



Review

Coordination chemistry of gold(II) with amidinate, thiolate and ylide ligands

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ABSTRACT

Various reagents such as Cl₂, Br₂, I₂, benzoyl peroxide and CH₃I add to the dinuclear gold(I) amidinate complex [Au₂(2,6-Me₂Ph-form)₂] to form oxidative-addition gold(II) metal–metal bonded complexes. The gold–gold distance in the dinuclear complex decreases upon oxidative-addition with halogens from 2.7 to 2.5 Å, similar to observations made with dithiolate and ylide ligands. The sodium salt of the guanidinate Hhpp ligand, Hhpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine reacts with (THT)AuCl in THF or CH₂Cl₂ to form a Au(II) complex, [Au₂(hpp)₂Cl₂], either by solvent oxidation or disproportionation of the Au(I) to Au(II) and the metal. Density functional theory (DFT) and MP2 calculations on [Au₂(hpp)₂Cl₂] find that the highest occupied molecular orbital (HOMO) is predominately hpp and chlorine-based with some Au–Au δ* character. The lowest unoccupied molecular orbital (LUMO) has metal-to-ligand (M–L) and metal-to-metal (M–M) σ* character (approximately 50% hpp/chlorine, and 50% gold). The charge-transfer character of the deeply colored solutions is observed in all the oxidative-addition products of the dinuclear gold(II) nitrogen ligands. This contrasts with the colors of the gold(II) ylide oxidative-addition products which are pale yellow. The colors of the crystalline gold(II) nitrogen complexes are dark orange to brown. This review will focus on the chemistry of gold(II) with nitrogen ligands and compare this with the well reviewed chemistry of gold(II) thiolate and ylide complexes.

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1. Introduction

Dinuclear gold(I) complexes containing either one or two bridging ligands such as ylides and thiolates and their oxidative-addition products have attracted considerable attention for many years [1,2]. Nitrogen ligands have been little used in gold(II) chemistry and almost no studies describe results using anionic, bridging nitrogen ligands. Only very few examples of other gold(II) complexes with nitrogen compounds are known. There is one nitrogen bonded gold(II) nitrite complex, Au₂(ylide)₂(NO₂)₂ [2].

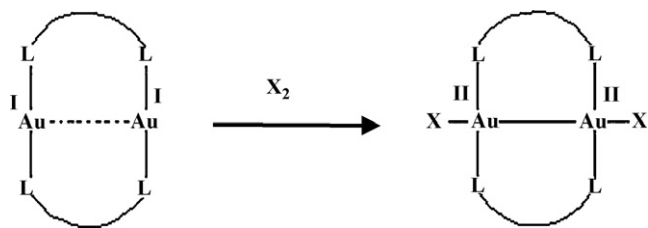
The great majority of compounds with gold nitrogen bonds occur with gold in the oxidation states +I and +III with the elec-

tronic configurations [Xe]4f¹⁴5d¹⁰ and [Xe]4f¹⁴5d⁸, respectively [3]. There is a strong tendency for disproportionation from Au(II) to Au(I) and Au(III) in mononuclear complexes [4] because of the odd electron in these 5d⁹ metal complexes. Several dinuclear gold(II) amidinate complexes have been produced. These metal–metal bonded Au(II) complexes have various anionic ligands, including a methyl group coordinated to the Au(II), and are stable at room temperature [5].

The oxidative-addition of halogens to dinuclear Au(I) ylide and thiolate ligand compounds, [AuL]₂, has been described thoroughly in several reviews [1,2]. Three new bonds form from the two Au(I) atoms and the X₂. One pair of electrons forms the metal–metal bond in this system (Scheme 1) [6]. In the Goddard–Low bonding argument [7], the two gold electrons available for the metal–metal bond are a result of promotion from the filled orbital on each Au(I) to the hybrid (d–sp) orbital along the Au–Au axis [1]. In these dinuclear

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Scheme 1. General drawing for the oxidative-addition to the dinuclear gold(I) complexes.

Au(I) complexes, this is a low lying, anti-bonding orbital directed along the internuclear axis which generally is the HOMO for these systems. However, this does not appear to be the case with the amidinate complexes (*vide infra*).

There are several published reviews on the chemistry of gold(II) ylide and thiolate complexes [2a,2b,8]. This review will focus on the chemistry of gold(II) with nitrogen ligands and compare this chemistry with the chemistry of gold(II) thiolate and ylide complexes.

2. Brief history of gold(II) ylide and thiolate complexes

Extensive studies have been published on dinuclear gold complexes containing one or two bridging ligands. The oxidative-addition reactions with gold(I) dimers containing anionic bridging ligands such as ylides, dialkyldithiocarbamates and dithiophosphinates have attracted much attention (Chart 1) [7,8]. It is believed that the σ -donor capability of carbon atoms on the ylide anion ligands and the presence of phosphorus onium centers adjacent to the four Au–C σ -bonds contribute to the unexpected stabilization found [1,2].

In the case of sulfur ligands, π -bonding or anti-bonding as well as σ bonding may occur. With weakly donating thiolate ligands such as xanthates, and dithiocarbamates, stable Au(II) products are not formed. With dithiophosphonates, and 1,1-dithiolates, chemically reversible oxidative-addition has been observed. These gold(I) dithioate dimers are structurally similar to the ylide dimer., but solutions of the Au(II) complexes disproportionate and with a mixed-ligand dithiophosphonate/ylide complex, the halogen can be lost from the solid upon heating. The methylhalide addition products of the ylides reversibly lose methyl halide upon heating.

The X-ray structures of the dinuclear gold(II) ylide and thiolate complexes reveal a short gold–gold distance of about 2.5 Å. The dinuclear Au(II) complexes $[\text{Au}(\text{CH}_2)_2\text{PPh}_2\text{X}]_2$ and $[\text{Au}(\text{MTP})\text{X}]_2$ (MTP = $\text{CH}_2(\text{S})\text{PPh}_2$; X = Cl, Br, I) have Au(II)–Au(II) bonds with dis-

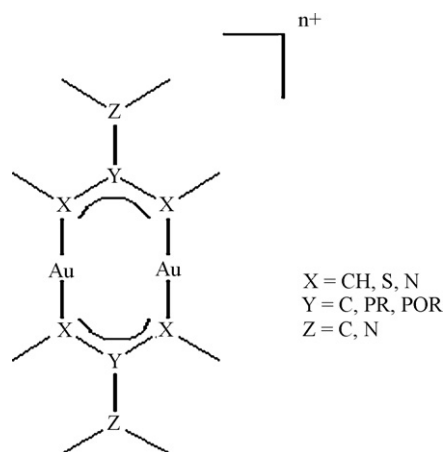


Chart 1. Bidentate monoanionic ligands known to form dinuclear gold(I) complexes which can be oxidized to gold(II) species.

tances around 2.6 Å. The Au(I) precursors in all these systems have gold–gold distances close to 3.0 Å [9]. This dramatic decrease in distance results from the formation of the Au–Au bond along a common X–Au–Au–X axis. In 1988, the short Au(II)–Au(II) distance of 2.55 Å was found in $[\text{Ph}_4\text{As}]_2[\text{Au}_2(i\text{-MNT})_2\text{Cl}_2]$, MNT = $\text{S}_2\text{C}_2(\text{CN})_2^{2-}$, a product formed by chlorine oxidation of the corresponding digold(I) dithiolate [10].

3. Oxidative-addition reactions to a dinuclear gold(I) amidinate complex

Oxidative-addition reactions to the dinuclear gold(I) amidinate complex, $[\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2]$, results in the formation of metal–metal bonded Au(II) complexes. The Au(II) amidinate complexes are the first gold(II) species isolated with nitrogen ligands [11]. The complexes are stable at room temperature. Various reagents such as Cl_2 , Br_2 , I_2 , benzoyl peroxide and CH_3I add to the dinuclear gold(I) amidinate complex to form the gold(II) products, $[\text{Au}_2\text{XY}(2,6\text{-Me}_2\text{Ph-form})_2]$ (Scheme 2) [11,12,13].

The reaction of the dinuclear complex, $[\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2]$, with the halogenated solvents, CH_2X_2 , $\text{XCH}_2\text{CH}_2\text{X}$, CX_4 (X = Cl, Br, I) also forms Au(II) products (Figs. 1 and 2). With the iodide derivatives the reaction occurs in the time of mixing. The analogous reactions with chloride and bromide derivatives take approximately 2–3 days, and 7 days with CH_2Cl_2 in order to oxidize all the Au(I) material. A crystalline product in which there are equal amounts of oxidized and unoxidized complexes in the same unit cell, $[\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2\text{X}_2][\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2]$, X = Cl and X = Br (Fig. 1) is isolated when the reaction is stopped after 3–4 h of stirring. In the reaction of the haloalkyls CH_nX_m , the qualitative order of reactivity with the dinuclear gold complex (I > Br > Cl) follows inversely the order of carbon–halogen bond dissociation energy, C–Cl > C–Br > C–I. X-ray crystallography of the gold(II) amidinate complexes shows a decrease in the Au–Au distance from 2.71 Å in the starting dinuclear complex to 2.51–2.57 Å in the oxidized species. The Au–X distances are Au–Cl = 2.36 Å, Au–Br = 2.47 Å, and Au–I = 2.68 Å (Table 1). The Au–N distance decreases from 2.035(7) Å in the dinuclear complex to 2.00–2.004 Å in the oxidative-addition products.

The oxidative-addition of benzoyl peroxide, $(\text{PhCOO})_2$, leads to the isolation of $[\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2(\text{PhCO}_2)_2]$ [12]. An analogous ylide complex, $[\text{Au}_2((\text{CH}_2)_2\text{PPh}_2)_2(\text{PhCO}_2)_2]$ is known [14]. The benzoate amidinate product $[\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2(\text{PhCO}_2)_2]$ was obtained, Fig. 3, by adding an equivalent amount of benzoyl peroxide to a toluene solution of the dinuclear Au(I) amidinate. The bonding of the benzoates to the dinuclear gold(II) amidinate is similar to the unidentate bonding of the carboxylate observed in the ylide complexes, which also adopt an *anti*-geometry in the solid state.

The oxidative-addition of benzoyl peroxide to the dinuclear gold(I) ylide complex forms a gold(II) complex with the shortest Au–Au distance observed, 2.56–2.58 Å, for the dinuclear Au(II) ylide complexes. Similarly, the Au–Au distance in the oxidized amidinate product $[\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2(\text{PhCO}_2)_2]$, 2.48 Å [12], is the shortest Au–Au distance in the Au(II) amidinate system although we have recently observed that the Au(II)–Au(II) bond

Table 1
Dinuclear Au(II) amidinate complexes characterized by X-ray studies.

Complex	$d(\text{Au}^{\text{II}} \cdots \text{Au}^{\text{II}})$	$d(\text{Au}-\text{X})$	$d(\text{Au}-\text{R})$
$[\text{ClAu}(2,6\text{-Me}_2\text{Ph-form})_2\text{AuCl}]$	2.517(7)	2.356(2)	
$[\text{BrAu}(2,6\text{-Me}_2\text{Ph-form})_2\text{AuBr}]$	2.525(15)	2.470(2)	
$[\text{IAu}(2,6\text{-Me}_2\text{Ph-form})_2\text{AuI}]$	2.579(4)	2.682(4)	
$[(\text{CH}_3)\text{Au}(2,6\text{-Me}_2\text{Ph-form})_2\text{AuI}]$	2.529(11)	2.50	2.12
$[\text{PhCO}_2\text{Au}(2,6\text{-Me}_2\text{Ph-form})_2\text{AuO}_2\text{CPh}]$	2.489(10)	2.045(8)	

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