

Oxidative Addition of Small Molecules to a Dinuclear Au(I) Amidinate Complex, $\text{Au}_2[(2,6\text{-Me}_2\text{Ph})_2\text{N}_2\text{CH}]_2$. Syntheses and Characterization of Au(II) Amidinate Complexes Including One Which Possesses Au(II)–Oxygen Bonds

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The dinuclear Au(I) amidinate complex $\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2$ (**1**) is isolated in quantitative yield by the reaction of (THT)AuCl and the potassium salt of 2,6-Me₂Ph-form in a 1:1 stoichiometric ratio. Various reagents such as Cl₂, Br₂, I₂, CH₃I, and benzoyl peroxide add to the dinuclear Au(I) amidinate complex $\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2$ to form oxidative-addition Au(II) metal–metal-bonded complexes **2**, **3**, **4**, **5**, and **6**. The Au(II) amidinate complexes are stable as solids at room temperature. The structures of the dinuclear $\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2$ and the Au(II) oxidative-addition products $\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2\text{X}_2$, X = Cl, Br, I, are reported. Crystalline products with an equal amount 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, **2m**, or Br, **3m**, are isolated and their structures are presented. The structure of $[\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2\text{X}_2][\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2]$, X = Cl has a Au(II)–Au(II) distance slightly longer, 0.05 Å, than that observed in the fully oxidized product $\text{Au}_2(2,6\text{-Me}_2\text{-form})_2\text{Cl}_2$, **2**. 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 the Au(I) dithiolates and ylides. The oxidative addition of benzoyl peroxide leads to the isolation of the first stable dinuclear Au(II) nitrogen complex possessing Au–O bonds, $\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2(\text{PhCOO})_2$, **6**, with the shortest Au–Au distance known for Au(II) amidinate complexes, 2.48 Å. The structure consists of unidentate benzoate units linked through oxygen to the Au(II) centers. The replacement of the bromide in **3** by chloride, and the benzoate groups in **6** by chloride or bromide also occurs readily. The unit cell dimensions are, for **1**, $a = 7.354(6)$ Å, $b = 9.661(7)$ Å, $c = 11.421(10)$ Å, $\alpha = 81.74(5)^\circ$, $\beta = 71.23(5)^\circ$, and $\gamma = 86.07(9)^\circ$ (space group $P\bar{1}$, $Z = 1$), for **2**·**1.5C₆H₁₂**, $a = 11.012(2)$ Å, $b = 18.464(4)$ Å, $c = 19.467(4)$ Å, $\alpha = 90^\circ$, $\beta = 94.86(3)^\circ$, and $\gamma = 90^\circ$ (space group $P2_1/c$, $Z = 4$), for **2m**·**ClCH₂CH₂Cl**, $a = 16.597(3)$ Å, $b = 10.606(2)$ Å, $c = 19.809(3)$ Å, $\alpha = 90^\circ$, $\beta = 94.155(6)^\circ$, and $\gamma = 90^\circ$ (space group $P2_1/n$, $Z = 2$), for **3m**, $a = 16.967(3)$ Å, $b = 10.783(2)$ Å, $c = 20.060(4)$ Å, $\alpha = 90^\circ$, $\beta = 93.77(3)^\circ$, and $\gamma = 90^\circ$ (space group $P2_1/n$, $Z = 2$), for **4**·**THF**, $a = 8.0611(12)$ Å, $b = 10.956(16)$ Å, $c = 11.352(17)$ Å, $\alpha = 84.815(2)^\circ$, $\beta = 78.352(2)^\circ$, and $\gamma = 88.577(2)^\circ$ (space group $P\bar{1}$, $Z = 1$), for **5**, $a = 16.688$ Å, $b = 10.672(4)$ Å, $c = 19.953(7)$ Å, $\alpha = 90.00(6)^\circ$, $\beta = 94.565(7)^\circ$, and $\gamma = 90.00^\circ$ (space group $P2_1/n$, $Z = 4$), for **6**·**0.5C₆H₆**, $a = 11.160(3)$ Å, $b = 12.112(3)$ Å, $c = 12.364(3)$ Å, $\alpha = 115.168(4)^\circ$, $\beta = 161.112(4)^\circ$, and $\gamma = 106.253(5)^\circ$ (space group $P\bar{1}$, $Z = 1$).

Introduction

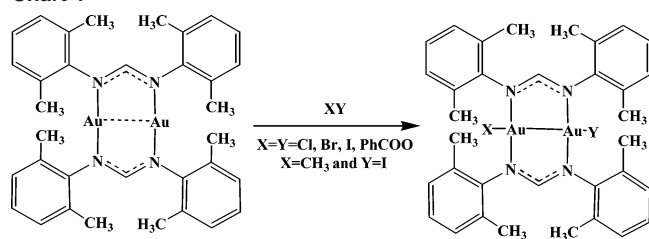
Gold–nitrogen compounds with Au(II)–to–nitrogen bonds are very scarce.¹ The great majority of gold–nitrogen

compounds occur with gold in the oxidation states +I and +III, which have electronic configurations $[\text{Xe}]4f^{14}5d^{10}$ and $[\text{Xe}]4f^{14}5d^8$, respectively.¹ It has been known that there is a strong tendency for Au(II) products to disproportionate to form Au(I) and Au(III) materials.² However, oxidative addition results in the formation of a Au(II)–Au(II) bond. The Au_2^{4+} core derivatives are the most stable and most

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Chart 1



commonly found Au(II) complexes.² The formation of metal–metal-bonded Au(II) products is strongly dependent on the type of the ligands bonded to the Au(I) centers. The charge on the metal centers and the metal–metal distance, which result from the ligand type bonded to the Au(I) atoms, both influence the oxidation process. Anionic ligands such as the ylides are known to support this process and even allow further oxidation to stable dinuclear Au(III) products. It has been suggested³ that the strong σ -donor capability of carbon atoms in the ylide ligands, promoted by the presence of the four-coordinate onium phosphorus ylide centers, is responsible for the ease of the reactions and stability of the products.^{3a,b} Mixed sulfur–carbon methylene thiophosphonate ligands also produce Au(II) products, but these are somewhat less stable.³

With other sulfur ligand complexes such as the dithiocarbamates, 1,1-dithiolates, and the mixed-ligand dithiophosphinate-ylide species, formation of metal–metal-bonded Au(II) products has been observed.² However, these sulfur ligand products are considerably less stable than the Au(II) ylides. Electron delocalization associated with the π system of these ligands appears to play a role in stabilizing the Au(II) products. The structurally similar dinuclear Au(I) xanthate⁴ shows no evidence of formation of stable Au(II) products, presumably because charge delocalization onto the ligand oxygen atoms is greatly diminished relative to the charge on the P atoms of the ylides and other phosphorus compounds or the N atoms of the dithiocarbamates. Dinuclear cationic diphosphine Au(I) complexes such as $[\text{Au}_2(\text{diphos})_2]^{2+}$, $\text{diphos} = \text{CH}_2(\text{PPh}_2)_2$, show no tendency at all to form Au(II) products.²

Recently there has been a growing interest in another class of anionic bridging ligands, the amidinates $[\text{ArNHC(H)NAr}]^-$. The amidinate ligands have the ability to bridge the metal ions and bring the metal ions close together, facilitating the formation of short metal–metal distances and Au(II)–Au(II) bond formation.⁵ In addition, these ligands can delocalize electron density through their B-bonding network and strongly donate π electron density to the metal atoms.⁵ The use of these amidinate ligands in the coordination chemistry

Table 1. X-ray Data Collection and Structure Refinement for Complexes **1**, **2**·**1.5C₆H₁₂**, and **2m**·**ClCH₂CH₂Cl**

compound	1	2 · 1.5C₆H₁₂	2m · ClCH₂CH₂Cl
empirical formula	C ₃₄ H ₃₈ Au ₂ N ₄	C ₄₃ H ₅₆ Au ₂ Cl ₂ N ₄	C ₇₀ H ₈₀ Au ₄ N ₈ Cl ₄
fw	896.62	1093.76	1962.1
cryst syst	triclinic	monoclinic	monoclinic
space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	7.354(6)	11.012(2)	16.597(3)
<i>b</i> (Å)	9.661(7)	18.464(4)	10.606(2)
<i>c</i> (Å)	11.421(10)	19.467(4)	19.809(3)
α (°)	81.74(5)	90.00	90.00
β (°)	71.23(5)	94.86(3)	94.155(6)
γ (°)	86.07(9)	90.00	90.00
<i>V</i> (Å ³)	760.1(11)	3943.7(14)	3477.9(11)
<i>Z</i>	1	4	2
R1, wR2	0.047, 0.124	0.0689, 0.1707	0.1104, 0.2956
GOF	1.044	1.015	1.334

of the transition metals has produced complexes with extraordinarily short M–M distances.⁶ Preliminary work with oxidative addition to Au–N has been reported recently by our group.^{7,8}

Our work with Au(I) amidinates has been found to be successful in producing products of various nuclearity such as dinuclear, trinuclear, and tetranuclear species.^{7,9–11} The tetranuclear Au(I) clusters $\text{Au}_4(\text{ArNC(H)NAr})_4$, Ar = C₆H₄-4-OMe,⁹ C₆H₃-3,5-Cl₂,⁹ C₆H₄-4-Me,⁹ C₆H₄-2-CF₃,¹⁰ C₆F₅,¹⁰ C₁₀H₇,¹⁰ and ArNC(Me)NAr, Ar = C₆H₅,¹¹ and ArNC(Ph)NAr, Ar = C₆H₅,¹⁰ have been synthesized and described structurally. The dinuclear and trinuclear Au(I) amidinates can be isolated when the amidinate has sterically bulky groups in the ortho positions of the aryl groups.⁷ The trinuclear species $\text{Au}_3(2,6\text{-Me}_2\text{Ph-form})_2(\text{THT})\text{Cl}$ and $\text{Au}_3(2,6\text{-}i\text{pr}_2\text{Ph-form})_2(\text{THT})\text{Cl}$ were isolated by the reaction of the potassium salt of the formamidinate ligand with (THT)AuCl in a 1:1.5 stoichiometric ratio.⁷ Tetranuclear Au(I) complexes with mixed pyrazolate-amidinate nitrogen ligands, $\text{Au}_4(3,5\text{-Ph}_2\text{pz})_2(2,6\text{-Me}_2\text{Ph-form})_2$ and $\text{Au}_4(3,5\text{-Ph}_2\text{pz})_3(2,6\text{-Me}_2\text{Ph-form})$, also have been prepared.¹²

Preliminary studies of the oxidative addition of several small molecules to the dinuclear Au(I) amidinate, $\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2$, have been communicated.^{7,8} Here we report details of the syntheses of dinuclear Au(II) amidinate complexes formed by addition of Cl₂, Br₂, I₂, and CH₃I, and the first example involving a Au(II)–oxygen bond formed

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Table 2. Details of X-ray Data Collection and Structure Refinement for Complexes **3m**, **4·THF**, **5**, and **6·0.5C₇H₈**

compound	3m	4·THF	5	6·0.5C₇H₈
empirical formula	C ₆₈ H ₇₆ Au ₄ Br ₂ N ₈	C ₃₈ H ₄₆ Au ₂ I ₂ N ₄ O	C ₃₅ H ₄₁ Au ₂ N ₄ I	C ₄₈ H ₄₈ Au ₂ N ₄ O ₄
fw	1951.03	1150.43	1038.62	1210.90
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	16.967(3)	8.0611(12)	16.688(6)	11.160(3)
<i>b</i> (Å)	10.783(2)	10.956(16)	10.672(4)	12.112(3)
<i>c</i> (Å)	20.060(4)	11.352(17)	19.953(7)	12.364(3)
α (°)	90.00	84.815(2)	90.00	115.168(4)
β (°)	93.77(3)	78.352(2)	94.565(7)	161.112(4)
γ (°)	90.00	88.577(2)	90.00	106.253(5)
<i>V</i> (Å ³)	3662.1(13)	977.9(3)	3542(2)	1355.4(6)
<i>Z</i>	2	1	4	1
R1, wR2	0.100, 0.2429	0.0422, 0.1204	0.0581, 0.1329	0.0691, 0.1964
GO F	0.966	1.062	1.133	1.193

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complexes **1**, **2**, and **2m**

Au₂(2,6-Me₂Ph-form)₂, 1			
N(2)–Au(1)–N(1)	171.1(6)	N(2)–C(1)–N(1)	127.8(15)
Au(1)–N(2)	2.026(13)	Au(1)–N(1)	2.018(13)
N(1)–C(1)	1.36(2)	Au(1)···Au(1)	2.712(2)
N(2)–C(1)	1.31(2)		
Au₂(2,6-Me₂Ph-form)₂Cl₂, 2			
N(1)–Au(1)–N(3)	175.0(4)	N(2)–Au(2)–N(4)	174.4(4)
N(1)–C(1)–N(2)	124.3(10)		
Au(2)–Cl(2)	2.366(3)	N(2)–C(1)	1.328(14)
Au(2)–Au(1)	2.5176(7)	N(1)–C(1)	1.318(14)
Au(1)–N(1)	2.022(8)		
[Au₂(2,6-Me₂Ph-form)₂][Au₂(2,6-Me₂Ph-form)₂Cl₂], 2m			
Au(1)–N(1)	1.99(3)	Au(2)–N(4)	2.03(3)
Au(1)–Au(1A)	2.5671(19)	Au(2)–Au(2A)	2.7098(15)
N(2)–C(1A)	1.30(4)	C(1)–N(1)	1.36(3)
N(1)–Au(1)–N(2)	174.6(10)	N(3)–Au(2)–N(4)	169.1(7)
N(3)–Au(2)–Au(2A)	83.5(5)	N(2)–Au(1)–Au(1A)	87.4(7)
N(2)–C(1A)–N(1A)	127(3)		

by the reaction with benzoyl peroxide, Chart 1. These materials are relatively stable as solids and in solution. Attempts to oxidatively add thiolate ligands with tetraethylthiuram disulfide failed to give the expected oxidative-addition product [Au₂(2,6-Me₂-form)₂][S₂CNEt₂]₂,¹³ as in the case of the dinuclear Au(I) ylide, [Au(CH₂)₂PPhMe]₂[S₂CNEt₂]₂,¹⁴ and resulted in the formation of the dinuclear complex Au₂[S₂CN(C₂H₅)₂]₂, which was reported previously by the reaction of Au(THT)Cl with KS₂CN(C₂H₅)₂ in THF.¹⁵ The diethyldithiocarbamate ligand replaced the bulky amidinate ligand, (2,6-Me₂-form), in the dinuclear Au(I) amidinate **1**, but the oxidation product was not identified.¹³ The reaction with Hg(CN)₂ results in the formation of the 2D mercury-(II) cyanide coordination polymer, [Au₂(*o*-Me₂-form)₂]₂·2Hg(CN)₂·2THF,¹⁶ not the oxidative addition product expected as had been observed with the ylide complex.¹⁶

Experimental

General Procedures. All glassware was oven-dried prior to use. Triethylorthoformamate (orthoester) and 2,6-dimethylaniline were purchased from Aldrich and used as received. Tetrahydrothiophene

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Table 4. Selected Bond Distances (Å) and Angles (deg) for Complexes **3m**, **4**, **5**, and **6**

[Au₂(2,6-Me₂Ph-form)₂][Au₂(2,6-Me₂Ph-form)₂Br₂], 3m			
Au(1)–N(1)	2.004(17)	N(1)–Au(1)–N(2)	173.4(6)
Au(1)–N(2)	2.023(18)	N(1)–Au(1)–Br(1)	93.1(4)
Au(1)–Br(1)	2.470(2)	N(1)–Au(1)–Au(1A)	86.9(4)
Au(1)–Au(1A)	2.5251(15)	Br(1)–Au(1)–Au1A	179.62(10)
N(1)–C(1)	1.32(3)	C(1)–N(1)–Au(1)	121.2(14)
C(1)–N(2A)	1.28(2)		
Au₂(2,6-Me₂Ph-form)₂I₂, 4			
N(2)–C(1A)–N(1A)	126.1(5)	N(2)–Au(1)–N(1)	173.36(16)
Au(1)–Au(1A)	2.5794(4)	Au(1)–N(1)	2.027(4)
Au(1)–I(1)	2.6828(4)	N(2)–C(1)	1.310(7)
N(1)–C(1)	1.325(7)		
[Au₂(<i>o</i>-Me₂-form)₂CH₃I], 5			
N(2A)–Au(1A)–N(1A)	174.8(4)	N(2AA)–Au(1B)–I(1)	92.5(3)
N(1A)–Au(1A)–C(1)	92.3(3)	I(1)–Au(1B)–Au(1A)	178.72(7)
Au(1A)–Au(1B)	2.5293(11)	Au(1A)–C(1)	2.120(10)
N(2AA)–C(10A)	1.318(16)	Au(1B)–I(1)	2.499(3)
Au(1A)–N(2A)	2.011(10)		
Au₂(2,6-Me₂Ph-form)₂(PhCOO)₂, 6			
O(2)–C(18)–O(1)	130.4(11)	N(2)–Au(1)–N(1)	175.5(4)
O(1)–C(18)	1.284(14)	Au(1)–Au(1A)	2.4899(10)
N(1)–C(1)	1.323(16)	Au(1)–N(1)	2.010(10)
O(2)–C(18)	1.264(15)	Au(1)–O(1)	2.045(8)

ligand was purchased from TCI, Tokyo. The solvents THF, CH₂-Cl₂, cyclohexane, toluene, and ether were purchased from Aldrich and used as received. Br₂, I₂, CH₃I, CCl₄, CBr₄, Cl₄, CH₂Br₂, CH₂I₂, ClCH₂CH₂Cl, BrCH₂CH₂Br, ICH₂CH₂I, PhI₂, Bu₄NBr, (PhCOO)₂, and KOH were purchased from Aldrich. Elemental analyses were performed by Guelph Chemical Laboratories, Ltd. and Chemisar Laboratories Inc, Guelph, Ontario, Canada. UV–vis spectra were recorded on a Shimadzu UV-2501 PC spectrometer. ¹H spectra were recorded on a Unity Plus 300 NMR spectrometer using solvent peaks to reference the chemical shifts (δ).

Synthesis of Au₂(2,6-Me₂Ph-form)₂, 1. *N,N'*-Bis(2,6-dimethylphenyl)formamidine (126 mg, 0.5 mmol) was stirred with (28 mg, 0.5 mmol) of KOH in 20 mL of THF for 24 h. The solution was colorless. Au(THT)Cl (160 mg, 0.5 mmol) was added and stirring continued for an additional 4–5 h. The solution was filtered and cyclohexane was added to form an off-white precipitate. The product was filtered and recrystallized from THF/cyclohexane to give colorless crystals. Yield: 75%. Anal. Calcd for C₃₄H₃₈-Au₂N₄: C, 45.53; H, 4.24. Found: C, 45.67; H, 4.45. ¹H NMR (CDCl₃, ppm): 2.48 (3H, 8(CH₃)), 6.91–6.99 (m, 12H (CH, phenyl)), 7.44 (1H, 2(CH) amidine). UV–vis (CH₂Cl₂): λ_{max} (nm), ε (L/M⁻¹ cm⁻¹): 259, 60 800.

Au₂(2,6-Me₂Ph-form)₂Cl₂, 2·1.5C₆H₁₂, and [Au₂(2,6-Me₂-form)₂Cl₂][Au₂(2,6-Me₂-form)₂], 2m·ClCH₂CH₂Cl. Compound **2·1.5C₆H₁₂** is prepared by using any of several oxidizing agents, PhI·Cl₂, CCl₄, CH₂Cl₂, ClCH₂CH₂Cl, and aqua regia. For example,

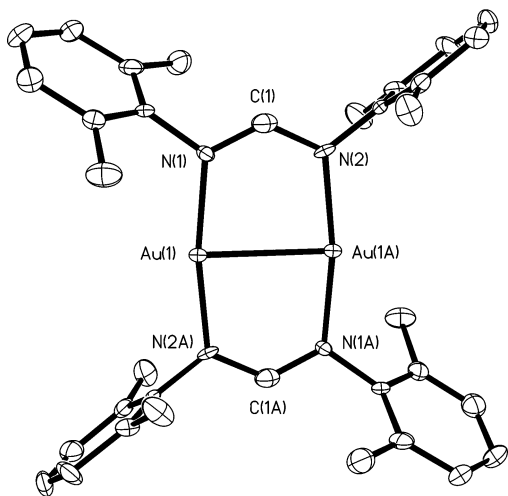


Figure 1. Thermal ellipsoid plot of **1** is drawn at the 50% probability level. Hydrogen atoms are removed for clarity. Selected distances (Å): Au(1)···Au(1A) 2.712 (2); Au–N(av) 2.022.

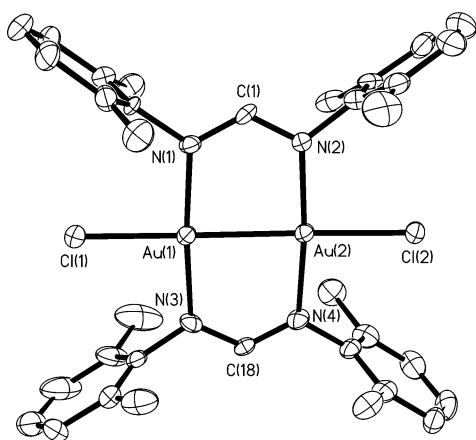


Figure 2. Thermal ellipsoid plot of **2** is drawn at the 50% probability level. Hydrogen atoms are removed for clarity. Selected distances (Å): Au(1)···Au(2) 2.517(2); Au(2)–Cl(2) 2.366(3); Au(1)–N(1) 2.022 (8).

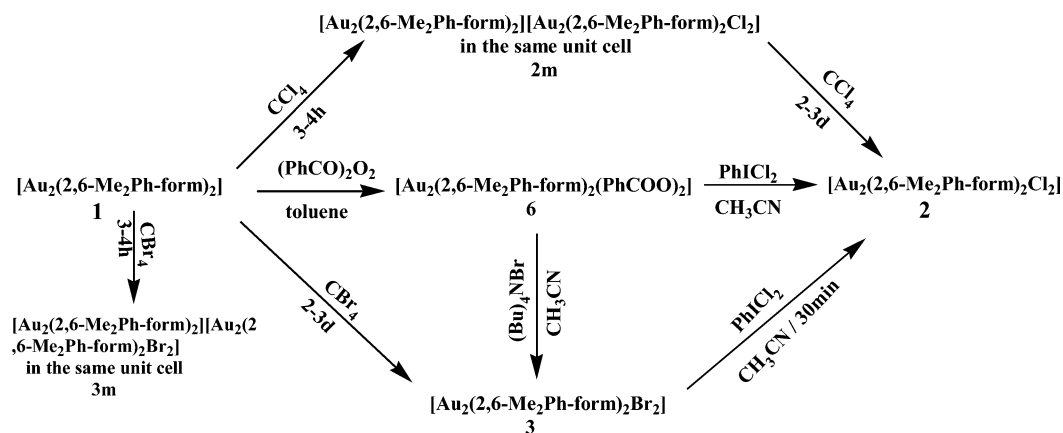
$\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2$, (0.31 g, 0.03×10^{-2} mol) was dissolved in 5 mL THF and stirred for 15 min. $\text{PhI}\cdot\text{Cl}_2$ (0.095 g, 0.03×10^{-2} mol) was added, and the color of the solution changes to dark green immediately. The reaction mixture was stirred for 3 h, then filtered. The solvent was removed under vacuum and the product was collected. Brown crystals of **2**·**1.5C**₆**H**₁₂ formed at room temperature by slow evaporation of a THF/cyclohexane solution. The oxidation by halogenated solvents CCl_4 , CH_2Cl_2 , and $\text{ClCH}_2\text{-}$

CH_2Cl , (0.31 g, 0.03×10^{-2} mol) of $\text{Au}_2(2,6\text{-Me}_2\text{-form})_2$ was mixed with 5–10 mL (excess) of the solvent and the mixture stirred for 2–3 days (7 days in the case of CH_2Cl_2), then filtered. The solvent was removed under vacuum, and the product was collected. Yield: 80%. Anal. Calcd For **2**·**1.5C**₆**H**₁₂, $\text{C}_{43}\text{H}_{56}\text{Au}_2\text{Cl}_2\text{N}_4$: C, 42.20; H, 3.95. Found: C, 41.77; H, 3.88. $^1\text{H NMR}$ (CDCl_3 , ppm): 2.51 (s, 24H (CH₃)), 6.99 (br, 12H (CH, phenyl)), 7.97 (s, 2H (CH amidinate)). UV–vis (CH_2Cl_2): λ_{max} (nm), ϵ ($\text{L/M}^{-1}\text{ cm}^{-1}$): 346, 29 400; 456, 5535. The crystalline product $[\text{Au}_2(2,6\text{-Me}_2\text{-form})_2\text{-Cl}_2][\text{Au}_2(2,6\text{-Me}_2\text{-form})_2]$, **2m**·**ClCH**₂**CH**₂**Cl**, which contains an equal amount of oxidized and unoxidized complexes in the same unit cell, was isolated when the reaction of the dinuclear with the halogenated solvents $\text{ClCH}_2\text{CH}_2\text{Cl}$ was stopped after 3–4 h of stirring (before oxidizing all the Au(I) material).

$\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2\text{Br}_2$, **3**, and $[\text{Au}_2(2,6\text{-Me}_2\text{-form})_2\text{Br}_2][\text{Au}_2(2,6\text{-Me}_2\text{-form})_2]$, **3m**. Several oxidizing agents, Br_2 , CBr_4 , $\text{BrCH}_2\text{CH}_2\text{Br}$, and CH_2Br_2 , can be used to prepare compound **3**. An example is given here. $\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2$ (0.22 g, 2.5×10^{-4} mol) was dissolved in 10 mL of THF, and CBr_4 (0.08 g, 2.5×10^{-4} mol) was added. After 20 min of stirring, the color of the reaction mixture changed to light brown. The reaction mixture was stirred for 2–3 days, then filtered. The THF solvent was removed under vacuum, and the product was collected. Brown crystals of **3** were formed by slow evaporation of a THF/cyclohexane solution at room temperature. Yield: 85%. Anal. Calcd for **3**, $\text{C}_{68}\text{H}_{76}\text{Au}_4\text{N}_8\text{Br}_2$: C, 41.81; H, 3.92. Found: C, 42.22; H, 3.54. $^1\text{H NMR}$ (CDCl_3 , ppm): 2.54 (s, 24H, (CH₃)), 6.99 (br, 12H (CH, phenyl)), 8.13 (s, 2H (CH amidinate)). UV–vis (CH_2Cl_2): λ_{max} (nm), ϵ ($\text{L/M}^{-1}\text{ cm}^{-1}$): 379, 27 200. The crystalline product **3m**, which contains an equal amount of oxidized and unoxidized dinuclear complexes in the same unit cell, was isolated when the reaction of the dinuclear with the halogenated solvents was stopped after 3–4 h of stirring before all the Au(I) material was oxidized.

$\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2\text{I}_2$, **4**·**THF**. Several oxidizing agents, I_2 , Cl_4 , CH_2I_2 , and $\text{ICH}_2\text{CH}_2\text{I}$, can be used to prepare compound **4**·**THF**. An example is given here. $\text{Au}_2(2,6\text{-Me}_2\text{Ph-form})_2$ (0.22 g, 2.5×10^{-4} mol) was dissolved in 10 mL of THF and stirred for 15 min. I_2 (0.07 g, 2.5×10^{-4} mol) was added. The color of the reaction mixture changed to dark green after 5 min. The stirring was continued for 2 h, and the reaction mixture was filtered. The solvent was removed under vacuum, and the product was collected. Brown crystals of **4**·**THF** were formed by slow evaporation at room temperature of a THF solution. The oxidation also was achieved with halogenated solvents Cl_4 , CH_2I_2 , and $\text{ICH}_2\text{CH}_2\text{I}$. $\text{Au}_2(2,6\text{-Me}_2\text{-Ph-form})_2$ (0.22 g, 2.5×10^{-4} mol) was mixed with 5–10 mL (excess) of the solvent, and the mixture was stirred for 2 h then

Chart 2



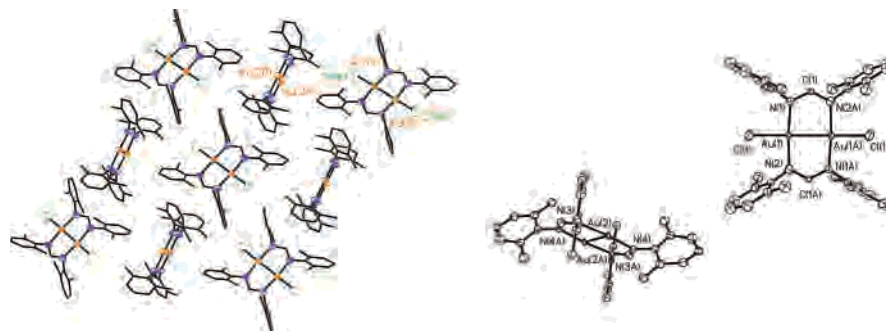


Figure 3. Thermal ellipsoid plot of **2m**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are removed for clarity.

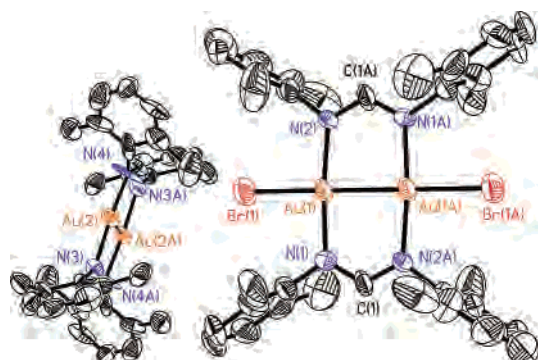


Figure 4. Thermal ellipsoid plot of **3m** drawn at the 50% probability level. Hydrogen atoms are removed for clarity.

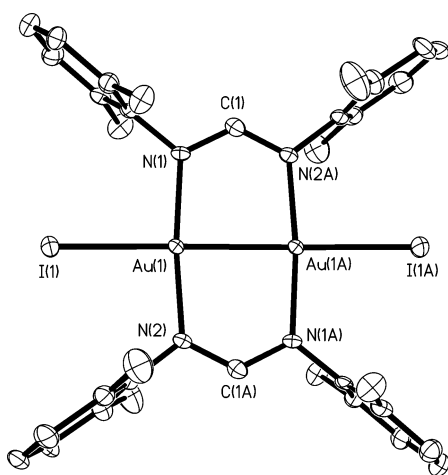


Figure 5. Thermal ellipsoid plot of **4** is drawn at the 50% probability level. Hydrogen atoms are removed for clarity. Selected distances (Å): Au(1)⋯Au(1A) 2.579(4); Au(1)–I(1) 2.682(4)

filtered. The solvent was removed under vacuum and the product was collected. Yield: 80%. Anal. Calcd For **4·THF**, $C_{38}H_{46}Au_2I_2N_4O$: C, 35.49; H, 3.32. Found: C, 34.73; H, 3.66. 1H NMR ($CDCl_3$, ppm): 2.55 (s, 24H (CH₃)), 6.99 (br, 12H (CH, phenyl)), 8.19 (s, 2H, (CH amidinate)). UV–vis (CH_2Cl_2): λ_{max} (nm), ϵ ($L/M^{-1}cm^{-1}$): 379, 17 300.

Au₂(2,6-Me₂Ph-form)₂CH₃I, 5. To 0.23 g (2.5×10^{-4} mol) of the dinuclear gold amidinate $Au_2(2,6-Me_2Ph-form)_2$ in 20 mL of freshly distilled ether in round-bottom flask, 0.5 mL (excess) of CH_3I was added. After stirring for 2 h under a N_2 stream in an ice bath, *in the absence of light*, a brown product was formed and then filtered, 85% yield. 1H NMR ($CDCl_3$, ppm): 1.37 (s, 3H (Au–CH₃)), 2.39 (s, 24H (CH₃)), 6.78 (br, 12H (CH, phenyl)), 8.10 (s, 2H, (CH amidinate)). Anal. Calcd for **5**, $C_{35}H_{41}Au_2IN_4$: C, 40.47; H, 3.97. Found: C, 39.91; H, 4.05.

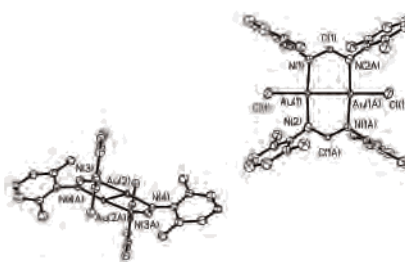


Figure 6. Thermal ellipsoid plot of **5** is drawn at the 50% probability level. Hydrogen atoms are removed for clarity. The structure has a disorder in the positions of the CH_3 and iodide atoms. Selected distances (Å): Au(1A)⋯Au(1B) 2.529(11).

Table 5. Au(II)–Au(II), Au(I)⋯Au(I), and Au–Cl Bond Distances (Å) in $[Au_2(2,6-Me_2Ph-form)_2X_2][Au_2(2,6-Me_2Ph-form)_2]$, X = Cl, **2m**, and $Au_2(2,6-Me_2Ph-form)_2$, **1**

oxidizing reagent	Au(II)–Au(II)	Au(I)⋯Au(I)	Au–Cl
CH_2Cl_2	2.527(3)	–	2.360(18), 2.345(16)
aqua regia	2.5242(7)	–	2.368(3), 2.355(3)
$PhICl_2$	2.5176(6)	–	2.365(2), 2.356(2)
$ClCH_2CH_2Cl$	2.5671(19)	2.7098(15)	2.321(8)
CCl_4	2.5502(13)	2.7132(14)	2.342(6)

Au₂(2,6-Me₂Ph-form)₂(PhCOO)₂, 6·0.5C₇H₈. $Au_2(2,6-Me_2Ph-form)_2$ (0.11 g, 1.2×10^{-4} mol) was dissolved in 10 mL of toluene and stirred for 15 min. $[Ph(CO)O]_2$ (0.03 g, 1.2×10^{-4} mol) was added, and the color of the reaction mixture gradually changed to dark brown. The reaction mixture was stirred for 3 h, then filtered. The solvent was removed under vacuum and the product was collected. Dark brown crystals of **6** were formed by slow evaporation of a toluene solution. Yield: 85%. Anal. Calcd for **6·0.5C₇H₈**, $C_{55}H_{56}Au_2N_4O_4$: C, 52.20; H, 4.42. Found: C, 52.40; H, 4.67. 1H NMR ($CDCl_3$, ppm): 2.54 (s, 24H (CH₃)), 6.71–6.79 (m, 10H (CH, benzoyl phenyl)), 6.92–7.00 (m, 12H (CH, phenyl)), 7.97 (s, 2H (CH amidinate)). UV–vis (CH_2Cl_2): λ_{max} (nm), ϵ ($L/M^{-1}cm^{-1}$): 345, 30 600.

Crystallographic Studies. Cell parameters and refinement results of the gold amidinate complexes **1**, **2**, **2m**, **3m**, **4**, **5**, and **6** are summarized in Tables 1 and 2. Tables 3 and 4 present important interatomic distances and angles. X-ray data were collected using a Siemens (Bruker) SMART CCD (charge-coupled device)-based diffractometer equipped with a LT-2 low-temperature apparatus operating at 110 K. A suitable crystal was chosen and mounted on a glass fiber using cryogenic grease. Data were measured using ω scans of $0.3^\circ/frame$ for 60 s. The first 50 frames were recollected

Table 6. Dinuclear Au(II) Ylide and Amidinate Complexes Characterized by X-ray Studies

complex	$d(\text{Au}^{\text{II}}\cdots\text{Au}^{\text{II}})$	$d(\text{Au}-\text{X})$	$d(\text{Au}-\text{R})$	ref
[ClAu(CH ₂ PPh ₂ CH ₂) ₂ AuCl]	2.600(1)	2.388(8)		2
[BrAu(CH ₂ PPh ₂ CH ₂) ₂ AuBr]	2.614(1)	2.516(1)		2
[IAu(CH ₂ PPh ₂ CH ₂) ₂ AuI]	2.650	2.693(8)		2
[(CH ₃)Au(CH ₂ PPh ₂ CH ₂) ₂ AuI]	2.695(4)			2
[(CH ₃)Au(CH ₂ PMe ₂ CH ₂) ₂ AuI]	2.695(4)	2.894(5)	2.13(5)	2
[PhCO ₂ Au(CH ₂ PPh ₂ CH ₂) ₂ AuO ₂ CPh]	2.561(2)	2.117(13)		2
[ClAu(2,6-Me ₂ Ph-form) ₂ AuCl], 2	2.517(7)	2.356(2)		^a
[BrAu(2,6-Me ₂ Ph-form) ₂ AuBr], 3m	2.525(15)	2.470(2)		^a
[IAu(2,6-Me ₂ Ph-form) ₂ AuI], 4	2.579(4)	2.682(4)		^a
[(CH ₃)Au ₂ (2,6-Me ₂ Ph-form) ₂ AuI], 5	2.529(11)	2.50	2.12	^a
[PhCO ₂ Au(2,6-Me ₂ Ph-form) ₂ AuO ₂ CPh], 6	2.489(10)	2.045(8)		^a

^a This work

at the end of data collection as a monitor for decay. No decay was detected. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections.¹⁷ Data reductions were performed using SAINT software.¹⁸ The structures were solved by direct methods using SHELXS-97 and refined by least-squares on F^2 , with SHELXL-97 incorporated in SHELXTL-PC V 5.03.^{19,20} The structures were determined in the space groups reported in Tables 1 and 2 by analysis of systematic absences. Hydrogen atom positions were calculated by geometrical methods and refined as a riding model.

Results

Syntheses. The dinuclear complex Au₂(2,6-Me₂Ph-form)₂, **1**, is isolated in a nearly quantitative yield by the reaction of (THT)AuCl with the potassium salt of 2,6-Me₂Ph-form in a 1:1 stoichiometric ratio. The addition of 1 molar equiv of Cl₂, Br₂, or I₂ to the dinuclear amidinate, **1**, in a THF solution at room temperature produces an immediate color change from colorless or light yellow to a very deep, dark green or brown. Recrystallization produces dark orange or brown crystals from which the X-ray crystallography established Au(II) products **2–4**, containing solvents such as THF or cyclohexane in the lattice. Thermal gravimetric analysis and differential thermal analysis showed the release of the solvent followed by the loss of the halogen. The reactions of the dinuclear complex with the halogenated solvents, CH₂X₂, XCH₂CH₂X, and CX₄ (X = Cl, Br, I) also formed Au(II) products. With the iodide derivative the reaction occurs in the time of mixing. The analogous reactions with chloride and bromide derivatives takes ~2–3 days and 7 days with CH₂Cl₂ in order to oxidize all of the Au(I) material. No bridged CH₂ product was observed as had been formed when CH₂Cl₂ reacts with the dinuclear Au(I) ylides.³ Crystalline products in which there are equal amounts of oxidized and unoxidized complexes in the same unit cell, [Au₂(2,6-Me₂Ph-form)₂X₂][Au₂(2,6-Me₂Ph-form)₂], X = Cl, **2m**; X = Br, **3m**, are isolated when the reaction is stopped after 3–4 h of stirring (Chart 2). Continuous stirring of the reaction mixture

for several days produced the completely oxidized products, Au₂(2,6-Me₂Ph-form)₂X₂, X = Cl, **2**; X = Br, **3**, as was confirmed by the UV–vis spectroscopy. In the reaction of the halo-alkyls CH_nX_m to produce the dihalides, the qualitative order of reactivity with the gold complexes (I > Br > Cl) follows inversely the order of carbon–halogen bond dissociation energy, C–Cl > C–Br > C–I.²¹

The replacement of the bromide from Au₂(2,6-Me₂Ph-form)₂Br₂, **3**, by chloride is achieved by adding 1 mol of PhICl₂ to 1 mol of **3** in polar solvent, CH₃CN. After 30 min of mixing the UV–vis peak of the bromide derivative, **3** at 379 nm in CH₂Cl₂ was shifted to 346 and 456 nm (shoulder), indicating the formation of the dichloride product, **2**. This product also was obtained by metathesis (see below and Chart 2).

The dropwise addition of methyl iodide, CH₃I, to a solution of Au₂(2,6-Me₂Ph-form)₂ in ether generates CH₃Au(2,6-Me₂Ph-form)₂AuI, **5**, in quantitative yield under nitrogen at 0 °C and in the absence of light.⁸ Crystal growth from ether was successful at 0 °C after one week. The dark orange brown crystals, which form as large blocks, are stable at room temperature. A gold metal mirror forms around the wall of the reaction vessel if the reaction is carried out in open air at room temperature.

The benzoate addition product **6** was obtained by adding an equivalent amount of benzoyl peroxide to a toluene solution of the dinuclear amidinate complex. The reaction was stirred for a few hours before the solvent was slowly evaporated to form crystals. A brown product was isolated in a good yield. The Au(II) product is stable at room temperature. Infrared spectroscopic studies of the Au(II) benzoate complex showed two intense bands at 1628 and 1578 cm⁻¹ due to $\nu(\text{C}=\text{O})$ and at 1320–1295 cm⁻¹ for the $\nu(\text{C}-\text{O})$ frequencies. The separation between the two bands, ~300 cm⁻¹, is typical of unidentate benzoate bonding, a “pseudo ester” character.²² The bonding of the benzoates to the dinuclear Au(I) amidinate is similar to the unidentate bonding observed in the ylide complexes which also adopt a anti geometry.²³ A facile metathesis replacement of the benzoate groups in **6** by chloride or bromide was achieved

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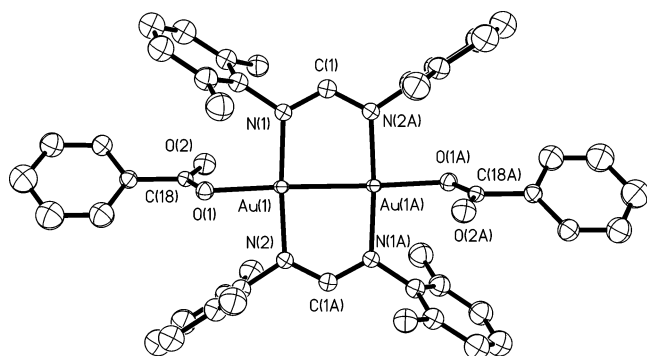


Figure 7. Thermal ellipsoid plot of **6** is drawn at the 50% probability level. Hydrogen atoms are removed for clarity. Selected distances (Å): Au(1)···Au(1A) 2.489(10); Au(1)–O(1) 2.045(8).

by adding equivalent amounts of PhICl₂ or Bu₄NBr to **6** in polar solvents such as CH₃CN, Chart 2.

After 5 min of mixing of PhICl₂ with **6** in CH₃CN/THF, the color of the reaction mixture changed from yellow to bright green, indicating the formation of the dichloride product, **2**, as confirmed by the UV–vis spectrum. The reaction of **6** with Bu₄NBr formed the dibromide derivative, **3**, after 7 days of mixing (Chart 2).

Structure Results and Discussion. The dinuclear complex **1** is crystallized in the space group *P* $\bar{1}$, Figure 1. The Au···Au distance is 2.711(3) Å, and the N–Au–N angle is 170.2(3)°. To our knowledge, there is only one other example of a symmetrically bridged dinuclear Au(I) nitrogen complex, Au₂[(Me₃SiN)₂C(Ph)]₂; it has a Au···Au distance of 2.646 Å.²⁴ In complex **1**, the Au···Au distance, 2.711 Å, is shorter than in the xanthate, Au₂(ⁿBu-xanthate)₂ (2.849 Å),²⁵ the dithiophosphinate (AuS₂PPh₂)₂ (3.085 Å),²⁶ ylide [Au(CH₂)₂-PPh₂]₂ (2.977 Å),²⁷ and dithiophosphonate [AuS₂PPh(OEt)]₂ (3.042 Å),²⁸ however, closer to the bond distance in the dithiolates [PPN]₂[Au₂(μ²-η²-CS₃)₂] (2.799 Å),²⁹ [*n*-Bu₄N][Au(S₂C=C(CN))₂] (2.796 Å),³⁰ and [Au(S₂C–N(C₅H₁₁))₂] (2.769 Å).³¹

The Au(II) amidinate complexes **2**, **3**, and **4** readily form crystals suitable for X-ray diffraction. X-ray crystallography established the formation of Au(II) products containing solvent such as THF or cyclohexane. The Au···Au distance decreases from 2.71 Å in the starting dinuclear complex to 2.51–2.57 Å in the oxidized species. The X-ray structures of **2** and **4** are shown in Figures 2 and 5. The X-ray structure of **3**, even at 77 K, is not sufficiently well resolved due to a

disorder to be reported here. However, the X-ray structure of **3** can be seen clearly in the X-ray structure of the oxidized and unoxidized complexes **3** and **3m** in the same unit cell shown in Figure 4. The Au–X distances, Au–Cl = 2.36 Å, Au–Br = 2.47 Å, Au–I = 2.68 Å, are typical for these Au(I) halide distances.² The N–Au–N angles of 173.9° (av) show a deviation from linearity. The Au–N distances decreased from 2.035(7) Å in the dinuclear complex to 2.000–2.004 Å in the oxidative-addition products. The Au(II) atoms have nearly square planar coordination geometries with formation of bonds to a second Au center, two N atoms, and one halide atom.

A crystalline product in which there is an equal amount of oxidized and unoxidized complexes in the same unit cell, **2m** or **3m**, was isolated when the reaction of dinuclear complex with the halogenated solvents, CH₂X₂, XCH₂CH₂X, and CX₄ (X = Cl, Br), was stopped after 3–4 h of stirring before oxidizing all the Au(I) material. The X-ray structures of **2m** and **3m** are shown in Figures 3 and 4, respectively. The Au–Au and the Au–Cl distances in **2m** changed from 2.52 (av) and 2.35 Å (av) in the fully oxidized complex, **2**, to 2.55 (av) and 2.34 Å (av), respectively, Table 5. The reasons for these differences are small and presumably relate to crystallographic difficulties.

Growing crystals of the methyl iodide addition product, **5**, was successful at 0 °C over 1 week. Although well-shaped, brown-black crystals were grown from ether, which diffracted well, the spatial volume occupied by CH₃ and I is approximately identical. This leads to a disorder in the positions of the CH₃ and iodide atoms. While the Au(II) atoms and the amidinate ligand atoms refine well, the CH₃ and I atom positions remain uncertain regarding their exact distances from the Au(II) atoms. The X-ray structure of **5** shows oxidized and unoxidized molecules in the same unit cell of **1** and **5**, respectively. Figure 6 shows the structure of the oxidized product, **5**, only. The Au–CH₃ and Au–I distances in **5** appear to be 2.12 and 2.50 Å, respectively, while in the dinuclear Au(I) ylide, [(CH₃)Au(CH₂PMe₂CH₂)₂-AuI], the Au–CH₃ and Au–I distances are 2.13(5) and 2.894(5) Å, respectively, Table 6.² This apparent lack of an amplified structural trans effect in the amidinate complex may be related to the fact that the HOMO in this system involves little M–M σ bonding as it is in the ylide complex³ but contains substantial M–L π* character. Unfortunately, the crystallography is not sufficiently good due to the disorder to dwell further on this point with this interesting observation. The Au(II)–Au(II) distance increased consistently for the addition products of the dinuclear Au(I) ylide with chloride, bromide, iodide, and methyl iodide having values of 2.600, 2.614, 2.650, and 2.69 Å, respectively, Table 6. With the dinuclear Au(I) amidinate, **1**, the Au(II)–Au(II) distances of the addition products with chloride, bromide, and iodide increased to values of 2.517, 2.525, and 2.579 Å, respectively but decreased for methyl iodide product to 2.529 Å, Table 6. Since this latter distance is relatively unaffected by disorder, we suspect that the M–L π* character of the HOMO plays an important role structurally, just as the LUMO of the Au(I) amidinate, which has largely

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Oxidative Addition to a Dinuclear Au(I) Amidinate Complex

amidinate carbon character, not M–M antibonding character as in the ylides, influences the emission spectrum of the complexes.

The structure of **6**, Figure 7, consists of unidentate benzoate units linked through oxygen to the Au(II) centers; the two benzoate units are anti to each other. The carbon-to-oxygen atom distances in the carbonyls are longer by 0.02 Å compared with free carbonyl O atoms (1.28 vs 1.264 Å).²² The Au–N distances decrease from 2.035(7) Å in the dinuclear complex to 2.01 and 2.008 Å in the oxidative-addition product. The Au–O distance is 2.045 Å. The Au atoms have nearly square planar coordination geometries considering formation of bonds to a second Au center, two N atoms, and one O atom. The oxidative addition of benzoyl peroxide to the dinuclear Au(I) ylide complex, Au₂(CH₂-PPh₂CH₂)₂ formed a Au(II) product with the shortest

Au···Au distance observed, 2.56–2.58 Å,² in the dinuclear Au(II) ylide complexes, Table 6. Similarly, the Au···Au distance in the oxidized product, **6**, 2.48 Å, is the shortest Au···Au distance in the Au(II) amidinate complexes. The short Au···Au distance in these complexes is due to the weak trans influencing ability of the carboxylate ligand.²³

Acknowledgment. The Robert A. Welch Foundation of Houston, Texas is acknowledged for financial support of this work. The DFT calculations were performed by Dr. Lisa Perez who it thanked.

Supporting Information Available: X-ray crystallographic files, in cif format, for complexes **2**, **3**, **4**, **5**, and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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