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Some Attempted Auration Reactions

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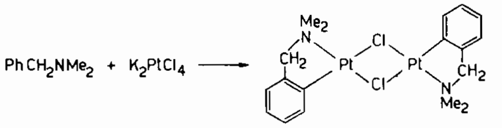
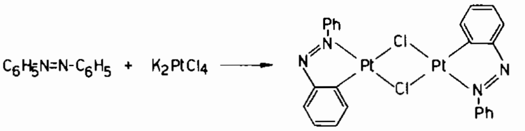
Gold(III) bromide reacts with NMe_2CH_2Ph to give $[AuBr_3(NMe_2CH_2Ph)]$, $[NMe_2(CH_2Ph)H][AuBr_4]$ or $[NMe_2(CH_2Ph)H][AuBr_2]$ depending on the reaction conditions, with azobenzene to give $[AuBr_3$(azobenzene)$]$ and with 2-vinylpyridine to give $[AuBr_3$(2-vinylpyridine)$]$, which with bromine gives $[AuBr_3\cdot$ 2-(1,2-dibromoethyl)pyridine$]$. Unsuccessful attempts to rearrange these complexes to the products of auration of the aryl- or vinyl-substituents of the ligands are described. Evidence is presented that the product of reaction of allyl methyl sulphide with gold(III) bromide arises from bromoauration of the allylic group.

Introduction

In 1931 Kharasch and Isbell[1] reported that anhydrous gold(III) chloride reacts rapidly with benzene to give the product of auration $[C_6H_5AuCl_2]$. This has recently been confirmed[2] and stable derivatives of the type $C_6H_5AuCl_2L$ (L = pyridine, chloride *etc.*) have been isolated. More recently[3] Cope and co-workers showed that metallation of aromatic rings substituted onto a nitrogen donor ligand could take place readily in palladium(II) and platinum(II) complexes, and such *ortho*-metallation reactions have since been thoroughly studied[5–7] (equations 1 and 2).



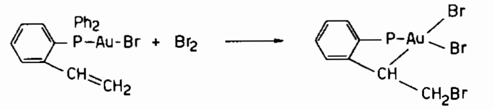
(1)



(2)

Surprisingly, these reagents do not readily give *ortho*-metallated derivatives with gold(III) halides. Kharasch and Beck reported[8] that benzonitrile with Au_2Cl_6 gave a complex $[NCC_6H_4AuCl_2]_n$ arising from metallation of the aromatic ring but a recent investigation[9] has shown the product to be the simple nitrile complex $PhCNAuCl_3$.

Another method of preparing compounds with gold–carbon bonds by auration of alkene-substituted ligands is shown in equation (3)[10].



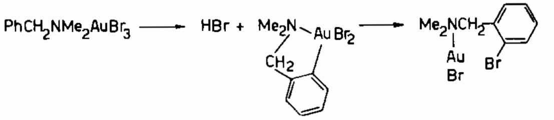
(3)

In an attempt to find new methods for preparing organogold complexes by auration reactions we have investigated reactions of N,N-dimethylbenzylamine, azobenzene, 2-vinylpyridine and allyl(methyl)sulphide with anhydrous gold(III) halides.

Results and Discussion

N,N-dimethylbenzylamine reacted with anhydrous gold(III) bromide or chloride in dichloromethane solution to give some decomposition to gold and form the N,N-dimethylbenzylammonium tetrahalogenaurate(III) as the chief product isolated after chromatography over silica gel. With gold(III) bromide the complex $[AuBr_3(NMe_2CH_2Ph)]$ could also be isolated and was the major product when the reaction took place in solvent methanol or ethanol. On addition of a large excess of N,N-dimethylbenzylamine in methanol the initial red-brown colour due to $[AuBr_3(NMe_2CH_2Ph)]$ slowly faded and a colourless solution was obtained. From this could be crystallised the complex $[PhCH_2NMe_2H]^+[AuBr_2]^-$. Tetraalkylammonium salts of the dibromoaurate(I) anion have been isolated recently by Braunstein and Clark and our complex has similar properties to those reported[11]. Thus it is unstable in aqueous solution, disproportionating to Au and $[AuBr_4]^-$, and reaction with bromine in dichloromethane or methanol gave a mixture of $[AuBr_3(NMe_2CH_2Ph)]$ and $[PhCH_2NMe_2H]^+[AuBr_4]^-$.

The mechanism by which the reduction of Au(III) to Au(I) takes place is not known. It is possible that *ortho*-metallation followed by reductive alimination could take place (equation 4).



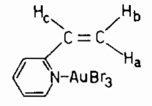
(4)

In the presence of excess amine, the brominated amine would presumably be displaced, but since other trialkylamines will also cause reduction of gold(III) bromide under these experimental conditions a mechanism not involving *ortho*-metallation is considered more likely.

Azobenzene reacted with gold(III) bromide to give a simple complex [(PhNNPh)$AuBr_3$]. The preparation of this complex was reported independently during the course of this work[12]. Neither we nor others have been successful in rearranging this complex to the *ortho*-metallated derivative. Our attempts include refluxing in chloroform, ethanol or ethyl acetate, but in each case slow decomposition to gold took place.

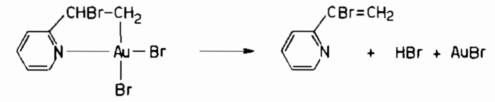
The low reactivity of the N,N-dimethylbenzylamine and azobenzene complexes towards *ortho*-metallation by gold(III) is perhaps surprising in view of the high reactivity of the gold(III) halides towards benzene, and the ease with which *ortho*-metallation of these ligands takes place with palladium(II) and platinum(II) complexes. It seems that blocking the fourth co-ordination site at gold greatly reduces the reactivity towards metallation reactions. This idea has previously been put forward to explain the low reactivity of the $[AuX_4]^-$ ions (X = Cl,Br) compared with $[Au_2X_6]$ towards benzene[1]. With platinum(II) and palladium(II) complexes $[LPtX_2]$ where L = azobenzene or N,N-dimethylbenzylamine could be formed as intermediates, and still have a vacant coordination site in the square plane of the metal atom at which the aromatic ring could complex prior to *ortho*-metallation. Interestingly, Shaw and co-workers have found that *ortho*-metallation of *chelating* benzylamines by platinum(II) takes place only under vigorous conditions[13]. They ascribed this to a lack of flexibility due to chelation, but it is also possible that the low reactivity is simply due to blocking of the fourth coordination site in the chelate complex. Working on this hypothesis, we have attempted to catalyse *ortho*-metallation in [$AuBr_3$(azobenzene)] by silver tetrafluoroborate, which should create a vacant coordination site by removing bromide from gold. However, in all cases only decomposition to gold took place in these reactions.

2-vinylpyridine gave an adduct (I) with gold(III) bromide. The vinyl group is not coordinated to gold in this complex, as evidenced by the nmr spectrum, which shows that the chemical shifts of the vinylic protons are downfield from the values in 2-vinylpyridine whereas an upfield shift is expected for a coordinated vinyl group. The coupling constants are also very similar to those in 2-vinylpyridine as shown in Table I.



(I)

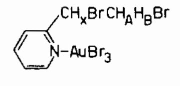
All attempts to rearrange (I) to give compounds containing a gold–carbon bond by treating with methanol or sodium methoxide in methanol (*cf.* the similar platinum complex[14]) or by heating in a veriety of organic solvents were unsuccessful. Thermolysis of the complex at 200° C did give HBr and a compound C_7H_6BrN, identified from its mass spectrum, which could arise through decomposition of the expected product of auration (II) by β-elimination (equation 5)



(5)

(II)

Reaction of (I) with bromine gave a complex $[AuBr_5C_7H_7N]$ which was identified as (III), formed by addition of bromine to the C=C double bond of the vinyl group by its nmr spectrum.



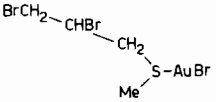
(III)

The protons of the resulting 1,2-dibromoethyl group gave an ABX nmr pattern with $\delta(H_X) = 6.10$ ppm, $^1/_2[\delta(H_A)+\delta(H_B)] = 4.55$ ppm, $\delta(H_A)-\delta(H_B) = 0.30$ ppm, $^2J(H_AH_B) = 10.8$ Hz, $^3J(H_AH_X) = 10.5$ Hz and $^3J(H_BH_X) = 6.0$ Hz. The chemical shifts and coupling constants have typical values for a group of this kind, and indicate that there is no direct interaction between the 1,2-dibromoethyl group and the gold atom. Thermolysis of the complex at 200° C gave 2-(1,2-dibromoethyl)pyridine and bromine as the volatile products as identified by mass spectrometry.

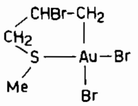
TABLE I. Nmr Spectra of L and $AuBr_3L$ (L = 2-vinylpyridine). Protons labelled as in (I).

Compound	$\delta(H_a)$ ppm	$\delta(H_b)$ ppm	$\delta(H_c)$ ppm	$^2J(H_aH_b)$ Hz	$^3J(H_aH_c)$ Hz	$^3J(H_bH_c)$ Hz
L	5.45	6.22	6.75	2	11	17
$AuBr_3L$	6.11	6.42	7.51	1	11	17

Allyl methyl sulphide reacted with gold(III) bromide to give a pale yellow solid of empirical formula [$AuBr_3$ (C_4H_8S)]. The pale yellow colour is inconsistent with the compound being the simple adduct (since complexes of the type $AuBr_3L$ are invariably deep red or red–brown in colour) and this is confirmed by the disappearance of an i.r. band due to C=C stretching at 1600 cm^{-1}observed in the parent sulphide. The likely structures are therefore (IV) and (V) by analogy with earlier work.



(IV)



(V)

Due to the low solubility of the complex it was not possible to obtain a satisfactory nmr spectrum of the product, but structure (V) is preferred for the following reasons: (i) (IV) was prepared independently by reaction of 2,3-dibromopropyl methyl sulphide (prepared by reaction of bromine with allyl methyl sulphide) with [$AuBr(SMe_2)$]. The product was an oil which was difficult to purify, but its properties were quite different from those of the above complex; (ii) the infrared spectrum of the complex contained bands in the region 600 cm^{-1} due to ν(CBr) which were considerably weaker than in the free ligand $MeSCH_2CHBrCH_2Br$ or in (IV), suggesting that only one bromine atom was incorporated into the sulphide ligand as in structure (V). The spectroscopic evidence (as well as the colour of the complex) is thus similar to that presented by Bennett and co-workers for the product of bromination of [AuBr(SP)] where (SP) is *o*-styryldiphenylphosphine, and which was proved to have a structure analogous to that of (V) by X-ray studies[10].

Experimental

Gold(III) bromide was prepared by shaking gold powder with excess bromine at room temperature for two days, and then removing excess bromine under vacuum. Gold(III) chloride was prepared by heating gold powder with excess chlorine in a Carius tube at 100° C for 1 week.

2-vinylpyridine was distilled immediately before use. Solvents and other reagents were purified by standard methods. Nmr spectra were recorded using a Perkin-Elmer R12B spectrometer. Chemical shifts are given in ppm downfield from internal TMS.

N,N-dimethylbenzylamine with Au_2Cl_6

Anhydrous gold(III) chloride (1.0 g) was treated with N,N-dimethylbenzylamine (0.4 g) in dichloromethane (10 cm^3). The mixture was stirred for 2 hr at room temperature, then filtered to remove some gold deposit. The solvent was removed under vacuum to give a yellow oil, which was purified by chromatography over silica using dichloromethane element and then by recrystallisation from chloroform. Yield 0.74 g. M.p. 142–143° C. Ir: ν(NH) 3120 cm^{-1}. Nmr in $CDCl_3$: $\delta(CH_3N)$ 1.63 ppm, $\delta(PhCH_2)$ 2.9 ppm, $\delta(C_6H_5)$ 7.50 ppm. *Anal.* Calcd. for $C_9H_{14}AuCl_4N$: C, 22.8; H, 3.0; Au, 41,5; Cl, 29,9; N, 3.0. Found: C, 22.6; H, 2.9; Au, 41.5; Cl, 30.1; N, 2.9%.

N,N-dimethylbenzylamine with Au_2Br_6

Treatment of Au_2Br_6 with N,N-dimethylbenzylamine as above gave a brown oil which could not be crystallised. Chromatography over silica gave two fractions. The first was eluted with dichloromethane/pentane (1/1), and gave orange–red crystals. M.p. 141–143° C. Yield 38%. Ir: ν(NH) 3170 cm^{-1}. Nmr in $CDCl_3$: $\delta(CH_3N)$ 1.62 ppm, $\delta(PhCH_2)$ 3.05 ppm, $\delta(C_6H_5)$ 7.50 ppm. *Anal.* Calcd. for $C_9H_{14}AuBr_4N$: C, 16.6; H, 2.2; Au, 30.2; N, 2.2. Found: C, 17.6; H, 2.1; Au, 30.0; N, 2.5%.

The second fraction was eluted with dichloromethane and gave a deep-brown oil, which slowly solidified to give deep purple–brown crystals. Yield 28%. M.p. 100–110° C. Ir showed no ν(NH). Nmr in $CDCl_3$: $\delta(CH_3N)$ 2.32 ppm; $\delta(PhCH_2)$ 3.87 ppm; $\delta(C_6H_5)$ 7.0 ppm (multiplet). *Anal.* Calcd. for $C_9H_{13}AuBr_3N$: C, 18.9; H, 2.3; Au, 34.4; N, 2.4. Found: C, 18.4; H, 2.5; Au, 33.5; N, 2.3%.

In another experiment a solution of gold(III) bromide in dry methanol was treated with excess N,N-dimethylbenzylamine. The initial red solution slowly decolorised. Evaporation of the solvent gave a colourless oil, which was washed thoroughly with ether and recrystallised from dichloromethane–ether as colourless, oily crystals. The crystals decomposed rapidly in water to give gold and the [$AuBr_4$]– ion. Ir: ν(NH) 3000 cm^{-1}. Nmr in CH_2Cl_2: $\delta(CH_3N)$ 2.65 ppm, $\delta(PhCH_2)$ 4.17 ppm, $\delta(C_6H_5)$ 7.28 ppm (multiplet), δ(NH) 9.92 ppm. *Anal.* Calcd. for $C_9H_{14}AuBr_2N$: C, 21.9; H, 2.9; Au, 39.9. Found: C, 22.1; H, 3.0; Au, 39.0%.

Tribromo(2-vinylpyridine)gold(III)

This was prepared by adding 2-vinylpyridine (0.12 cm^3) to a solution of Au_2Br_6 (0.40 g) in methanol (4 cm^3). The *product* precipitated from solution and was recrystallised from dichloromethane as red crystals. M.p. 95–100° C. *Anal.* Calcd. for $C_7H_7AuBr_3N$: C, 15.5; H, 1.3; Au, 36.4. Found: C, 15.85; H, 1.7; Au, 36.85%.

Tribromo[2-(1,2-dibromoethyl)pyridine]gold(III)

This was prepared by adding bromine (0.06 cm^3) to a solution of tribromo(2-vinylpyridine)gold(III)

(0.21 g) in dichloromethane (15 cm^3). The solution was set aside for 2 days in the refrigerator when red crystals of the *product* slowly formed. M.p. 135–139° C. *Anal.* Calcd. for $C_6H_7AuBr_5N$: C, 12,0; H, 1.0; Au, 28.1; Br, 57.0. Found: C, 12.1; H, 1.0; Au, 28.0; Br, 57.2%.

Tribromo(azobenzene)gold(III)

This prepared by reaction of Au_2Br_6 (0.38 g) with azobenzene (0.18 g) in dichloromethane (4 cm^3). After stirring for 1 hr at room temperature the solution was heated to give a clear red solution. On cooling red–brown crystals of the *product* formed. M.p. 189° C. *Anal.* Calcd. for $C_{12}H_{10}AuBr_3N_2$: C, 23.3; H, 1.6; Au, 31.8; Br, 38.7; N, 4.5. Found: C, 23.1; H, 1.5; Au, 31.5; Br, 39.4; N, 4.6%.

Allyl Methyl Sulphide with Au_2Br_6

Allyl methyl sulphide (0.15 cm^3) was added to a solution of Au_2Br_6 (0.57 g) in methanol (5 cm^3). The solution was warmed to redissolve the initial brown precipitate and then allowed to stand for 2 days. A yellow solid slowly precipitated. This was filtered off and dried under vacuum. M.p. 125–127° C. *Anal.* Calcd. for $C_4H_8AuBr_3S$: C, 9.1; H, 1.5; Au, 37.5; Br, 45.7; S, 6.1. Found: C, 9.8; H, 1.7; Au, 40.5; Br, 44.2; S, 6.4%.

2,3-dibromopropyl Methyl Sulphide

This was prepared by slow addition of bromine (0.35 cm^3) to a solution of allyl methyl sulphide (0.5 cm^3) in dichloromethane (5 ml). After 15 min, the solvent was removed and the product purified by vacuum distillation. Nmr in $CDCl_3$: $\delta(CH_3S)$ 2.72 ppm, $\delta(CH_2S)$ 3.56 ppm, doublet of doublets $^3J(HH)$ 6Hz, $\delta(CHBr)$ 4.68 ppm, $\delta(CH_2Br)$ 4.38 ppm, each a complex multiplet. Ir $\nu(CBr)$ 565, 610, 640 cm^{-1}, no band in 1600 cm^{-1} region.

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