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Review

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

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ABSTRACT

Various reagents such as Cl_2, Br_2, I_2, benzoyl peroxide and CH_3I add to the dinuclear gold(I) amidinate complex $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2]$ 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-2*H*-pyrimido[1,2-a]pyrimidine reacts with (THT)AuCl in THF or CH_2Cl_2 to form a Au(II) complex, $[Au_2(hpp)_2Cl_2]$, either by solvent oxidation or disproportionation of the Au(I) to Au(II) and the metal. Density functional theory (DFT) and MP2 calculations on $[Au_2(hpp)_2Cl_2]$ 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.

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, $Au_2(ylide)_2(NO_2)_2$ [2].

The great majority of compounds with gold nitrogen bonds occur with gold in the oxidation states +I and +III with the electronic configurations $[Xe]4f^{14}5d^{10}$ and $[Xe]4f^{14}5d^{8}$, 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 $5d^9$ 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 X_2. 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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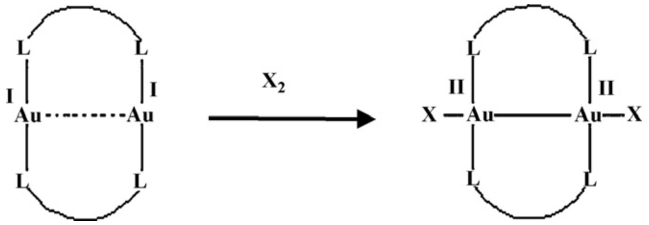


Scheme 1. General drawing for the oxidative-addition to the dinuclear gold(I) complexes.

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 (*vida 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 dithiophoshinates 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 $[Au(CH_2)_2PPh_2X]_2$ and $[Au(MTP)X]_2$ (MTP = $CH_2(S)PPh_2$; X = Cl, Br, I) have Au(II)–Au(II) bonds with distances 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 $[Ph_4As]_2[Au_2(i\text{-MNT})_2Cl_2]$, MNT = $S_2C_2(CN)_2^{2-}$, a product formed by chlorine oxidation of the corresponding digold(I) dithiolate [10].

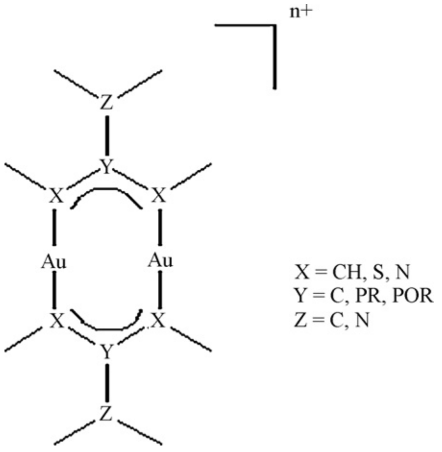


Chart 1. Bidentate monoanionic ligands known to form dinuclear gold(I) complexes which can be oxidized to gold(II) species.

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

Oxidative-addition reactions to the dinuclear gold(I) amidinate complex, $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2]$, 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, $[Au_2XY(2,6\text{-}Me_2Ph\text{-}form)_2]$ (Scheme 2) [11,12,13].

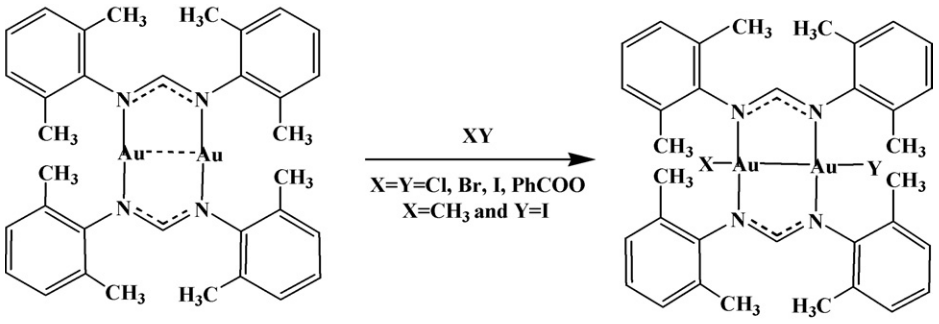
The reaction of the dinuclear complex, $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2]$, with the halogenated solvents, CH_2X_2, XCH_2CH_2X, CX_4 (X = Cl, Br, I) also forms Au(II) products (Figs. 1 and 2). With the iodide derivatives the reaction occurs in the time of mixing. The analogous reactions with chloride 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, $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2X_2][Au_2(2,6\text{-}Me_2Ph\text{-}form)_2]$, 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, $(PhCOO)_2$, leads to the isolation of $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2(PhCO_2)_2]$ [12]. An analogous ylide complex, $[Au_2((CH_2)_2PPh_2)_2(PhCO_2)_2]$ is known [14]. The benzoate amidinate product $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2(PhCO_2)_2]$ 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 $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2(PhCO_2)_2]$, 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	$d(Au^{II}\cdots Au^{II})$	d(Au–X)	d(Au–R)
$[ClAu(2,6\text{-}Me_2Ph\text{-}form)_2AuCl]$	2.517(7)	2.356(2)	
$[BrAu(2,6\text{-}Me_2Ph\text{-}form)_2AuBr]$	2.525(15)	2.470(2)	
$[IAu(2,6\text{-}Me_2Ph\text{-}form)_2AuI]$	2.579(4)	2.682(4)	
$[(CH_3)Au(2,6\text{-}Me_2Ph\text{-}form)_2AuI]$	2.529(11)	2.50	2.12
$[PhCO_2Au(2,6\text{-}Me_2Ph\text{-}form)_2AuO_2CPh]$	2.489(10)	2.045(8)	



Scheme 2. Synthesis of gold(II) amidinate complexes by oxidative-addition to the dinuclear gold(I) amidinate.

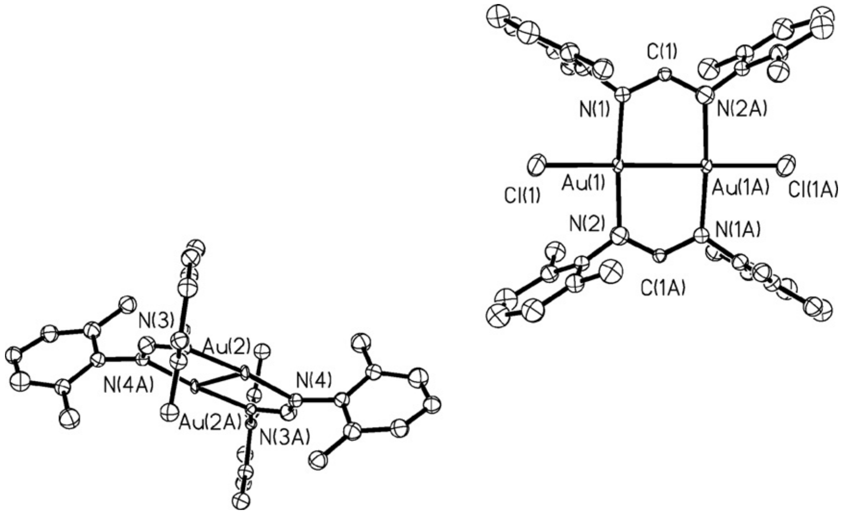


Fig. 1. Thermal ellipsoid plot of $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2Cl_2][Au_2(2,6\text{-}Me_2Ph\text{-}form)_2]$.

in the nitrate complex $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2(NO_3)_2]$ is about this same distance [15]. Only in the oxidized hpp complex (*vida infra*) has a slightly shorter Au(II)–Au(II) bond been observed. The short Au···Au distance in these complexes is due to the weak trans-directing and sigma covalent bonding ability of the oxygen coordinating ligands along the O–Au–Au–O axis.

A facile replacement of the benzoate groups in $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2(PhCOO)_2]$ by chloride or bromide is achieved by adding equivalent amounts of $PhICl_2$ or $[Bu_4N]Br$. The replacement of the bromide in $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2Br_2]$ by chloride is achieved by adding $PhICl_2$ in a polar solvent such as CH_3CN.

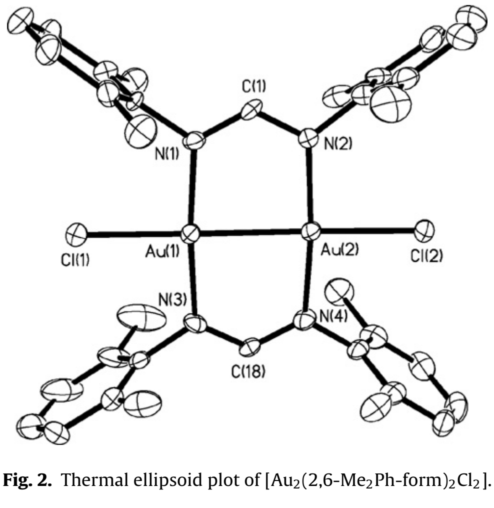


Fig. 2. Thermal ellipsoid plot of $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2Cl_2]$.

The reaction of methyl iodide, CH_3I, with $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2]$ in ether generates $[CH_3Au(2,6\text{-}Me_2Ph\text{-}form)_2AuI]$ in quantitative yield under nitrogen at 0 °C, in the absence of light [13]. While the Au(II) atoms and the amidinate ligand atoms refine well, unfortunately, the structure has a disorder in the CH_3 and iodide positions since the spatial volume occupied by CH_3 and I is approximately identical. As a result their positions remain uncertain with regard to their exact distances from the Au(II) atoms. The Au–CH_3 and Au–I distances appear to be 2.12 Å and 2.50 Å, while in the dinuclear gold(II) ylide, $[(CH_3)Au((CH_2)_2PMe_2)_2AuI]$, the Au–$CH_3$ and Au–I distances are 2.13(5) Å and 2.894(5) Å, respectively, and the Au(II)–Au(II) distance is 2.695(4) Å [8]. Surprisingly, the Au–I distance in the Au(II) amidinate complex appears to be much shorter than found in the ylide, $[IAu((CH_2)_2PMe_2)_2AuI]$. No stable organometallic alkyl halide oxidative-addition products of

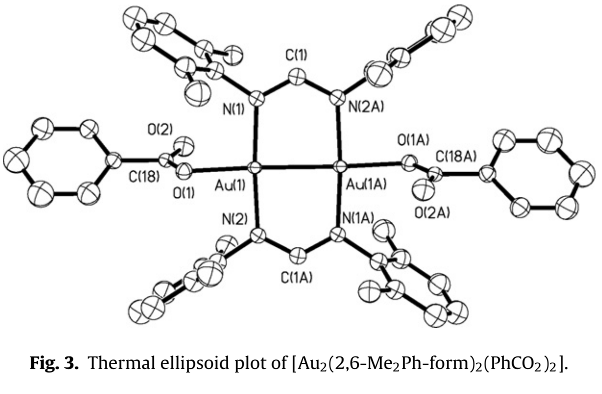
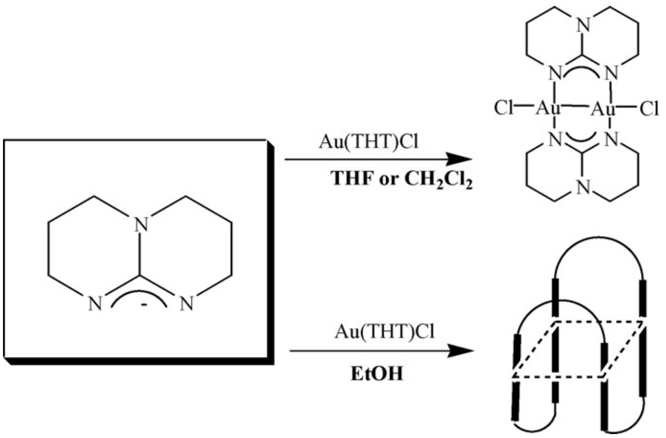


Fig. 3. Thermal ellipsoid plot of $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2(PhCO_2)_2]$.



Scheme 3. Synthesis of [Au$_2$(hpp)$_2$Cl$_2$] and [Au$_4$(hpp)$_4$].

dinuclear Au(I) complexes have been characterized with ligands other than the ylides and amidinates.

The chemistry of the Au–R and Au–X bonds in these dimers is largely associated with the σ bond framework along the Au–Au axis. The R–Au–Au–X segment of the gold(II) product has σ bonds polarized due to the differences in the electron-donating electron-withdrawing properties of the alkyl and halide subsitituents. Results from our laboratory showed that the chemistry of the Au(I) ylide dimers may be understood by recognizing that the LUMO is metal–metal bonding and the HOMO is σ anti-bonding. In the dinuclear Au(II) complexes, the polarization along the metal–metal axis is significantly associated with the electronic properties of the methyl halide, the methyliodide adduct being the most polarized, the bromide showing less polarization and the chloride showing only a small polarization. Hence the *trans* Au–X distances reflect this variation in halide polarization. However, the MeI addition product to the amidinate appears out of line with this observation, although the disorder observed in the structure produces some uncertainty in the result. Density functional calculations suggest that metal N-ligand pi interactions are much stronger in the amidinates, hence the sigma bonding polarization may be substantially reduced when compared with the ylide complexes.

The charge-transfer character of the deeply colored solutions has been noticed in all the oxidative-addition products of the dinuclear gold(II) amidinates. This contrasts with the colors of the gold(II) ylide complexes, which are pale yellow oxidative-addition products. The colors of the gold(II) amidinate complexes are dark orange to brown. It is apparent that the metal–ligand pi orbital mixing leads to a considerably reduced HOMO-LUMO separation in the Au(II) amidinates than the ylides.

4. Solvent influences on the oxidation and nuclearity of gold guanidinate derivatives

While we have been unsuccessful during many attempts by direct synthesis or reduction to isolate the dinuclear gold(I) guanidinate complex, [Au$_2$(hpp)$_2$], we have discovered that solvent conditions determine whether oxidation to the dinuclear Au(II) species, [Au$_2$(hpp)$_2$Cl$_2$], occurs or whether a tetranuclear Au(I) species, [Au$_4$(hpp)$_4$], forms [16,17]. It appears that the nuclearity

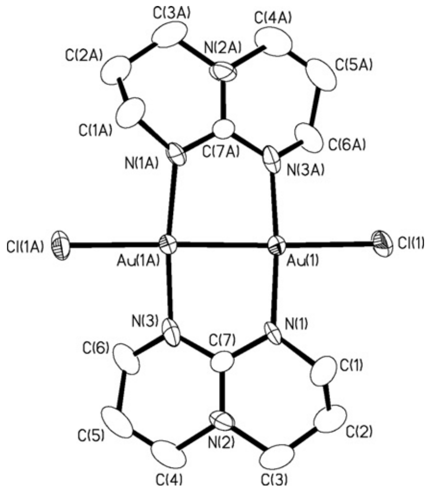


Fig. 4. Thermal ellipsoid plot of [Au$_2$(hpp)$_2$Cl$_2$].

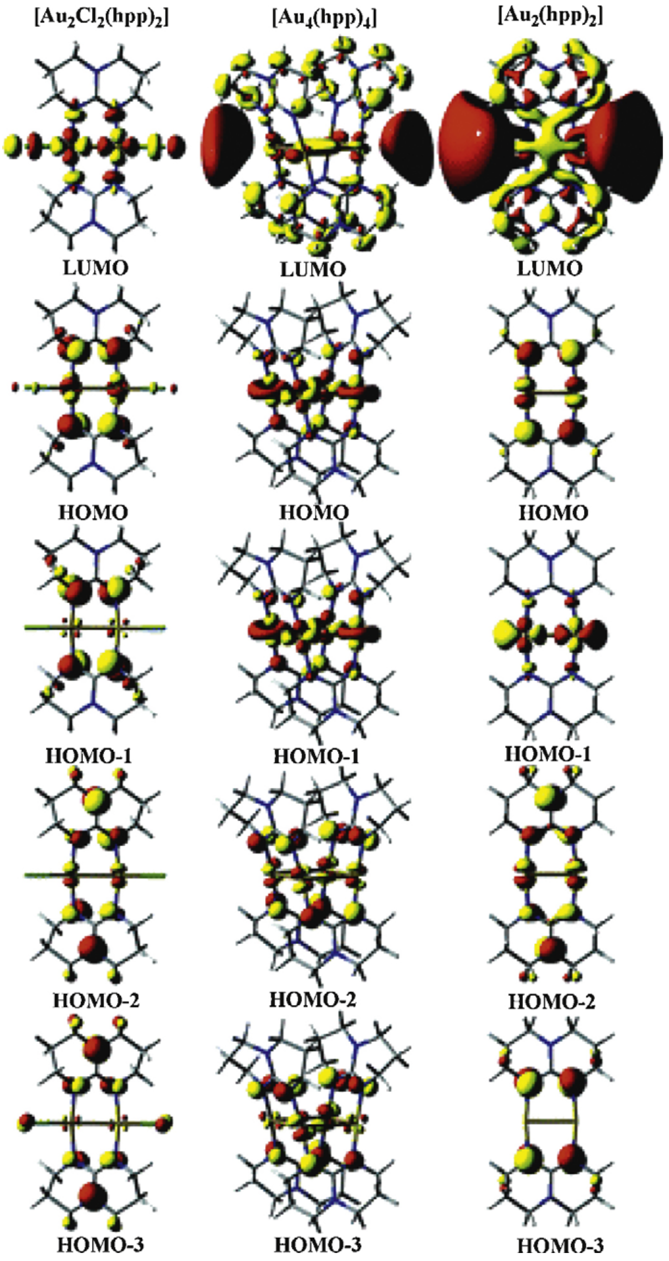


Fig. 5. Pictures of the 0.05 contour surface diagram at the MPW1PW91/BSII level for the HOMO-3 through the LUMO of [Au$_2$(hpp)$_2$Cl$_2$] and HOMO-3 through the HOMO of [Au$_4$(hpp)$_4$], and the theoretical model, [Au$_2$(hpp)$_2$]. The 0.01 contour surface diagram at the MPW1PW91/BSII of the LUMO for [Au$_4$(hpp)$_4$] and [Au$_2$(hpp)$_2$] is pictured instead of a value of 0.05 due to large gold s orbital contribution.

of the gold(I) hpp compound depends on factors such as the disproportionation rate of the Au(I) in a given solvent and the presence of oxidants. The short ligand N···N distance in hpp promotes tetranuclear product formation over Au(I) dinuclear species but in the presence of oxidizing solvents with the presence of coordinating ligands like chloride, a gold(II) product is isolated.

This solvent role regarding the formation of a dinuclear Au(II) or a tetranuclear Au(I) product is noted when Na[hpp] is reacted with (THT)AuCl. In THF the product is the dinuclear Au(II) species, $[Au_2(hpp)_2Cl_2]$, along with gold metal. In oxidizing solvents such as the chlorocarbon dichloromethane, $[Au_2(hpp)_2Cl_2]$ is produced in high yield without Au(0) formation (Scheme 3). If ethanol is used as the solvent, the product is the tetranuclear Au(I) species, $[Au_4(hpp)_4]$. A plausible rationalization of the different behavior in the two solvents is that ethanol solvates both the $[(THT)Au]^+$ and the Cl^-, reducing the potential of the cation for oxidation. The X-ray crystal structure of $[Au_2(hpp)_2Cl_2]$ revealed a Au(II)–Au(II) distance of 2.4752(9) Å, Fig. 4, which is shorter than the Au–Au distance observed in the amidinate, $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2Cl_2]$ (2.617 Å) and even the amidinates with terminal oxygen ligands.

The molecular structures of $Mo_2(hpp)_4$ and $W_2(hpp)_4$ studied by Cotton show M–M distances of 2.067(1) Å and 2.162(1) Å, respectively [18]. These two complexes contain the shortest ${Mo_2}^{4+}$ or ${W_2}^{4+}$ quadruple bonds known. The ready oxidation of these complexes and apparently the dinuclear gold(I) hpp complex clearly shows that ligands which favor short metal–metal distances promote reduction of the electron density between the metal atoms by electron loss.

Density functional theory (DFT) and MP2 calculations on $[Au_2(hpp)_2Cl_2]$ calculate reasonably well the Au(II)–Au(II) distance in this molecule [17]. The highest occupied molecular orbital (HOMO) is predominately hpp and chlorine-based with some Au–Au δ^* character with the filled orbital reflecting the sigma Au–Au bond energetically very deep. 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). Calculations on the hypothetical $[Au_2(hpp)_2]$ precursor show that unlike what was observed for the dinuclear Au(I) ylide complexes, the HOMO is largely delta anti-bonding. The HOMO-1 becomes the largely metal based σ^* anti-bonding orbital along the Au···Au axis that is the HOMO in the ylides, leading to a metal based emission spectra. With the amidinates the emission spectra are significantly ligand based. Theoretical results obtained for the Au(I) tetranuclear complex also are included in Fig. 5.

The calculated thermodynamics for the reduction of $[Au_2(hpp)_2Cl_2]$ to $[Au_2(hpp)_2]$ and $Cl_2(g)$ suggest the reaction is endothermic with a ΔH° of 50.0, 48.6, 45.8, and 69.5 kcal mol^{-1} and a ΔG° of 38.3, 37.5, 35.3, and 57.8 kcal mol^{-1} depending upon the level of theory used. The fact that the reaction is thermodynamically unfavorable is consistent with the difficulty in obtaining the Au(I) compound $[Au_2(hpp)_2]$.

Several reducing agents were used in attempts to reduce the Au(II) hpp complex to form the Au(I) product, including reagents such as KC_8 and K, but each produced gold metal. Using silver benzoate in a CH_3CN/THF solution to remove the chlorides formed a green hexanuclear product with mixed metals and ligands [19]. The gold(II)–silver(I) complex $[(PhCOO)_6Au_4(hpp)_4Ag_2]$ crystallized and was structurally characterized (Fig. 6). It has a very short Au–Au distance, 2.4473(19) Å. This dramatic decrease in distance results from the formation of two Au–O bonds along the common Au–Au bond axis, forming a stable d^9–d^9 system. The Au(II) hpp and Ag(I) benzoate parts are linked by carboxylate groups and gold–silver interactions.

5. Comparison of oxidative-addition to gold(I) nitrogen complexes with addition to gold(I) thiolate and ylide complexes

Attempts to oxidatively add chlorine to $[Au_2(xanthate)_2]$ using $PhICl_2$ at low temperature were unsuccessful and resulted in decomposition of the complexes [20]. These results agree with observations for most other neutral dithiolates. The $[n\text{-}Bu_4N]_2[AuS_2C{=}C(CN)_2]_2$ and the mixed-ligand dithiophosphonate/ylide complexes are the only dinuclear dithiolate Au(I) complexes which have produced Au(II) products sufficiently stable to be isolated and structurally characterized, although the former material does rearrange in solution to gold(III) and gold(I) products.

The reaction of the dinuclear gold amidinate complex with $Hg(CN)_2$ (1:2 stoichiometry) results in the formation of the 2D mercury(II) cyanide coordination polymer [21], $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2]\cdot 2Hg(CN)_2\cdot 2THF$ (Scheme 4), not the expected oxidative-addition product $[NCAu(2,6\text{-}Me_2Ph\text{-}form)_2AuCN]$, as in the case of the dinuclear gold(I) ylide. The mercury product is sparingly soluble in various organic solvents. This variation in the behavior of $Hg(CN)_2$ toward dinuclear gold(I) complexes requires comment. In the case of the mercury(II) cyanide reaction with the dinuclear gold(I) dithiophosphinate, the stability of the gold(I)–carbon bond compared with that of mercury(II)–carbon

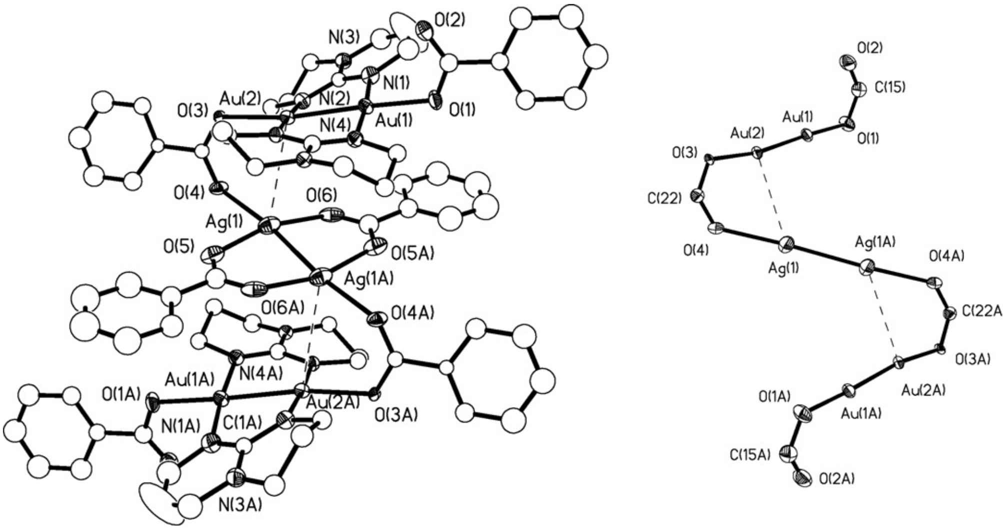
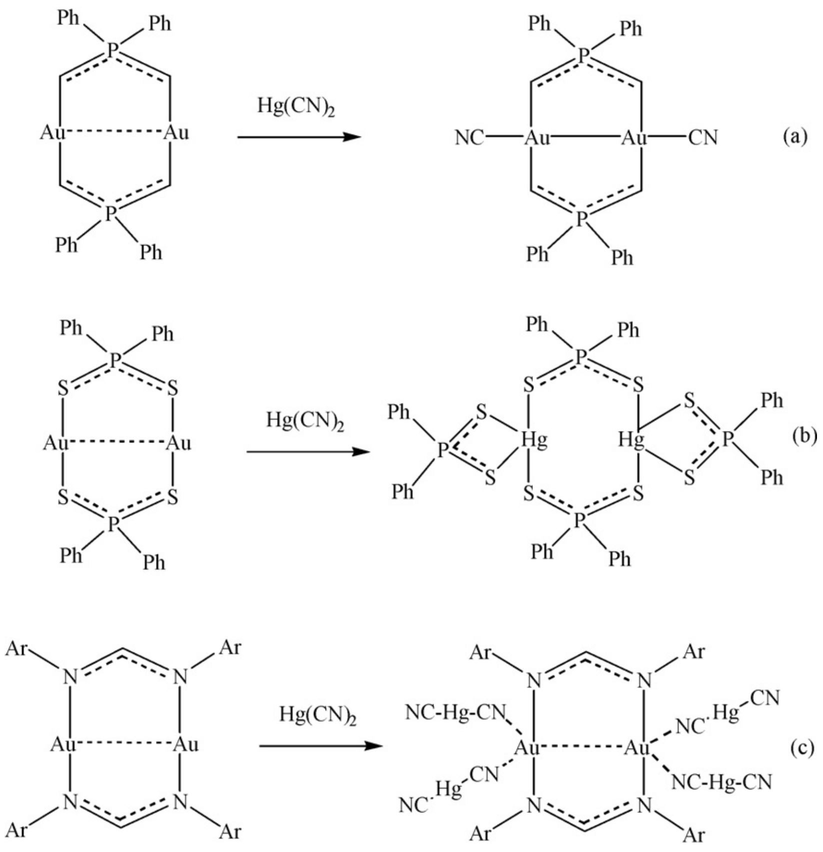


Fig. 6. Ellipsoid drawing of the structure of $[(PhCOO)_4Au_4(hpp)_4Ag_2(PhCOO)_2]$. The chain of atoms along the metal–metal axis also is shown.



Scheme 4. Reaction of $Hg(CN)_2$ with gold(I) ylide, dithiophosphinate and amidinate.

bond and the strength of the Hg(II)–S bonds compared with the labile Au(I)–S bonds appears to lead to the metathesis products observed, $[Hg_2(S_2PPh_2)_4]$ [22]. In the case of the ylide, oxidation of the Au(I) to Au(II) results in the formation of Hg(0) [23] and CN coordination to the Au(II). With the amidinate ligands, the cyanide IR stretching frequency appears at the same value, ~2147 cm^{-1}, as found in the Au(II) ylide complex but the oxidation of the dinuclear amidinate is much more difficult and the nitrogen of the mercury cyanide bonds to the gold.

Cyclic voltammetric studies bear out the relative difficulty in oxidizing the dinuclear Au(I) amidinate complex (*vida infra*) [24]. The differences in the chemistry of these dinuclear gold(I) complexes may be understood by recognizing that the HOMO in the ylide complex is metal–metal anti-bonding. In the dinuclear gold(I) amidinates the HOMO is δ^* anti-bonding with the LUMO primarily ligand in character [25]. Gold ylides are oxidized in 0.1 M Bu_4NBF_4/THF at low potentials of +0.11 and +0.23 V vs. Ag/AgCl (quasi-reversible). The situation, however, is complicated by the precipitation of a yellow material of unknown composition in the immediate vicinity of the Pt working electrode. The dinuclear amidinate $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2]$ oxidizes under the same conditions at +1.22 V vs. Ag/AgCl (irreversible). These large differences in chemical character of the metal ligand interactions in these dinuclear gold(I) complexes appear to explain the widely different behavior of these compounds toward oxidative-addition and reaction with mercury cyanide.

The reaction of the dinuclear amidinate complex $[Au_2(2,6\text{-}Me_2Ph\text{-}form)_2]$, with tetraethylthiuram disulfide in THF results in the formation of the dinuclear Au(I) dithiocarbamate complex $Au_2[S_2CN(C_2H_5)_2]_2$, not the expected oxidative-addition product as in the case of the dinuclear gold(I) ylide, $[Au(CH_2)_2PPhMe]_2[S_2CNEt_2]_2$ [26]. The tetraethylthiuram disulfide replaces the bulky amidinate ligand, 2,6-Me_2Ph-form, producing the same product that is formed by the reaction of Au(THT)Cl with $KS_2CN(C_2H_5)_2$ in THF [27].

6. Conclusion and remarks

Accumulated data regarding the reactivity of dinuclear and polynuclear metal complexes is consistent with the ability of both neighboring metal atoms and coordinated ligands to influence the oxidative-addition process. Cationic metal centers or electron-withdrawing ligands near the oxidation center can be expected to stabilize the HOMO or "closed-shell" ground state. This increases the HOMO–LUMO separation, thereby making oxidation less favorable. Electron-rich anionic complexes or complexes with strongly donating ligands decrease the HOMO–LUMO separation rendering oxidation and the oxidative-addition process more feasible.

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References

[1] (a) J.P. Fackler Jr., Inorg. Chem. 41 (2002) 6959;
(b) H.E. Abdou, A.A. Mohamed, J.P. Fackler Jr., Inorg. Synth. Wiley & Sons, Submitted for publication;
(c) H.E. Abdou, A.A. Mohamed, J.P. Fackler Jr., in: F. Mohr (Ed.), Gold Chemistry: Highlights and Future Directions, Wiley & Sons, 2009, p. 1 (Chapter 1).
[2] (a) H. Schmidbaur (Ed.), Gold Progress in Chemistry, Biochemistry, and Technology, Wiley: West Sussex, England, 1999;
(b) A. Grohman, H. Schmidbaur, E.W. Abel, F.G. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 3, Pergamon, Oxford, 1995, p. 1;

(c) B. Trzcinska-Bancroft, M.N. Khan, J.P. Fackler Jr., Organometallics 7 (1988) 993.
[3] R. Puddephatt, The Chemistry of Gold, Elsevier, 1978.
[4] F.A. Cotton, Basic Inorganic Chemistry, vol. 3, Wiley, New York, 1995.
[5] H.E. Abdou, A.A. Mohamed, J.P. Fackler Jr., J. Chin. Chem. Soc. 54 (2007) 1107.
[6] M.C. Gimeno, A. Laguna, in: J.A. McCleverty, T.J. Meyer, D.E. Fenton (Eds.), Silver and Gold in Comprehensive Coordination Chemistry II, vol. 6, Elsevier Pergamon, Oxford, UK, 2004.
[7] J.J. Low, W. Goddard III, J. Am. Chem. Soc. 108 (1986) 885, and reference therein.
[8] A. Laguna, M. Laguna, Coord. Chem. Rev. 193–195 (1999) 837.
[9] J.P. Fackler Jr., Polyhedron 16 (1997) 1.
[10] M.N.I. Khan, J.P. Fackler Jr., C. King, J.C. Wang, S. Wang, Inorg. Chem. 27 (1988) 1672.
[11] H.E. Abdou, A.A. Mohamed, J.P. Fackler Jr., Inorg. Chem. 44 (2005) 166.
[12] H.E. Abdou, A.A. Mohamed, J.P. Fackler Jr., Inorg. Chem. 46 (2007) 9692.
[13] H.E. Abdou, A.A. Mohamed, J.P. Fackler Jr., Z. Naturforsch, Chem. Sci. 59B (2004) 1480.
[14] L.C. Porter, J.P. Fackler Jr., Acta Cryst. 42 (1986) 1128.
[15] D. Melgarejo, G. Chiarella, J.P. Fackler Jr., Unpublished results.
[16] M.D. Irwin, H.E. Abdou, A.A. Mohamed, J.P. Fackler Jr., Chem. Commun. (2003) 2882.
[17] A.A. Mohamed, A. Mayer, H.E. Abdou, M.D. Irwin, L. Perez, J.P. Fackler Jr., Inorg. Chem. 46 (2007) 11165.
[18] (a) F.A. Cotton, N.E. Gruhn, J. Gu, P. Huang, D.L. Lichtenberger, C.A. Murillo, L.O. Van Dorn, C. Wilkinson, Science 298 (2002) 1971;
(b) C. Wilkinson, Ph.D. thesis, Texas A&M University, 2005;
(c) D.B. Soria, J. Grundy, M.P. Coles, P.B. Hitchcock, J. Organomet. Chem. 690 (2005) 2278;
(d) F.A. Cotton, J.C. Durivage, N.E. Gruhn, D.L. Lichtenberger, C.A. Murillo, L.O. Van, C. Wilkinson, J. Phys. Chem. B 110 (2006) 19793.
[19] A.A. Mohamed, H.E. Abdou, A. Mayer, J.P. Fackler Jr., J. Cluster Sci. 19 (2008) 551.
[20] A.A. Mohamed, I. Kani, A.O. Ramirez, J.P. Fackler Jr., Inorg. Chem. 43 (2004) 3833.
[21] A.A. Mohamed, H.E. Abdou, J.P. Fackler Jr., Inorg. Chem. 45 (2006) 11.
[22] (a) H.E. Abdou, A.A. Mohamed, J.P. Fackler Jr., Unpublished results;
(b) J.S. Casa, M.S. Garcia-Tasende, A. Sanchez, J. Sordo, E.M. Vazquez-Lopez, Inorg. Chim. Acta 256 (1997) 211.
[23] H.H. Murray, A.A. Mazany, J.P. Fackler Jr., Organometallics 4 (1985) 154.
[24] A.A. Mohamed, A.E. Bruce, M.R.M. Bruce, in: S. Patai (Ed.), The Chemistry of Organic Derivatives of Gold and Silver, John Wiley & Sons, 1999 (Chapter 9).
[25] H.E. Abdou, Ph.D. thesis, Texas A&M University, 2006.
[26] D.D. Heinrich, R.J. Staples, J.P. Fackler Jr., Inorg. Chim. Acta 229 (1995) 61.
[27] D.D. Heinrich, J. Wang, J.P. Fackler Jr., Acta Cryst. 46 (1990) 1444.