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# Synthesis of Stable Gold(III) Pincer Complexes with Anionic Heteroatom Donors

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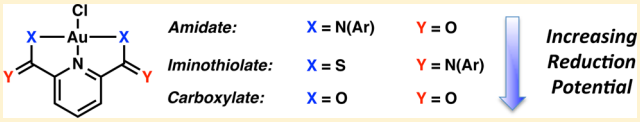
Supporting Information

**ABSTRACT:** A series of gold(III) complexes supported by pyridine-based bis(amidate), bis(carboxylate), and bis(iminothiolate) substituents is reported. These compounds represent rare examples of pincer-ligated gold(III) centers with multiple anionic heteroaom donors. Reactivity and electrochemical studies demonstrate the stability of these compounds and the marked difference in reduction potentials with varying ligand scaffolds.



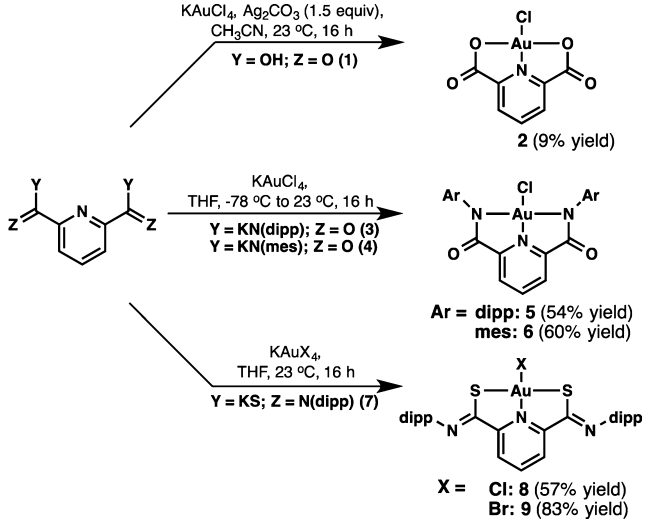

Coordination compounds of gold(III) are valuable in medicine,[1] materials science,[2] and catalysis.[3] Despite the utility of this high-valent metal, gold(III) remains underexplored in comparison to gold(I), due in part to the propensity of gold(III) complexes to undergo decomposition via reduction[4] and protodemetalation.[5] The development of new stabilizing ligands would improve understanding and better enable harnessing the potential of this metal center.

Pincer ligands,[6] members of a ligand class that have been exploited for decades in catalysis and in the preparation of structurally remarkable compounds across the transition metals, have received relatively little attention in advancing the chemistry of gold(III). The works of Che,[7] Yam,[2b,8] and Bochmann[9] have demonstrated that cyclometalated 2,6-diphenylpyridine complexes of gold(III) exhibit electronic properties of interest in the development of photoluminescent materials and the capacity to support highly reactive ligands. The chemistry of other pincer ligands on gold(III) has not been explored to such depth. Surprisingly, X-type heteroatom ligands have been utilized in only a few examples of gold(III) pincer complexes,[10] even though bidentate 2-pyridyl carboxylate[11] and 2-pyridyl amidate[12] complexes of gold(III) show catalytic and biological activity, respectively. Tridentate analogues of the ligands that support these compounds are well-documented in stabilizing other $d^8$ metal centers[13] and yet, to our knowledge, have not been extended to gold(III). This precedent and the use of other $X_2L$-type ligands to stabilize highly electrophilic metals[14] suggest that bis(anionic) heteroatom-rich ligands may serve as excellent ancillary ligands for gold(III). In addition, such ligands may prevent the reduction of gold(III) to gold(I), which would be of value, as the oxidation state of gold complexes can have a profound impact on product distributions in catalysis[15] and the potency of gold-containing therapeutics.[1a,16]

Herein we report the synthesis, structural characterization, electrochemical analysis, and reactivity studies of gold(III) pincer complexes stabilized by gold−heteroatom bonds. The results of this investigation demonstrate that gold(III) complexes supported by iminothiolate and amidate pincer ligands are remarkably stable and less susceptible to reduction than analogues with carboxylate linkages. These findings in turn can inform ligand design for the diverse applications of gold(III) complexes.

All pincer complexes were accessed via salt metathesis of commercially available tetrahaloaurate salts (Scheme 1). The

**Scheme 1. Synthesis of Gold(III) Pincer Complexes**




reaction of 2,6-pyridinedicarboxylic acid (**1**) with $KAuCl_4$ in the presence of $Ag_2CO_3$ yielded the desired compound **2**, albeit in low yield. Dipotassium bis(amidate) ligands **3** and **4** underwent salt metathesis with $KAuCl_4$ to yield complexes **5** and **6**, respectively. Similarly, bis(iminothiolate) complexes **8** and **9** were prepared in moderate to good yield by metalation of **7** with the appropriate tetrahaloaurate salt. For all compounds, one linkage isomer was formed, and the structures of **2**, **5**, and **8**

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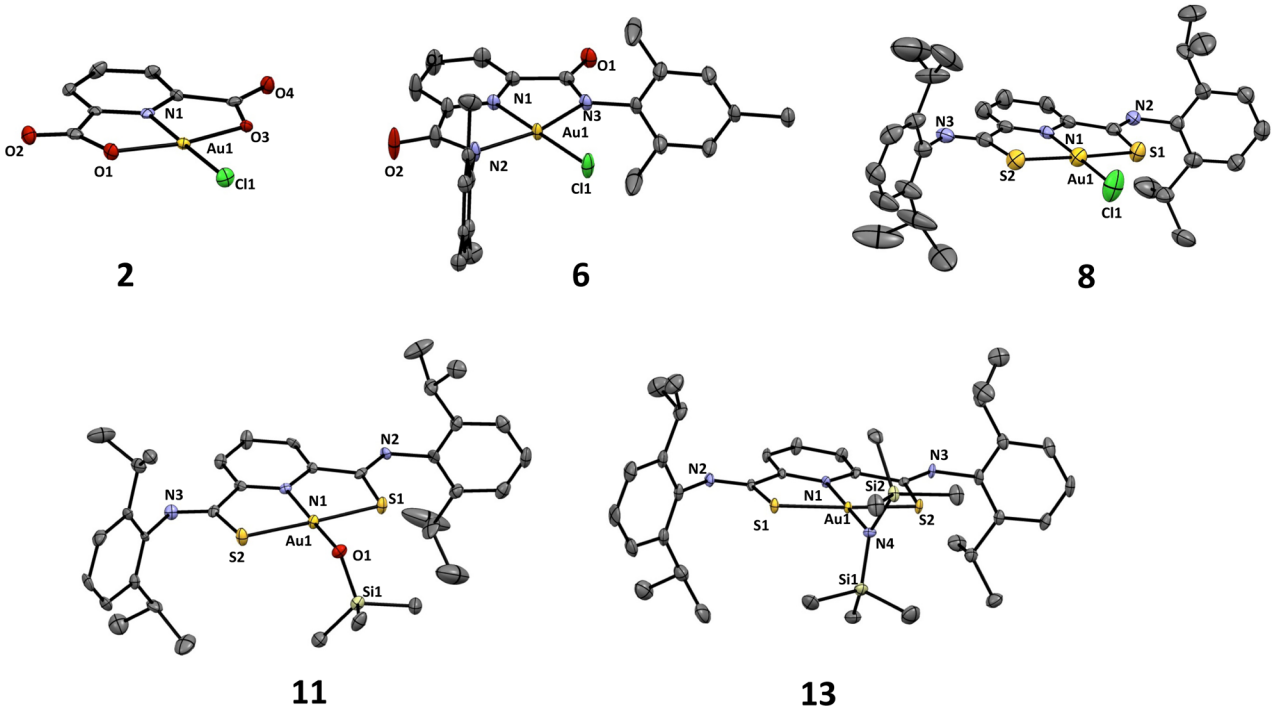
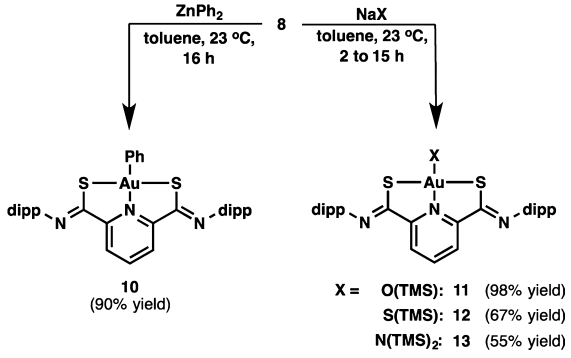



**Figure 1.** Solid-state structures of complexes **2**, **5**, **8**, **11**, and **13**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

were confirmed unambiguously by single-crystal X-ray diffraction (Figure 1).

We first sought to probe the fundamental reactivity of these new complexes (Scheme 2). Attempts to add new ligands to **5** and **6** via transmetalation were unsuccessful, presumably due to projection of the amidate aryl rings around the chloride; however, the less sterically congested coordination sphere of **8** permitted access to a variety of ligand substitutions. For example, complex **8** was treated with diphenylzinc to yield the organometallic compound **10**. Given our groups' interest in the reactivity of gold–heteroatom bonds,[17] we next attempted substitution of the chloride with X-type heteroatom donors. An initial survey of various alkyl and aryl thiolates, amides, and oxides led to no reaction or decomposition. Though previously reported methods designed to install heteroatom donors were unsuccessful,[18] it was found that salt metathesis with silyl amides, thiolates, and oxides yielded the first examples of gold(III) complexes with silyl-substituted heteroatoms as ligands (**11**–**13**), and silanoate **11** and silylamide **13** were subsequently characterized by X-ray diffraction in the solid state (Figure 1). The marked difference in reactivity between these ligands and their hydrocarbyl analogues remains unclear but may be attributed to attenuation of electron density at the heteroatom, which may in turn prevent reduction at the metal center.

**Scheme 2. Halide Substitution of 8**




Our interest in using these complexes to effect catalytic transformations led us to examine a number of reactions known to involve gold(III) precatalysts, such as C–H activation[19] and cycloadditions.[20] Halide abstraction from complexes **5**, **6**, **8**, and **9** to open a coordination site were unsuccessful, and treatment of complexes **10**–**14** with a host of electrophiles led to no reaction or decomposition (see the Supporting Information). Surprisingly, the reaction of **10** even with triflic acid did not lead to protonolysis to form benzene. Treatment of **5** and **8** with excess trifluoroacetic acid resulted in no reaction and reversible protonation at the ligand, respectively, indicating that the gold–heteroatom bonds in these compounds are not as susceptible to protonolysis as the gold–carbon bonds of cyclometalated 2,6-diphenylpyridine gold(III) complexes are.[5] It is likely that electrophiles react with the lone pairs of the supporting ligands of the complexes described in this work, as evidenced by modeling of the molecular orbitals of compounds **2**, **5**, and **8**.[21] In the course of canvassing the reactivity of these new complexes, it was discovered that **2** was reduced to gold(0) in the presence of *N*,*N*-diisopropylamine, while the other complexes were not. This prompted us to consider the susceptibility of these new compounds to reduction.

Electrochemical profiles of each of these complexes were investigated by cyclic voltammetry in order to determine their reduction potentials (Figure 2). Complexes **5** and **6** underwent reduction only at very negative potentials (−1.06 and −1.05 V, respectively), as did **8** and **9** (−0.96 and −0.95 V, respectively). In all cases these first reduction events were quasi-reversible. In contrast, complex **2** underwent an irreversible reduction at 0.15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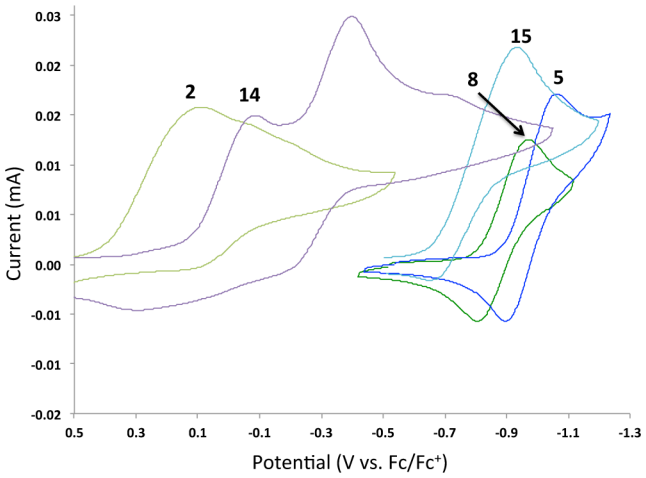


**Figure 2.** Cyclic voltammograms of complexes **2**, **5**, **8**, **14**, and **15** in THF. Conditions: 0.1 M $n$-$Bu_4NPF_6$; working electrode, glassy carbon; counter electrode, Pt; reference electrode, Ag/AgCl; scan rate, 100 mV/s.

V. (2-Picolinato)gold(III) dichloride (**14**) and the 2-pyridyl amidate complex **15** were analyzed as well (Figure 3). The

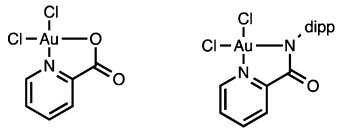


**Figure 3.** Structures of complexes **14** (left) and **15** (right).

former was also reduced at a relatively anodic potential (−0.07 V), whereas the latter underwent reduction at −0.92 V. Though these data have not been definitively identified as being ligand- or metal-based reductions, they show the minimal potential at which these gold complexes are reduced and, given that these events are not fully reversible regardless of scan rate, the point at which these compounds begin to decompose. These data suggest that amidate, bidentate or tridentate, and iminothiolate complexes of gold(III) are less susceptible to reduction, whereas carboxylate-supported complexes are reduced at relatively positive potentials. There are two major implications of these results. The first is that the identity of gold(III) picolinate catalysts is complicated by their high reduction potential, as Hashmi and co-workers have alluded to in a previous study[11] focused on the induction period observed with this class of precatalysts. A second insight is the importance of gauging the susceptibility to reduction of gold(III) complexes on the basis of the context in which they are used. Just as picolinate complexes serve as excellent precatalysts for many transformations, their lack of other applications may be attributed to their ease of reduction. This idea is particularly important, given recent advances in the controlled reduction of gold(III) to gold(I) for delivering biological probes[1e] and the divergent reactivity between gold(I) and gold(III) catalysts.[15,22]

In conclusion, a series of novel gold(III) complexes with ancillary pincer ligands bound by heteroatom linkages has been prepared. The bis(iminothiolate) scaffold was competent in stabilizing a number of complexes with varied substitution in the fourth coordination site. The stability of the pincer complexes with iminothiolate and amidate groups appears to preclude the use of these compounds in catalysis. This in turn led us to examine the electrochemistry of these pincer compounds and conclude that iminothiolate- and amidate-supported complexes have reduction potentials nearly 1 V more cathodic than those of their carboxylate analogues. We hope that these compounds will be exploited in other fields that require discrete gold(III) complexes.

## ■ ASSOCIATED CONTENT

### Supporting Information

Text, figures, tables, and CIF and MOL files giving X-ray diffraction data for all crystallographically characterized compounds, $^1$H and $^{13}$C NMR spectra of all compounds, experimental details, and details of DFT calculations. 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.

## ■ ACKNOWLEDGMENTS

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