MIXED VALENCE GOLD CHEMISTRY: STEPWISE OXIDATION OF A CYCLIC TRIGOLD(I) COMPLEX

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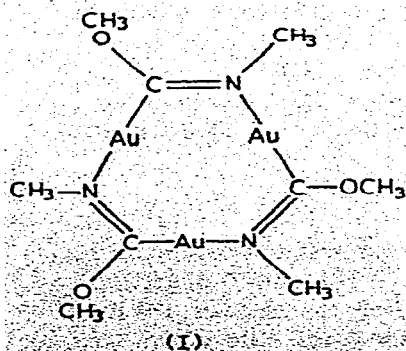*Department of Chemistry, University of California, Davis, California 95616 (U.S.A.)*

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Summary

Oxidation of the cyclic complex $Au_3(CH_3OC=NCH_3)_3$ by iodine or bromine produces three distinct complexes $Au_3(CH_3OC=NCH_3)_3X_n$ (n = 2, 4 or 6, X = Br or I) in which the gold atoms undergo stepwise oxidative halogen addition. The products have been characterized by elemental analysis, molecular weight determinations, proton magnetic resonance spectra and IR spectra. The complexes with n = 4 or 2 undergo spontaneous autodecomposition. In the case of $Au_3(CH_3OC=NCH_3)_3Br_4$ this decomposition produces gold metal, $Au_3(CH_3OC=NCH_3)_3Br_6$, methyl bromide, and methyl isocyanate in an extremely clean reaction.

Introduction

As part of our studies of mixed valence compounds and of interactions between metal centers, the halogen oxidation of the trimeric gold(I) complex I [1,2] has been examined. This complex is representative of a class of such planar trimers [3,4] all of which are believed to involve linear coordination about

(I)

each gold. Based on considerations of standard covalent radii and on the known structures of complexes II [5] and III [6], the gold centers in I should be separated by about 3.3 Å. In comparison the gold—gold bonds in a dimeric

(II)   (III)

gold(II) complex [7] and in gold cluster complexes are in the range 2.59—2.98 Å [8,9]. Consequently, it has been assumed that there will be no direct metal—metal interaction in I and its trinuclear derivatives. However, we have previously demonstrated that rhodium(I) centers separated by about 3.3 Å do have definite physical and chemical properties which can be ascribed to the close proximity of the two metal centers [10]. Here we demonstrate that the metal centers in I are able to affect one another. Additionally, since I is a flat and rather sterically unencumbered molecule, the possibility existed that it and its oxidation products might form solids with columar stacking similar to that displayed by the various tetracyanoplatinates [11]. In particular we anticipated, but did not observe, the formation of fractionally oxidized materials analogous to Krogmann's salt $(K_2Pt(CN)_4Cl_{0.32} \cdot 3H_2O)$.

Experimental

[$(CH_3OC=NCH_3)Au]_3$ was prepared as described previously [1]. The melting point of this complex cannot be used as a reliable property for characterization. Upon heating samples decompose, usually explosively, in the temperature range 110—220°C.

Molecular weights were measured by osmometry using a Mechrohm vapor pressure osmometer. The solvent was chloroform and triphenylphosphine gold(I) chloride was the standard. Under these conditions the molecular weight of the unhalogenated trimer $(CH_3OC=NCH_3)_3Au_3$ was measured as 784 (calculated: 807). IR spectra were obtained from mineral oil mulls or chloroform solutions and recorded on a Beckman IR-12 spectrophotometer. PMR spectra were recorded in chloroform-d_1 solutions on a JEOL JNM-MH-100 spectrometer operating at 100 MHz. Electronic spectra were recorded on a Cary 17 spectrophotometer.

[$(CH_3OC=NCH_3)_3Au_3I_6$]

A solution of 110 mg (0.453 mmol) of iodine in a minimum volume of boiling chloroform was added to a solution of 100 mg (0.124 mmol) of [$(CH_3OC=NCH_3)_3Au_3$] in 20 ml of hot chloroform. After cooling the mixture, the dark crystalline product was collected by filtration, washed with chloroform, and

dried under vacuum (yield 185 mg, 95%). The product forms very small crystals with a green reflectance; on grinding the solid product is red-brown. (Found: C, 7.40; H, 1.14; I, 48.14; N, 2.89. $Au_3C_9H_{18}I_6N_3O_3$ calcd.: C, 6.89; H, 1.16; I, 48.54; N, 2.68%.)

[(CH₃OC=NCH₃)₃Au₃I₄]

A solution of 50.4 mg (0.196 mmol) of iodine in 15 ml of chloroform was added to a solution of 80.1 mg (0.0992 mmol) of [(CH₃OC=NCH₃)₃Au₃] in 20 ml of hot chloroform. The solution was filtered and its volumn was reduced to 10 ml. Ether was added dropwise to the solution. The dark brown, micro-crystalline product which precipitated rapidly was collected by filtration, wash-ed with ether, and vacuum dried (yield: 110 mg, 85%). (Found: C, 8.18; H, 1.30; I, 38.57; Mol. wt. 1420. $Au_3C_9H_{18}I_4N_3O_3$ calcd.: C, 8.22; H, 1.38; I, 38.61%; Mol. wt. 1314.)

[(CH₃OC=NCH₃)₃Au₃I₂]

A solution of 48.4 mg (0.191 mmol) of iodine in 10 ml of chloroform was added to a solution of 154.0 mg of [(CH₃OC=NCH₃)₃Au₃] in 20 ml of hot chloroform. After filtration the volume of the red solution was reduced to 5 ml by evaporation and 20 ml of ether was added. The solution was stored at −10°C for 3 h. The dense, red, crystalline product which had separated was collected by filtration, washed with ether and vacuum dried (yield: 169 mg, 83%). (Found: Mol. wt. 1141. $Au_3C_9H_{18}I_2N_3O_3$ calcd.: Mol. wt. 1061.)

[(CH₃OC=NCH₃)₃Au₃Br₆]

A solution of 0.030 ml of bromine in 1 ml of chloroform was added to a solution of 153 mg (0.189 mmol) of [(CH₃OC=NCH₃)₃Au₃] in 20 ml of hot chloroform. The solution was filtered and the solution volume reduced to 7 ml by distillation. Ether was added to this solution slowly to precipitate the product as yellow crystals (yield 204 mg, 84%). (Found: C, 8.49; H, 1.28; Br, 37.68; Mol. wt. 1400. $Au_3Br_6C_9H_{18}N_3O_3$ calcd.: C, 8.40; H, 1.41; Br, 37.26%, Mol. wt. 1286.)

[(CH₃OC=NCH₃)₃Au₃Br₄]

A solution of 125.3 mg (0.0974 mmol) of [(CH₃OC=NCH₃)₃Au₃Br₆] in 10 ml of chloroform was added to a solution of 39.7 mg (0.0492 mmol) of [(CH₃OC=NCH₃)₃Au₃] in 20 ml of hot chloroform. After filtration, the volume of the solution was reduced to 5 ml by distillation and 20 ml of ether was added to the yellow solution. The product gradually separated from solution as yellow crystals which were collected by filtration, washed with ether and dried under vacuum (Found: C, 9.52; H, 1.42; Br, 29.37; Mol. wt. 1222. $Au_3Br_4C_9H_{18}N_3O_3$ calcd.: C, 9.59; H, 1.61; Br, 28.37%, Mol. wt. 1126.)

[(CH₃OC=NCH₃)₃Au₃Br₂]

A solution of 68.4 mg (0.0532 mmol) of (CH₃OC=NCH₃)₃Au₃Br₆ in 10 ml of chloroform was added to a solution of 86.3 mg (0.107 mmol) of [(CH₃OC= NCH₃)₃Au₃] in 20 ml of hot chloroform. The volume of the solution was re-duced to 5 ml by evaporation and 10 ml of cyclohexane was added. On storage at

—10°C the product gradually separated as pale yellow crystals. These were collected by filtration, washed with cyclohexane, and vacuum dried (yield 82 mg, 80%).

Results and discussion

Bromine or iodine oxidation of I produces a series of three new complexes whose characterization is described in detail below. On the basis of the available evidence we believe that these complexes represent the result of successive, stepwise oxidation of the gold atoms of the trimer. The anticipated structures are shown in Fig. 1. Two mixed valence species IV and V are produced in addition to the all gold(III) species VI. The coordination about gold(III) is square planar with the gold coordination plane expected to lie perpendicular to the plane of the nine-membered ring. The gold(I) centers retain linear coordination.

$Au_3(CH_3OC=NCH_3)_3X_6$

Treatment of I with an excess of iodine or bromine produces species to which six halogen atoms have been added. For these and the other new complexes, the IR spectra, the PMR spectra and the electronic spectra are reported in Tables 1, 2 and 3 respectively. Of the two complexes of type VI, the bromo complex is the more soluble and amenable to characterization. A molecular weight determination indicates that it is trimeric in chloroform solution. Complexes of type VI
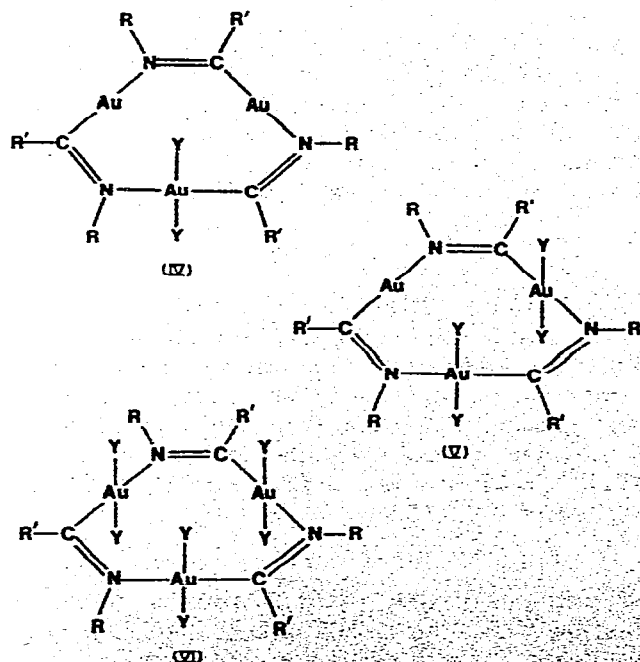

Fig. 1. Proposed structures for halogen oxidation products (R = CH₃, R' = OCH₃ and Y = either Br or I).

TABLE 1

IR SPECTRA OF GOLD COMPLEXES

Compound	ν(C=N) (CHCl$_3$ soln.)	1700—1500, 1300—700 cm^{-1} regions (hydrocarbon mull)
Au$_3$(CH$_3$OC=NCH$_3$)$_3$	1556	1560s, 1557(sh), 1211s, 1168m, 1120s, 1049m, 996w, 754m, 719m
Au$_3$(CH$_3$OC=NCH$_3$)$_3$I$_2$	1594, 1585	1600s, 1554s, 1226s, 1166m, 1143s, 1036w, 1027m, 906w, 979w, 755m, 720w
Au$_3$(CH$_3$OC=NCH$_3$)$_3$I$_4$	1596, 1585, 1575	1594s, 1678s, 1566w, 1231vs, 1166w, 1143s, 1026m, 991w, 977w, 752m, 729m
Au$_3$(CH$_3$OC=NCH$_3$)$_3$I$_6$	1592	1588s, 1242s, 1210(sh), 1169w, 1150m, 1023m, 980m, 753w, 743m, 712w
Au$_3$(CH$_3$OC=NCH$_3$)$_3$Br$_2$	1604, 1564	1602s, 1558s, 1227s, 1175m, 1138m, 1036m, 752w, 717m
Au$_3$(CH$_3$OC=NCH$_3$)$_3$Br$_4$	1608, 1597, 1570	1603s, 1589s, 1567s, 1234vs, 1172w, 1143m, 1029m, 993w, 978w, 763m, 718w
Au$_3$(CH$_3$OC=NCH$_3$)$_3$Br$_6$	1604	1598s, 1258vs, 1236(sh), 1158m, 1033m, 976m, 752, 720w

TABLE 2

PMR SPECTRA

Compound	τ (ppm) in $CDCl_3$	
	$CH_3\!-\!N=$	$CH_3\!-\!O\!-$
$Au_3(CH_3OC=NCH_3)_3$	7.10	6.08
$Au_3(CH_3OC=NCH_3)_3I_2$	6.62, 7.04, 7.15	5.93, 5.95, 6.03
$Au_3(CH_3OC=NCH_3)_3Br_2$	6.69, 7.02, 7.10	5.86, 5.94, 6.03
$Au_3(CH_3OC=NCH_3)_3I_4$	6.63, 6.66, 7.07	5.80, 5.92, 5.93
$Au_3(CH_3OC=NCH_3)_3Br_4$	6.68, 6.73, 7.06	5.76, 5.84, 5.92
$Au_3(CH_3OC=NCH_3)_3Br_6$	6.68	5.73

should have the same symmetry as I. Spectroscopically these are similar. Both I and VI (X = Br) exhibit a single proton resonance for the O—methyl and a second, equally intense resonance for the N—methyl groups. The IR spectra of I and VI (X = Br or I) are also similar. The most major difference occurs in the frequency of the vibration in the 1500—1600 cm^{-1} region. The vibration is ascribed to the C=N stretch and its frequency increases upon oxidation. Although the IR spectra of VI (X = Br or I) are similar in the solid state and in solution, the electronic spectrum of VI (X = I) in the solid differs from the solution spectrum. In a nujol mull of solid VI (X = I) electronic transitions are found at much lower energies (λ_{max} = 600(sh), 520, 370 nm) than are observed in chloroform solution (λ_{max} = 445, 330 nm). Apparently these are significant solid state intermolecular interactions in VI (X = I).

$Au_3(CH_3OC=NCH_3)_3X_4$

Oxidation of I with two moles of iodine produces V. A molecular weight determination supports the formulation. Because of its lower symmetry V (X = I) exhibits a more complex proton magnetic resonance and IR spectrum than do I and VI. Again in the IR spectrum, oxidation produces an increase in the frequency of the C=N stretching vibrations. As expected from the symmetry of V the PMR spectrum consists of three equally intense O—methyl resonances and three equally intense N—methyl resonances. The complex V also possesses a distinct electronic spectrum and, as with VI (X = I), the electronic spectrum of the solid (λ_{max} = 510(sh), 450, 360 nm) differs from that found for the solution.

TABLE 3

ELECTRONIC SPECTRA

Compound	$\lambda_{max}(\epsilon)$ Chloroform solution
$Au_3(CH_3OC=NCH_3)_3$	280 (3.5 × 10^3), 262 (1.09 × 10^4)
$Au_3(CH_3OC=NCH_3)_3I_2$	383 (6.5 × 10^3)
$Au_3(CH_3OC=NCH_3)_3I_4$	403 (7.8 × 10^3), 310 (1.39 × 10^4)
$Au_3(CH_3OC=NCH_3)_3I_6$	445 (6.7 × 10^3), 300 (2.1 × 10^4)
$Au_3(CH_3OC=NCH_3)_3Br_2$	331 (3.6 × 10^3), 270(sh) (5.9 × 10^3)
$Au_3(CH_3OC=NCH_3)_3Br_4$	330 (5.7 × 10^3), 292 (6.5 × 10^3)
$Au_3(CH_3OC=NCH_3)_3Br_6$	323 (8.6 × 10^3), 298 (9.3 × 10^3)

However, again the IR spectra of the solid V (X = I) and solutions of V (X = I) are similar. Consequently the solid state effects do not appear to alter the overall molecular geometry.
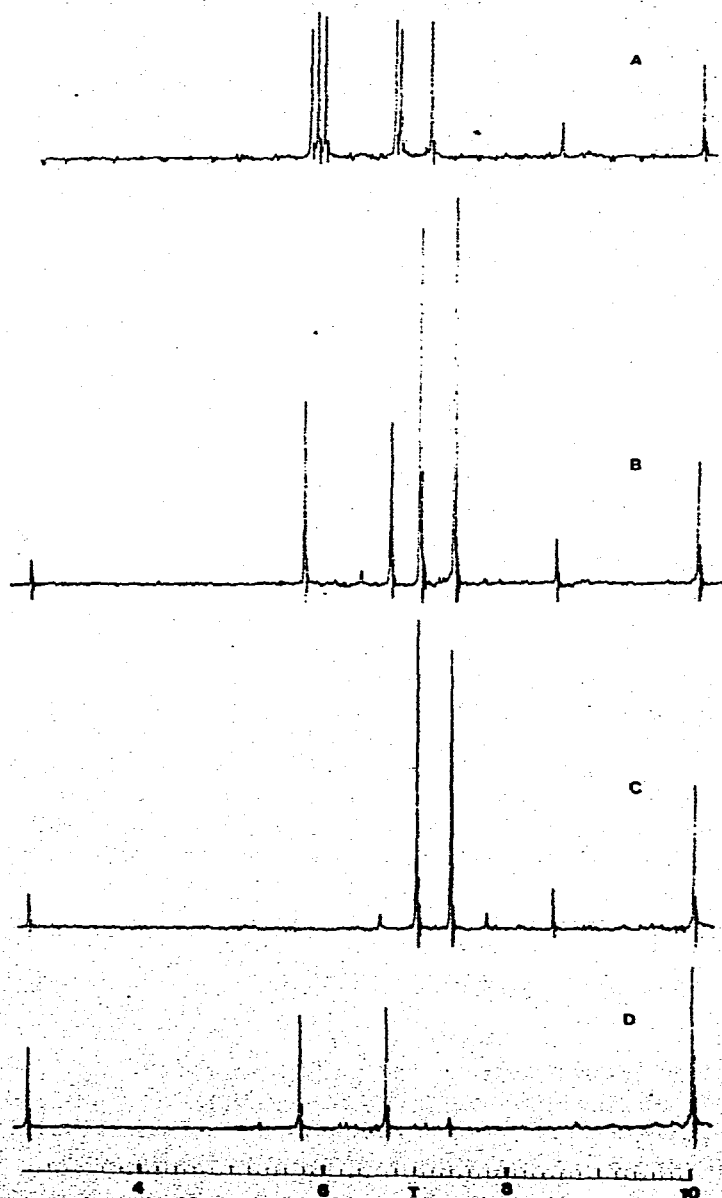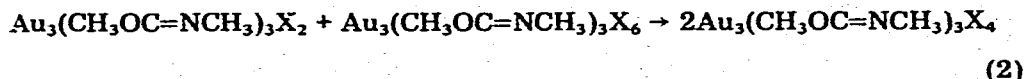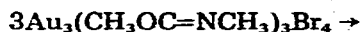

Fig. 2. PMR spectra of $Au_3(CH_3OC=NCH_3)_3Br_4$ in chloroform-d. A: Initial sealed evacuated sample; B: The same sample as in A after 25 days; C: Volatile products obtained by distillation of B; D: chloroform solution of the solid residue obtained after distillation of volatile material in sample B. Internal standard tetramethylsilane at τ 10, $CHCl_3$ at τ 2.8 and a solvent impurity at τ 8.45 also are present.

Complexes of the type V can also be formed via reactions 1 and 2.

$$Au_3(CH_3OC=NCH_3)_3 + 2Au_3(CH_2OC=NCH_3)_3X_6 \rightarrow 3Au_3(CH_3OC=NCH_3)_3X_4 \quad (1)$$

$$Au_3(CH_3OC=NCH_3)_3X_2 + Au_3(CH_3OC=NCH_3)_3X_6 \rightarrow 2Au_3(CH_3OC=NCH_3)_3X_4$$

$$(2)$$

In the case of the iodo complexes these reactions have been monitored by observing their electronic spectra. These reactions appear to be completed upon mixing of solutions. In both cases the equilibrium constants must be very large since only the product can be detected. Reaction 1 has been utilized as a convenient method of preparing V (X = Br). The IR and PMR spectra of V (X = Br) are analogous to those of V (X = I).

In solution and in the solid state V (X = Br or I) undergoes a spontaneous decomposition. This has been followed in detail for the bromo complex. Fig. 2 shows the PMR spectra of V (X = Br) under various conditions. Trace A shows the spectrum of the freshly prepared complex in a sealed, evacuated tube with chloroform-d as solvent. Trace B shows the spectrum of the same sample after twenty-five days of standing at ca. 25°C. At this point all traces of the starting complex have vanished and a quantity of gold metal has precipitated. The products were characterized by the following experiments. The sample was distilled into a second sample tube. The PMR spectrum of the volatile materials is shown in trace C. From comparison with authentic material the peak at τ 7.34 is identified as being due to methyl bromide and the peak at τ 6.95 is identified as methyl isocyanate. Further confirmation of the presence of methyl isocyanate comes from the IR spectrum of the distillate which shows a strong CN absorption at 2286 cm^{-1}. The solid residue remaining after distillation was dissolved in chloroform-d and separated from the metallic gold present. The PMR spectrum of this solution is shown in trace D. The chemical shifts observed correspond to those of VI (X = Br). From these observations along with the integration of spectrum B, which indicates that VI, methyl bromide and methyl isocyanate are present in the ratio of 1 : 2 : 2, we conclude that the decomposition of V proceeds via eq. 3. In view of the complexity of this reaction, which results in the destruction of two of the trigold complexes, the cleanliness of the process is remarkable.

$$3Au_3(CH_3OC=NCH_3)_3Br_4 \rightarrow$$

$$6Au(s) + Au_3(CH_3OC=NCH_3)_3Br_6 + 6CH_3NCO + 6CH_3Br \quad (3)$$

$Au_3(CH_3OC=NCH_3)_3X_2$

The iodo complex of this type was obtained as well formed, red crystals from the reaction of I with one mole of iodine. The bromo analog was obtained from the reaction between I and VI (X = Br) according to eq. 4. Both of these complexes undergo spontaneous decomposition in solution and in the solid

$$2Au_3(CH_3OC=NCH_3)_3 + Au_3(CH_3OC=NCH_3)_3Br_6 \rightarrow 3Au_3(CH_3OC=NCH_3)_3Br_3$$

$$(4)$$
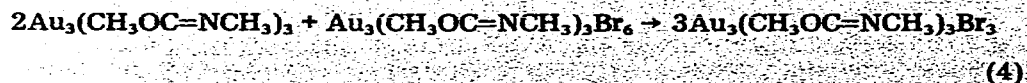
state even when rigorously protected from the atmosphere. Preliminary observa-

tions indicate that the decomposition is more complex than the decomposition reaction established for V (X = Br). The speed of this decomposition reaction has precluded the acquisition of elemental composition data since the samples decomposed during the time required for mailing to an analyst. However we believe that the available data do adequately characterize these compounds. A molecular weight determination for the iodo complex supports its formulation. The IR spectra of the two complexes are similar and are distinct from those of the other complexes in this series. The CN stretching frequencies of these two species are, as expected, increased in comparison to I. Both complexes exhibit similar PMR spectra with three C—methyl and three N—methyl resonances which all have equal intensity.

For these complexes the alternate structure VII might be considered in view of the sequence of oxidations involving Au(II) shown in eq. 5 [7]. However the
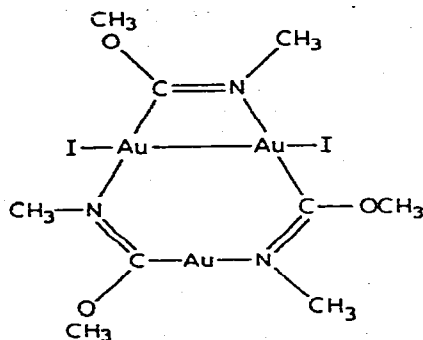
(VII)

gold—gold separation in the dimers in eq. 5 is much less than in our cyclic tri-

(VIII)

(5)
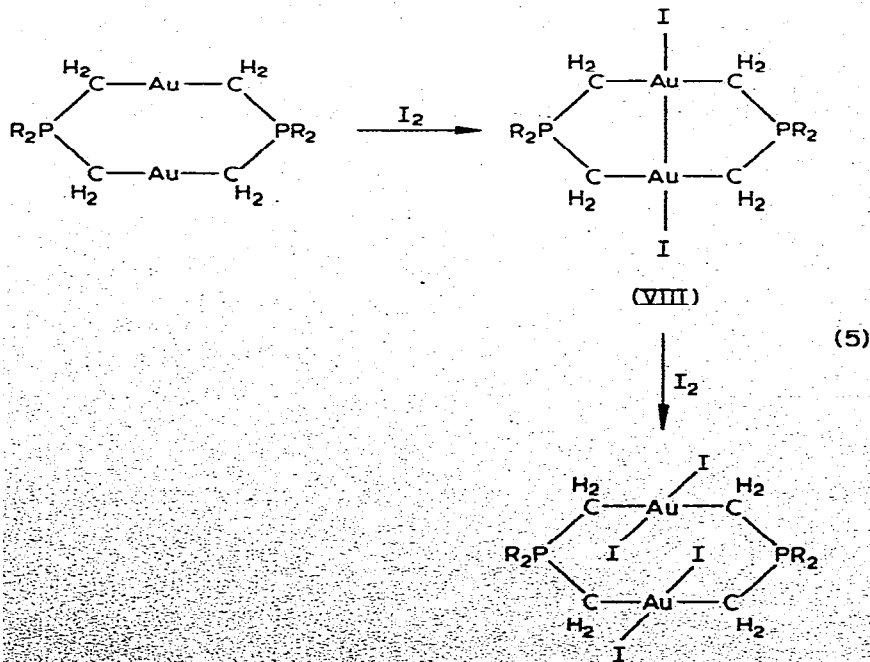
gold species. In VIII the gold—gold distance is 2.59 Å [7]. Moreover the rigidity of the cyclic trigold species is expected to oppose any shortening of gold—gold separation. Consequently a transannular oxidation to give VII is extremely unlikely and we reject this structure in favor of VI.

Each of the gold atoms in IV is in a chemically distinct environment. Because of the speed of reactions such as 1, 2 and 4 the formation of V probably involves IV as an intermediate. It is possible that halogen addition to form V from IV involves either specific addition to just one of the two different gold(I) centers or oxidation of both gold(I) centers. Due to the symmetry properties of this cyclic system only a single product V can result regardless of which gold(I) center is oxidized.

The separation and isolation of three distinct halogen oxidation products of I indicates that the three gold centers can communicate the differences in their chemical environment. This interaction could occur through direct gold—gold interactions or through the π system of the bridging ligands. The effect however could also be transmitted directly by the halogen ligands. The van der Waals radii of bromine and iodine are 1.95 and 2.15 Å respectively [12] with a separation of only 3.3 Å between metal centers, the halogen—halogen separation on one side of these planar species is clearly less than the sum of the van der Waals radii of the two halogens.

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