Nucleophilic T-Shaped (LXL)Au(I)-Pincer Complexes: Protonation and Alkylation

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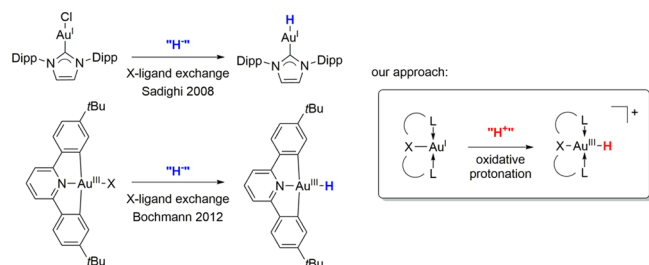[‖]Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg 2050, South Africa

S *Supporting Information*

ABSTRACT: We report the synthesis and reactivity of unusual T-shaped (LXL)Au(I)-pincer complexes, based on a carbazole framework flanked by two mesoionic carbenes (MICs). In contrast to other Au(I) complexes, these complexes react with electrophiles. Protonation and alkylation occur either at the metal or the ligand, depending on steric factors. Of particular interest, protonation at gold leads to an unprecedented cationic Au(III) hydride, which gives a ^{1}H NMR resonance at δ −8.34 ppm. The reactivity of this "hydride", however, shows protic and not hydridic behavior.

The understanding of gold catalysis has tremendously improved thanks to the isolation of complexes previously thought to be only transient intermediates.[1] Among them are gold hydrides,[2] which have been postulated as intermediates in catalytic cycles,[3] such as β-hydride elimination processes.[4] The first stable monomeric Au(I) hydride was isolated in 2008 by Sadighi et al. through the addition of a hydride source to an (NHC)Au(I)-Cl complex (Scheme 1).[5] In 2012, using a similar synthetic approach, Bochmann et al. were able to prepare a Au(III) hydride supported by a XLX pincer ligand,[6] and this family[7] remains the only one reported. On the other hand, there has been pronounced interest in the search for mild Au(I)-Au(III) oxidation reactions. Some recent strategies involve chelate assisted oxidative addi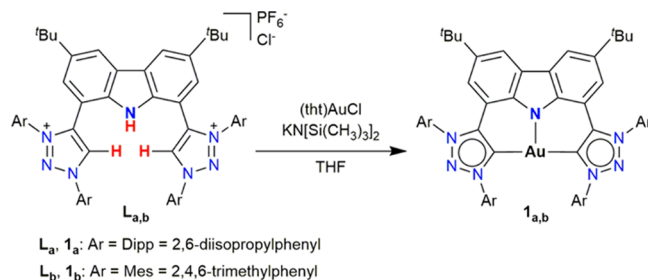tion,[8] and the use of reactive partners such as strained biphenylene[9] or aryldiazonium salts under photoactivation[10] or thermally controlled processes.[11]

In 2014, we reported the synthesis of a monoanionic LXL-pincer ligand featuring two 1,2,3-triazol-5-ylidenes[12] flanking a carbazolide scaffold.[13] The ligand was shown to stabilize reactive late transition metal complexes as a result of the donating ability of both the mesoionic carbenes (MICs) and the central coordinating amido moiety.[14] Herein we show this ligand allows for the preparation of (LXL)Au(I) complexes, which in contrast to the well studied Au(III)-pincer complexes[15] are not known. The strong electron-donating properties of the ligand, coupled with its peculiar geometry, makes the Au(I) center reactive toward electrophiles. It is shown that, depending on steric factors, protonation and alkylation occur either at the metal or the ligand.

One-pot tris-deprotonation of L_a and L_b with excess KHMDS followed by addition of (tht)AuCl, yielded the corresponding dark purple-red pincer Au(I) complexes 1_a and 1_b which are air-stable (Scheme 2). Single crystals of 1_a and 1_b suitable for X-ray

Scheme 1. Previous Strategies to Au Hydrides Involved a Hydride Source without Change of Oxidation State, In Contrast to Our Approach

Scheme 2. Synthesis of T-Shaped Au(I) Complexes 1_a and 1_b

L_{a}, 1_a: Ar = Dipp = 2,6-diisopropylphenyl
L_b, 1_b: Ar = Mes = 2,4,6-trimethylphenyl

diffraction analysis were obtained by slow evaporation of a toluene solution (Figure 1). Both complexes feature an unusual three-coordinate T-shaped geometry around the metal center, with a long Au-N bond distance [1_a, 2.325(2); 1_b, 2.412(3) Å].[16] Note that three-coordinate Au(I) complexes are not uncommon; however, all known examples display trigonal planar geometries (albeit distorted).[17,18]
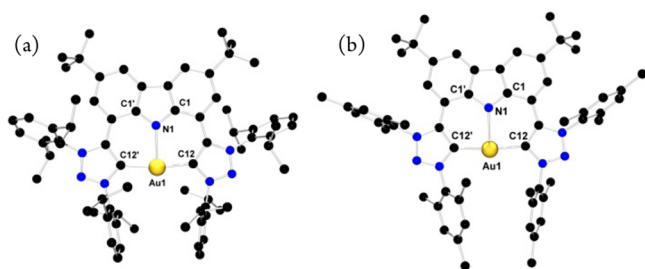
**Figure 1.** Solid-state structures of 1_a (a) and 1_b (b). Hydrogen atoms are omitted for clarity.

We reasoned that both the strong electron-donating ligand and the T-shaped geometry should favor oxidation processes leading to d^8-square-planar Au(III) complexes. Treatment of 1_a with excess trifluoromethanesulfonic acid (6 equiv) in THF resulted in a color change from red-purple to lime-green, and after workup, the cationic Au(III) hydride complex 2_a was isolated in 35% yield (Scheme 3). Just like Bochmann's complex, 2_a is air-stable both in solution and in the solid-state. An X-ray diffraction study allowed for the unambiguous localization of the H atom, and revealed a Au-N distance $[2.051(2)$ Å$]$ much shorter than in 1_a $[2.325$ Å$]$; the other parameters show very little deviation from the ideal square-planar geometry (Figure 2). The carbene carbons of 2_a

Scheme 3. Protonation of T-Shaped Au(I) Pincer Complex 1_a To Give the Cationic Au(III) Hydride 2_a
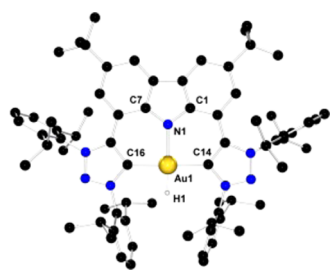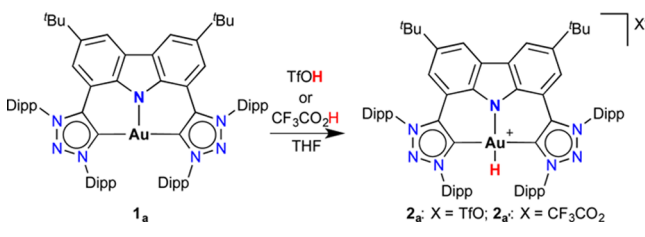

Figure 2. Solid-state structure of Au-hydride 2_a. Counter-anion $[OTf^-]$ and hydrogen atoms are omitted for clarity.

give a ^{13}C NMR signal at δ 149.8 ppm,[19] significantly upfield shifted compared to the carbene carbon resonance of 1_a (δ 175.1 ppm). The hydride NMR signal appears at δ −8.34 ppm, upfield of the reported value (−6.58 ppm) for Bochmann's neutral hydride complex.[4] The FT-IR spectrum displays the ν(Au-H) absorption at 2197 cm^{-1} which is comparable to the band reported by Bochmann (2188 cm^{-1}).[4] Note that protonation of 1_a also occurred with weaker acids, such as the trifluoroacetic acid, affording $2_{a'}$.

Like Bochmann's Au(III)-H and Sadighi's Au(I)-H complexes,[3] 2_a features a covalent Au-H bond that is unreactive toward excess acid (trifluoromethanesulfonic acid, trifluoroacetic acid or HCl). Interestingly, addition of NaH to a d_8-THF solution of $2_{a'}$

resulted in the regeneration of 1_a and formation of H_2 (g) after 3 days at room temperature (see SI, section S3). This result clearly illustrates the protic and not hydridic character of 2_a (Scheme 4).

Scheme 4. Protic and Not Hydridic Character of 2_a
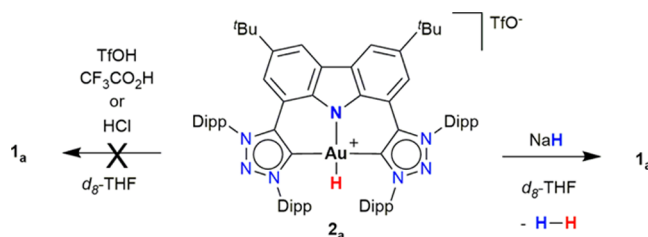

Two mechanisms could rationalize the formation of 2_a. A direct protonation of the Au(I) center of 1_a, or alternatively a protonation of the nucleophilic nitrogen of the amido ligand, followed by oxidative addition of the N-H bond across the Au(I) center (Scheme 5). NMR spectroscopic evidence for the

Scheme 5. Postulated Mechanism for the Protonation of 1_a
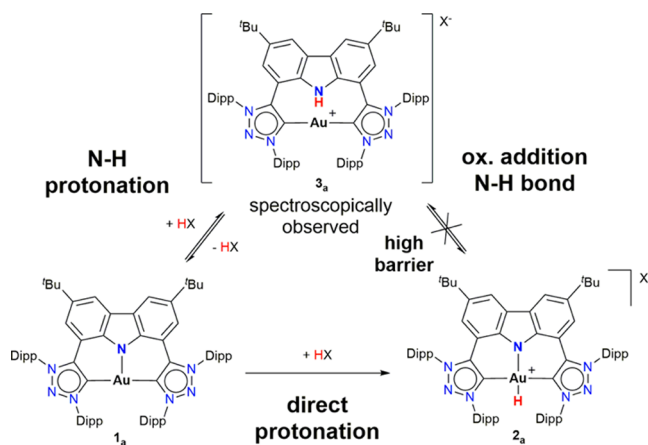
formation of the Au(I) complex 3_a featuring a protonated amido N-H was obtained when 1_a was treated with a stoichiometric amount of TfOH in THF (see SI, section S5). The NH resonance was observed as a singlet at δ 10.94 ppm, and the carbene carbons give a signal at δ 177.8 ppm. Complete conversion of 3_a into 2_a occurs in solution over an extended period of time. At first glance, these experimental data suggest an N-H oxidative addition, similar to the C-X insertion at gold recently reported by Bourissou et al.[8] However, calculations at the B3PW91-SMD/SDD(Au)-6-31G**(other atoms) level of theory predict a slightly exergonic reaction from 3_a to 2_a ($\Delta G \sim$ −1 kcal/mol) but with a high energy barrier $[\Delta G^{\ddagger} \sim 50$ kcal/mol$]$ that clearly disfavors this mechanism. The difficulty for the N-H insertion might be the requirement for the H to migrate trans (over the gold). Therefore, we propose the protonation can occur both at the nitrogen and gold center, a hypothesis that is supported by the visualization of the HOMO of 1. Of particular interest, Figure 3 shows that the anti-bonding interaction between N and Au results in a significant polarization of the corresponding occupied d-orbital at gold. This interaction can be seen as a "remote basicity" that renders the Au-side nucleophilic.[20] Then, there is an equilibrium between the cationic NH (3_a) and the neutral complex 1_a leading to the AuH complex 2_a.
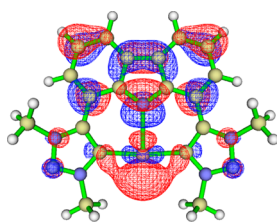
Figure 3. Visualization[22] of the HOMO of **1** at the B3PW91/SDD(Au)-6-31G** (other atoms) level of theory.

For the deprotonation of the cationic Au(III)-hydride, two mechanistic scenarios can be proposed: (i) direct deprotonation of the hydride at the metal center; (ii) coordination of a second hydride to form a Au(III)-dihydride followed by reductive elimination of H_2. Calculations support the first hypothesis because the pentacoordinate gold dihydride[21] features a trans-configured square-pyramidal geometry (see SI), which makes a trans-elimination process very unlikely.

We then expanded our study to other electrophiles. Treatment of **1$_a$** with a slight excess of MeOTf led to complex **4$_a$** in which the amido moiety was alkylated (Scheme 6). The methyl hydrogens

Scheme 6. Alkylation of 1$_{a,b}$ To Form 4$_{a,a'}$ and 5$_b$, Respectively
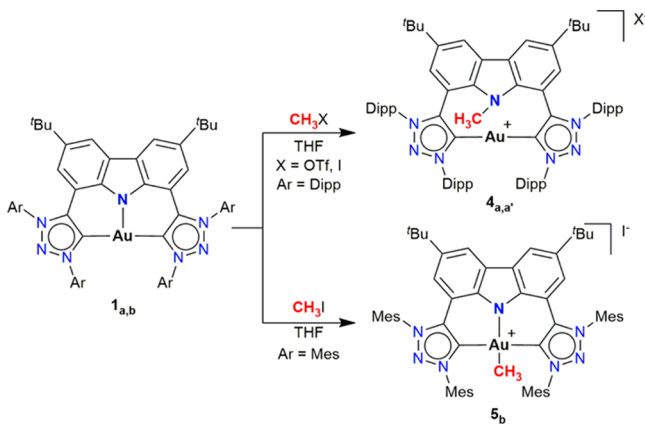
appear at δ 2.93 ppm, and the downfield ^{13}C chemical shift of the carbene signal (δ 177.5 ppm) is in agreement with a Au(I) oxidation state. The structure was confirmed by X-ray diffraction, which shows that the methyl group points out of the plane of the carbazole ring (Figure 4a). The Au···N distance [2.67(1) Å] is significantly longer than in **1$_a$**/**1$_b$** and **2$_a$** (<2.412 Å), indicating a weak interaction, if any. Alkylation of the amido moiety also readily occurred with iodomethane to form **4$_{a'}$**, as shown by NMR spectroscopy, albeit longer reaction times where required. All
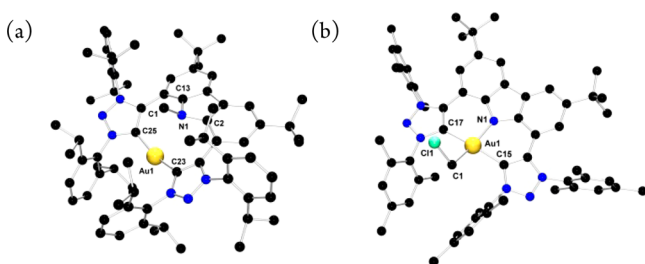

Figure 4. Solid-state structure of (a) *N*-methylated complex **4$_a$** and (b) the alkylation product **6$_b$**. Hydrogen atoms and counter-anion (a) [OTf⁻] and (b) (Cl⁻) are omitted for clarity.

attempts to form the corresponding Au(III) methyl complex failed, despite heating the reaction up to 60 °C for 2 days. However, upon addition of iodomethane to the Au(I) complex **1$_b$**, we observed the immediate and clean formation of the Au(III)-Me complex **5$_b$**. The methyl hydrogens and carbon appear at δ +0.19 and −3.8 ppm, respectively, and the upfield ^{13}C chemical shift of the carbene signal (δ 146.3 ppm) is in agreement with a Au(III) oxidation state. It is quite likely that the regioselectivity observed is based on steric factors, and in contrast to the protonation reaction, the alkylation is not reversible.

The influence of steric factors has been further substantiated by the lack of reactivity of complex **1$_a$** with dichloromethane, whereas with **1$_b$**, the Au(III) complex **6$_b$** was readily obtained (Scheme 7).

Scheme 7. Alkylation of 1$_b$ with CH_2Cl_2
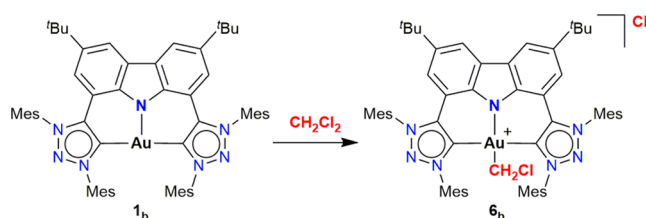
In agreement with a Au(III) complex, the carbene carbons resonate significantly upfield (δ 145.7 ppm), and the -CH_2Cl protons give a signal at δ 3.03 ppm. The X-ray diffraction study of crystals obtained in CD_2Cl_2 revealed a short N-Au bond distance [2.078(5) Å] as observed in the Au(III)-hydride **2$_a$**, but the expected square-planar geometry is significantly distorted [N-Au-C 166.2(2)°], possibly because of excessive steric bulk (Figure 4b). Note that a chloromethyl gold complex has previously been prepared by salt metathesis from the Grignard reagent.[23] The oxidative addition of CH_2X_2 to gold was previously only observed with binuclear gold dimers leading to mixed Au(I)/Au(III) compounds.[24]

In conclusion, we present the synthesis of unusual T-shaped (LXL)Au(I) complexes, which in contrast to other Au(I) complexes, react with electrophiles, either at the ligand or the metal. Importantly, protonation leads to the first cationic Au(III) hydride complex, which shows protic and not hydridic behavior. We are currently exploring the reactivity of the cationic Au(III) hydride and wish to take advantage of the facile oxidation of Au(I) to Au(III) that is enabled by the MIC-based pincer ligand.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Notes

The authors declare no competing financial interest.

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