM $[CN\text{-}4\text{-}C_6H_4N{\equiv}N]AuCl_4$ observed at −0.06 V versus Ag/AgCl in CH_3CN/0.1 M $[Bu_4N]PF_6$ encompasses both gold(0) deposition and diazonium reduction. Repeated scans showed the absence of the reduction peak on the second run, which indicates that surface modification with a blocking gold aryl film has occurred and is largely complete.

Modification of surfaces by the electrochemical reduction of diazonium salts is a progressing area of materials chemistry.[1] Organic films generated by diazonium reduction and grafting demonstrated a distinctive performance in the formation of a superior corrosion inhibitor film on iron surfaces,[2] graphene surface modification,[3] the preparation of diazonium-modified enzyme electrodes,[4] immobilization of proteins,[5] the grafting of polymers to surfaces,[6] the attachment of oligonucleotides to surfaces,[7] and the printing of gold surfaces via soft lithography.[8] Heck reactions involving diazonium salts have been extensively developed and widely used in the synthesis of natural products and other organic compounds.[9]

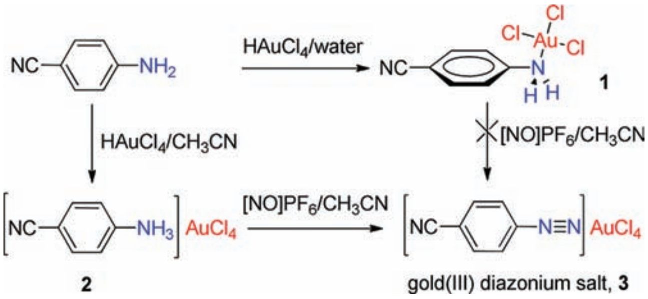
In the electrochemical reductive grafting process, one-electron reduction of an aryldiazonium ion results in the attachment of the aryl group to the electrode. Electrochemical reduction of a cobaltocenium diazonium complex resulted in the covalent attachment of the cobaltocenium ion to a glassy carbon surface and the formation of an "organometallic electrode".[10] Some of the limitations that arise from the low stability of the aryldiazonium salts have been overcome by in situ diazotization, followed by the cathodic deposition process.[10] Electrochemical reduction of the aryldiazonium salts to grafted films has been studied at carbon,[3,12] semiconductors,[13] and metals.[14]

Despite the advantages of self-assembled monolayer grafting to gold, there are some serious limitations, and an alternative modification strategy has shown great success: diazonium grafting.[15] Strong and stable adhered films derived from diazonium salt reduction on gold surfaces are due to the C−Au covalent bond.[1] Density functional theory structure and bonding studies between an aryl group and the gold surface shows that the phenyl favors a C−Au σ bond in a vertical pattern and facilitates the perpendicular growth of the aryl layers compared with grafting to other metals such as iron.[16]

Conversely, the drawback of a modification approach based on the aryldiazonium salts is their synthesis and isolation, which is not always simple. More broadly, many diazonium complexes are incompatible with the extremely harsh conditions for diazotization, which involve either strong acids, oxidizing agents, or both. In comparison with the extensive literature on the synthesis and application of gold−nitrogen complexes, gold diazonium complexes have not been synthesized.[17] We describe a facile procedure for the synthesis of stable gold(III) diazonium complexes and the success in the in situ "synthesis" of an aryl-modified gold surface. Thus, the synthesis of easily reduced diazonium salts containing metal complex anion-based anions is very important from the preparative and application standpoint.

Diazotization necessitates an acidic medium, which can be provided by the chloroauric acid $H[AuCl_4]\cdot 3H_2O$ (Scheme 1).

Scheme 1. Synthesis of Gold(III) Diazonium Salt 3



The gold precursor plays several important roles in this chemistry; it provides the acidic medium necessary in the diazotization reactions, a stabilizing counteranion, and a gold surface for aryl grafting. One more advantage of the chloroauric acid is the ability to dissolve the amine completely as an ammonium salt. The trial to protonate $CN\text{-}4\text{-}C_6H_4NH_2$ with $H[AuCl_4]\cdot 3H_2O$ by suspending in water resulted in the loss of one HCl molecule and the formation of the gold(III) trichloride amine complex $CN\text{-}4\text{-}C_6H_4NH_2AuCl_3$ (**1**). Because of the absence of the acidic medium necessary for diazotization,

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1 was not susceptible to oxidation by [NO]PF_6 in CH_3CN (Supporting Information). However, the protonation of CN-4-$C_6H_4NH_2$ with H[$AuCl_4$]·$3H_2O$ in CH_3CN formed the tetrachloroaurate ammonium salt [CN-4-$C_6H_4NH_3$]$AuCl_4$ (**2**), which was oxidized by [NO]PF_6 to form the yellow gold(III) diazonium salt [CN-4-$C_6H_4N{\equiv}N$]$AuCl_4$ (**3**) in 92% yield.

The gold(III) diazonium complex **3** was synthesized for the first time in the present work and without the need for mineral or organic acids. *Although caution should be exercised when handling all diazonium salts, there were no indications that this compound is particularly hazardous.* Complex **3** is stable to air and light in the solid state and in a CH_3CN solution. The IR spectrum of **3** showed the $\nu_{N\equiv N}$ stretching frequency at 2277 cm^{-1}, and the ^1H NMR spectrum in $CDCl_3$/dimethyl sulfoxide displayed two doublets assigned to the phenyl protons at 7.71 and 8.33 ppm, which are noticeably shifted from 6.65 and 7.45 ppm in the 4-aminobenzonitrile ligand (Supporting Information).

To the best of our knowledge, this work reports the first X-ray structure of an amine-$AuCl_3$ complex, **1** (Figure 1).[16]

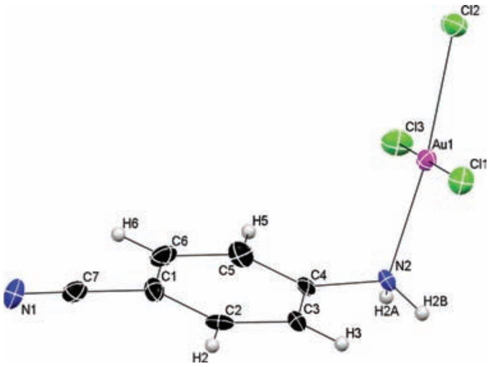

Figure 1. Structure of **1** at 50% probability. Bond distances (Å): Au1−N2 2.073(9), C4−N2 1.443(13), and C7−N1 1.139(14). Bond angles (deg): Au1−N2−C4 109.0(6), Cl3−Au1−Cl1 177.33(11), and Cl2−Au1−N2 173.3(3).

Coordination of gold(III) trichloride to the CN-4-$C_6H_4NH_2$ ligand caused a difference in the bond angles about the gold atom in the square-planar arrangement. The Cl−Au−N and Cl−Au−Cl bond angles measure 173.3(3)° and 177.33(11)°, respectively. Protonation of the amine by tetrachloroauric acid resulted in a slight increase in the C−N bond distance, 1.479(8) Å in **2** versus 1.443(13) Å in **1** (Figure 2). The close proximity to the N≡N group, the Cl···N≡N bond distance 3.23 Å, and the fact that the halide is less nucleophilic in the tetrachloroaurate anion than the free chloride are presumably the contributing factors for the increased stability of the diazonium salt (Figure 3).

The irreversible electrochemical reduction of 0.1 mM complex **2** in CH_3CN/0.1 M [Bu_4N]PF_6 at a glassy carbon electrode at a scan rate of 500 mV/s was observed at −0.56 V versus Ag/AgCl. The prepeak at −0.1 V probably indicates the two-step reduction of gold(III). The $Au^{III} \rightarrow Au^0$ reduction in **2** was confirmed by the presence of a black gold deposit on the glassy carbon (GC) electrode surface after several runs. The peak assigned to the gold(III) reduction is known to be sensitive to the coordinating ligand, among many other factors,[18] and can proceed directly to gold(0) or in two distinctive steps.

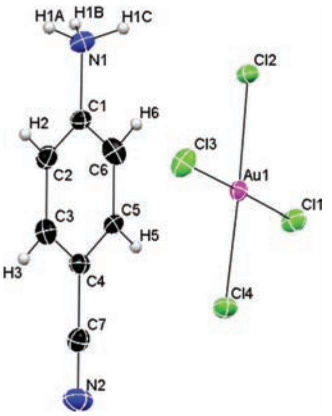

Figure 2. Structure of **2** at 50% probability. Bond distances (Å): C1−N1 1.479(8) and C7−N2 1.142(10).

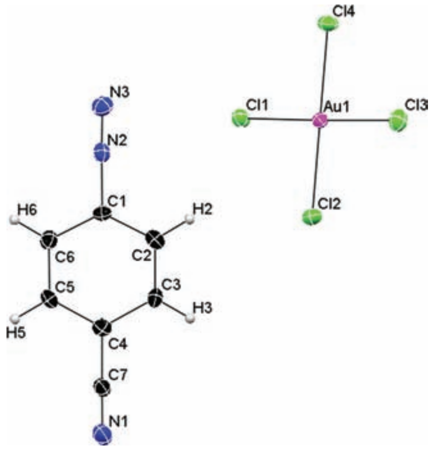

Figure 3. Structure of **3** at 50% probability. Bond distances (Å): N2−N3 1.087(5), N2−C1 1.414(6), and C7−N1 1.133(6). Bond angles (deg): N3−N2−C1 177.2(5) and N1−C7−C4 177.4(5).

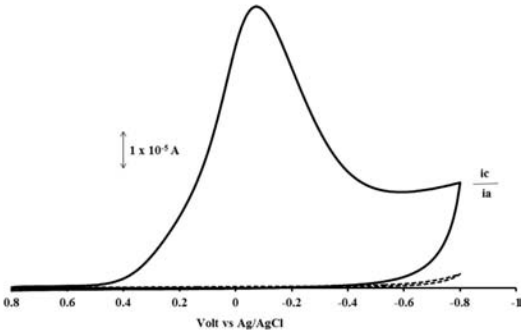

Figure 4. Cyclic voltammogram of 0.1 mM **3** at a GC electrode in CH_3CN/0.1 M [Bu_4N]PF_6 at 100 mV/s versus Ag/AgCl. Top: Reduction at the first cycle. Bottom: Reduction at the second cycle.

The highly irreversible reduction potential of 0.1 mM **3** occurs at −0.06 V versus Ag/AgCl in CH_3CN/0.1 M [Bu_4N]PF_6 (Figure 4). The reduction potential of the diazonium tetrafluoroborate salt is observed at 0.16 V versus SCE.[12b] The first scan of **3** showed the reduction of gold(III) and diazonium and the formation of black deposits on the glassycarbon working electrode surface. The absence of the irreversible reduction peak after repeated scans indicates that surface modification with a blocking gold−aryl film has occurred and is largely complete. The gold film is stable to oxidation in the anodic backward scan from 0 to +1.8 V presumably because of its protection by the grafted aryl layer. The oxidation of gold(0) films at ~1.0 V has been reported in gold halide complexes.[18]

The electrochemical reduction of the diazonium tetrafluoroborate salt [CN-4-$C_6H_4N{\equiv}N$]BF_4 at a glassy carbon electrode showed the one-electron peak at 0.16 V to the fifth run, in contrast to the gold(III) diazonium salt, which is completely reduced at the electrode surface before the second run.[12b] The fact that the gold(III) halides such as **2**, H[$AuCl_4$]·$3H_2O$, and PPN[$AuCl_4$] showed reduction after repetitive cycles is in support of the role of gold in the diazonium salt reduction efficiency.[18] The irreversible reduction potential of **3** observed close to 0 V is assumed to encompass the gold and diazonium.

It cannot be concluded from this study whether gold was completely deposited before the diazonium reduction. More detailed studies are underway to support the sequence of the deposition as concerted or stepwise. Chronoamperometry measurements for **3** showed a sharp decrease in the current within a short time (~5 s), which indicates that the first monolayer of grafted aryl is completed rather quickly. The current change after the turning point is much smaller because electron transfer through the first grafted aryl monolayer is strongly suppressed. The modified electrode does not appear to undergo a significant loss of the gold–aryl layer if it is washed with organic solvents, and it retains its coverage even when subjected to sonication in water for 1 h.

In summary, we synthesized a gold diazonium complex that showed electrochemical reduction behavior typical of grafting onto the in situ deposited gold film on a glassy carbon electrode. Synthesis of the gold diazonium complex following our procedure is simple and can be carried out without the need for mineral or organic acids.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, characterization, and CIF files for **1**–**3**. 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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