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Thermally Stable Gold(I) β-Diketiminate Complexes

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The synthesis and X-ray structures of gold(I) adducts supported by β-diketiminates have been reported. $\{[HC\{(H)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Au\}_2$ and $\{[HC\{(H)C(Dipp)N\}_2]Au\}_2$ [Dipp = 2,6-(i-Pr)$_2$C$_6$H$_3$] are easily isolable solids and feature 12-membered macrocyclic ring structures. β-Diketiminate ligands adopt a W-shaped conformation. Gold atoms are bonded to the nitrogen atoms in a linear fashion. ^{1}H NMR signals corresponding to the protons at the β-diketiminate ligand β-C position of the gold adducts appear at a notably high downfield region.

The β-diketiminates are one of the most useful groups of monoanionic, nitrogen-based ligands in chemistry.[1] They are excellent auxiliary ligands for the isolation of a wide variety of transition-metal complexes including a number of copper derivatives with interesting structures and useful catalytic properties.[2−28] However, β-diketiminates have yet to play a major role in the heavier coinage metal (i.e., silver and gold) chemistry. In 2005, Itoh and co-workers reported the isolation of the first β-diketiminatosilver(I) complexes using $[HC\{(H)C(Dipp)N\}_2]^-$ [Dipp = 2,6-(i-Pr)$_2$C$_6$H$_3$], $[NCC\{(H)C(Dipp)N\}_2]^-$, and $[O_2NC\{(H)C(Dipp)N\}_2]^-$ ligands.[29] These molecules display interesting dinuclear, tetranuclear, and polymeric structures with W- or U-shaped ligand backbones. They also described some of the difficulties encountered during the isolation of such adducts as a result of facile silver(I) → silver(0) reduction accompanied by the oxidative dimerization of the β-diketiminate ligand. Monomeric silver(I) β-diketiminates have also been reported recently.[30]

In contrast to copper and silver, there are no structurally characterized β-diketiminate complexes of gold in the literature. There is, however, an important recent discovery concerning the catalytic properties of gold(I) supported by $[HC\{(Me)C(Dipp)N\}_2]^-$ (the adduct has been detected by electrospray ionization mass spectrometry).[31] It serves as an excellent catalyst for the selective aerobic oxidation of alcohols to carbonyl compounds. In this Communication, we report the successful utility of two β-diketiminates in the isolation of thermally stable gold(I) adducts, including X-ray crystal structures of $\{[HC\{(H)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Au\}_2$ (**1a**) and $\{[HC\{(H)C(Dipp)N\}_2]Au\}_2$ (**1b**).

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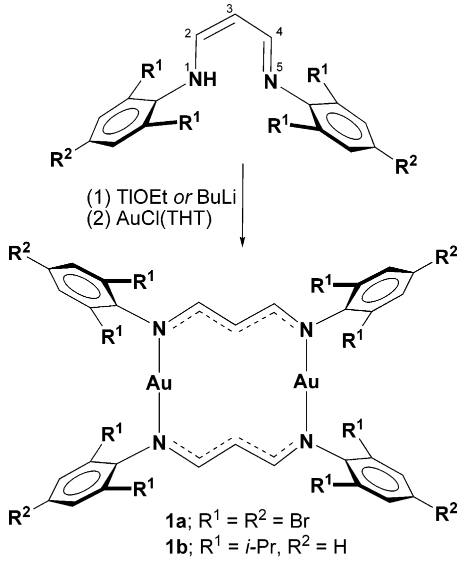
Scheme 1. Synthesis of Gold(I) Adducts Supported by β-Diketiminates



1a; $R^1 = R^2 = Br$
1b; $R^1 = i\text{-}Pr$, $R^2 = H$

In order to improve the chances of stabilizing a gold(I) β-diketiminate adduct, we first focused on the use of a bulky and somewhat weakly donating diketimine $[HC\{(H)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]H$ (which contains large and electron-withdrawing bromine atoms at the ortho/para positions of the *N*-aryl groups). The free ligand and the corresponding thallium(I) adduct $[HC\{(H)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Tl$ were obtained in good yields using readily available starting materials. The treatment of $[HC\{(H)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Tl$ with Au(THT)Cl led to **1a** in about 50% yield (see Scheme 1). It is a yellow solid with an unexpectedly high air, light, and thermal stability. For example, a solid sample of **1a** did not show any signs of decomposition even after 1 week in open air under ambient light.

The X-ray analysis revealed that the gold β-diketiminate "$[HC\{(H)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]Au$" units form dimers of the type **1a** with a planar 12-membered $Au_2N_4C_6$ core as shown in Figure 1. **1a** molecules sit on a center of symmetry. The β-diketiminate ligand adopts a W-shaped conformation. The two-coordinate gold atoms exhibit nearly linear geometry [average N−Au−N angle = 174.89(11)°]. The intramolecular and closest intermolecular Au···Au separations are at 4.96 and 7.00 Å, respectively. The closest intramolecular Au···H distance between the gold and hydrogen atoms at the β-diketiminate ligand backbone β-C position is short at 2.65 Å (cf. the sum of the van der Waals radii of gold and hydrogen based on Bondi values = 2.86 Å).[32]

Encouraged by the remarkable stability of **1a**, we also explored the utility of a better known and somewhat electron-rich $[HC\{(H)C(Dipp)N\}_2]^-$ in gold chemistry.[33] Interestingly, the reaction between $[HC\{(H)C(Dipp)N\}_2]Li$ and Au(THT)Cl also gave an air and thermally stable gold(I) β-diketiminate adduct **1b** (Scheme 1) in reasonable yield (~50%). **1b** also features a planar 12-membered macrocyclic $Au_2N_4C_6$ core and has a center of symmetry (Figure 2). The N−Au−N angles are essentially linear [175.17(10)°]. The intramolecular and closest intermolecular Au···Au separations are at 4.95 and 10.66 Å, respectively. The gold and hydrogen atoms at the β-diketiminate ligand backbone β-C position are in close proximity, separated just by 2.70 Å.

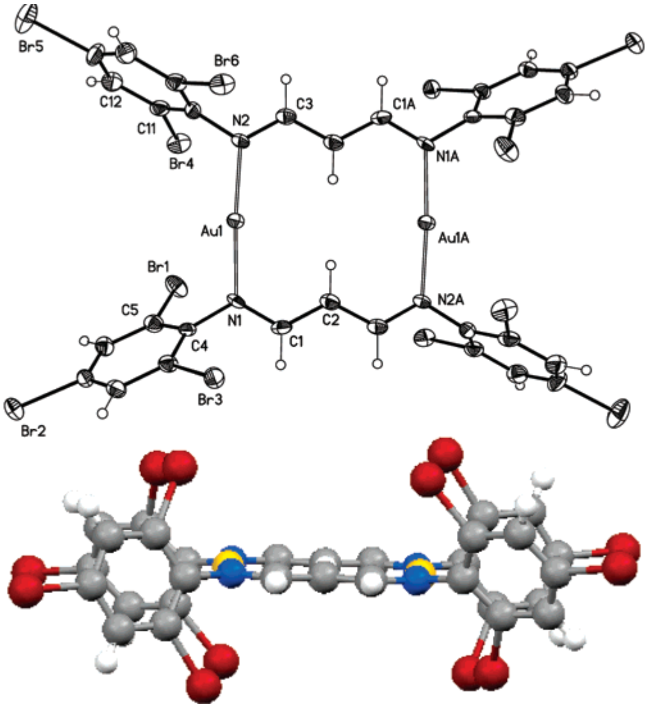


Figure 1. Top: ORTEP diagram of **1a** with 50% probability thermal ellipsoids. Bottom: Side view showing the planarity of the macrocyclic ring. Selected bond lengths (Å) and angles (deg): Au1−N2 2.029(5), Au1−N1 2.036(5), N1−C1 1.327(7), N2−C3 1.324(7), C1−C2 1.384(8); N2−Au1−N1 175.94(19), C1−N1−C4 119.4(5), C1−N1−Au1 120.8(4), C4−N1−Au1 119.7(4), C3−N2−C10 119.0(5), C3−N2−Au1 122.5(4), C10−N2−Au1 118.5(4), N1−C1−C2 121.8(5), C1−C2−C3A 123.8(5), N2−C3−C2A 123.5(5).

The lighter coinage metal analogues of **1b** are known.[29,34] These homoleptic metal adducts are useful for examining coinage metal group trends. The basic structures of $\{[HC\{(H)C(Dipp)N\}_2]M\}_2$ (M = Cu, Ag, Au) are very similar (see the Supporting Information for selected structural parameters). The M−N distances of these coinage metal β-diketiminates [average Cu−N = 1.870(8) Å, Ag−N = 2.111(8) Å, and Au−N = 2.026(3) Å] vary as expected based on the covalent radii of silver(I) >gold(I) > copper(I).[35,36] The transannular ligand separation follows the same trend (i.e., the silver adduct has the longest distance between the two β-diketiminate ligands). The intramolecular M···M distance is similar, indicating that the W-shaped backbone does not change significantly despite the change in the size of the metal ion.

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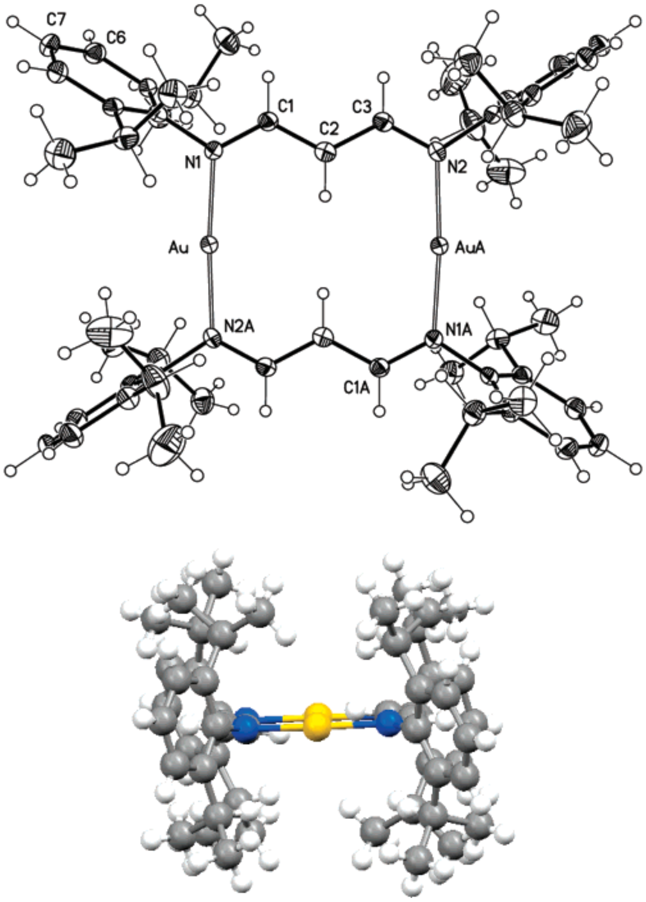

Figure 2. Top: ORTEP diagram of **1b** with 50% probability thermal ellipsoids. Bottom: Side view showing the planarity of the macrocyclic ring. Selected bond lengths (Å) and angles (deg): Au−N2A 2.025(3), Au−N1 2.027(3), N1−C1 1.325(4), N1−C4 1.436(4), N2−C3 1.320(4), N2−C16 1.448(4), N2−AuA 2.025(3), C1−C2 1.390(5), C2−C3 1.394(5); N2A−Au−N1 175.17(10), C1−N1−C4 118.5(3), C1−N1−Au 121.1(2), C4−N1−Au 120.2(2), C3−N2−C16 117.8(3), C3−N2−AuA 120.4(2), C16−N2−AuA 121.4(2), N1−C1−C2 123.9(3), C1−C2−C3 124.0(3), N2−C3−C2 123.8(3).

^{1}H NMR signals corresponding to the protons at the β-diketiminate ligand β-C position of **1a** and **1b** appear as triplets at a notably high downfield region (δ 8.76 and 9.01, respectively). However, the resonances corresponding to the ligand backbone protons at the α positions do not show such high downfield chemical shift values (e.g., δ 7.32 and 7.19 for **1a** and **1b**, respectively). Furthermore, protons on the β-C position of the free ligands and the metal adducts with U-shaped ligand backbones (e.g., $\{[HC\{(H)C(Dipp)N\}_2]ZnOCH_3\}_2$, δ 4.40;[33] $[HC\{(H)C(2,4,6\text{-}Br_3C_6H_2)N\}_2]CuCO$, δ 4.98) were observed at significantly upfield positions. Overall, these data point to a link between the high downfield ^{1}H NMR shifts (of protons at the ligand β-C position) and the inward-pointed C−H bonds enforced by the rigid W-shaped ligand backbone.

The ^{1}H NMR signal corresponding to the protons at the β-diketiminate ligand β-C position of the copper adduct $\{[HC\{(H)C(Dipp)N\}_2]Cu\}_2$ has been observed at δ 7.91.[34] However, this peak overlaps with aryl proton signals in the silver adduct $\{[HC\{(H)C(Dipp)N\}_2]Ag\}_2$ (i.e., it is reported to be in a much more upfield region, δ 7.05−7.32).[29] This trend in the chemical shift values appears to follow the electron affinities of coinage metal ions [9.22, 7.59, and 7.72 eV for gold(I), silver(I), and copper(I), respectively], which correlates with the metal ion σ-acceptor ability.[37] However, because of the limited amount of data, we are not certain whether this high downfield shift of endocyclic protons is a result of through-space M···H interaction [note that these protons are in a peri position with the gold atoms just as in 1-naphthyl- or 9-anthrylgold(I) compounds][38] or some other factors such as the deshielding caused by two contributing transannular π systems (i.e., because these protons are sandwiched by two conjugated W-shaped ligand backbones). We are currently synthesizing related molecules with different ligand backbone conformations to further examine this NMR spectroscopic feature.

In conclusion, here we show that it is possible to isolate thermally stable β-diketiminate complexes of gold(I). **1a** and **1b** also represent a rare group of gold(I) (a "soft" metal ion) adducts stabilized solely by a "hard" nitrogen-based ligand (without the aid of Au···Au interactions).[35,39]

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Supporting Information Available: Synthetic details and X-ray crystallographic data for **1a** and **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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