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Synthesis and Properties of Arylgold(III) Compounds

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Received December 13, 1973 AIC30894V

A preparative route to the complexes $R'_4N^+[RAuX_3^-]$ (X = Cl or Br; R = C_6H_5, p-ClC_6H_4, p-BrC_6H_4, or p-$NO_2C_6H_4$) is described. The route involves the reaction of (phenyl or substituted phenyl)hydrazine hydrochloride with the tetraethyl- or tetra-*n*-butylammonium salts of tetrachloro- or tetrabromoaurate(III). The arylgold(III) species were characterized by ^1H nmr, ir, and Raman studies. Vibrational assignments for various fundamentals of the complexes are given.

Introduction

Although the organometallic chemistry of gold(III) is of considerable interest, few arylgold compounds have been reported[1-3] and their properties are not known in detail. Most of the known arylgold(III) compounds have the formula $(RAuX_2)_2$ (R = aryl, X = halogen) and were obtained by direct reaction between anhydrous gold(III) chloride and an aromatic hydrocarbon.[4] Such compounds are rather unstable, and hence they were not characterized in detail. Starting from the compounds $(RAuCl_2)_2$, Liddle and Parkin[2,5] have prepared trichloroarylgold(III), $RAuCl_3^-$, and dichloroarylgold(III), $RAuCl_2L$, complexes.

It is well known that π-acceptor ligands such as phosphines may be used to stabilize complexes containing metal-carbon σ bonds. This generalization applies to gold(III) chemistry, *e.g.*,[6] $C_6H_5AuBr_2 \cdot P(C_6H_5)_3$ and $(CH_3)_3Au \cdot P(C_6H_5)_3$, and to platinum(II) chemistry, *e.g.*,[7] $[(C_2H_5)_3P]_2Pt(C_6H_5)_2$ and $[(C_2H_5)_3P]_2Pt(CH_3)_2$. σ-Alkyl and σ-aryl derivatives of gold(I) need also to be stabilized by ligands such as tertiary phosphines, *e.g.*,[8] $(C_6H_5)AuP(C_6H_5)_3$.

The present paper constitutes a report on a new reaction which leads directly to trihalogenoarylgold(III) complexes which are neither air nor moisture sensitive and which do not contain any stabilizing ligands such as phosphines. Note however that little is known about the actual strengths of metal-carbon σ bonds,[9] and there is no reason to believe that they are less strong in our complexes than in ones containing phosphine ligands. The key reaction (preliminary reports on which have appeared[3,10]) is

$$2C^+[AuX_4^-] + C_6H_5NHNH_2 \cdot HCl \rightarrow C^+[AuX_2^-] + C^+[C_6H_5AuX_3^-] + N_2 + 4HCl$$

It involves treatment of tetrahalogenoaurate(III) complexes $C^+[AuX_4^-]$ ($C^+ = (C_2H_5)_4N^+$ or $(n\text{-}C_4H_9)_4N^+$; X = Cl or Br) with phenylhydrazine hydrochloride, thereby affording the corresponding gold(I) halide $C^+[AuX_2^-]$ and the trihalogenogold(III) complex $C^+[C_6H_5AuX_3^-]$. The mechanism of this reaction has been discussed elsewhere.[3] The success of this reaction procedure is very much a function of the appropriate redox properties of phenylhydrazine and the AuX_4^- ion. The work has also been extended to include the para-substituted phenylhydrazines p-$YC_6H_4NHNH_2$, where Y = Cl, Br, or NO_2.

The resulting complexes $C^+[p\text{-}YC_6H_4AuX_3^-]$ have been studied by means of ^1H nmr, infrared, and Raman spectroscopy in order to assist in the establishment of the structures of the arylgold(III) anions and in order to allow vibrational assignments of various fundamentals to be made.

Experimental Section

Preparations of the Complexes. Tetraethylammonium trichlorophenylaurate(III) and tetra-*n*-butylammonium trichlorophenylaurate(III) were prepared as described previously.[10] Yields referred to the theoretically expected quantities (corresponding to half the $AuCl_4^-$ engaged) were 32 and 26%, respectively.

Tetraethylammonium Tribromophenylaurate(III). Tetraethylammonium tetrabromoaurate(III) (0.72 g, 1.11 mmol) was partly dissolved in absolute ethanol (15 ml) and gently heated. To this solution, a suspension of phenylhydrazinium hydrochloride (0.09 g, 0.62 mmol) in absolute ethanol (5 ml) was added with constant agitation. The solution changed from red to yellow during 2 hr heating at 45°. The slight excess of phenylhydrazinium hydrochloride was necessary in order to complete the color change. On cooling in a refrigerator, the solution deposited yellow plates, which were removed by filtration, washed with diethyl ether, and dried. These were $[(C_2H_5)_4N][C_6H_5AuBr_3]$; *yield 0.062 g, 17%.*

Tetra-*n*-butylammonium Tribromophenylaurate(III). The preparation was analogous to the previous one. The reaction solution deposited white needles on being cooled in a refrigerator. These were filtered off, washed with diethyl ether, and dried to give $[(n\text{-}C_4H_9)_4N][AuBr_2]$ in 85% yield. Addition of diethyl ether to the remaining solution afforded yellow prisms of $[(n\text{-}C_4H_9)_4N][C_6H_5AuBr_3]$ in 16% yield. As noted in the case of the chloride,[10] the aryl salt is less soluble than the AuX_2^- salt with tetraethylammonium cation but the reverse is true with the tetra-*n*-butylammonium cation.

Tetraethylammonium Triiodophenylaurate(III). Several attempts were made to effect reaction between $[(C_2H_5)_4N][C_6H_5AuCl_3]$ and LiI, NaI, or $[(C_2H_5)_4N]I$ in anhydrous dichloromethane. Owing to its solubility, $[(C_2H_5)_4N]I$ appeared to be the most convenient reagent with which to carry out this metathesis. To a solution of $[(C_2H_5)_4N][C_6H_5AuCl_3]$ (0.33 g, 0.65 mmol) in CH_2Cl_2 (25 ml) was added dropwise a solution of $[(C_2H_5)_4N]I$ (0.51 g, 1.98 mmol) in CH_2Cl_2 (30 ml). The first drops gave an orange color, which turned yellow within seconds. After being stirred for 15 min, diethyl ether (10 ml) was added to the solution, which was then placed in a refrigerator for 10 hr. About 25 mg of orange-red crystals was precipitated, filtered off, washed with diethyl ether, and dried. On addition of more diethyl ether to the filtrate, white and yellow crystals (identified as $[(C_2H_5)_4N]Cl$ and $[(C_2H_5)_4N]AuI_2$, respectively) were precipitated. Evaporation of the mother liquor on a rotary evaporator yielded an orange-yellow oil containing iodobenzene.

The original orange-red crystals are decomposed by water, melt at 85-86°, and appear (ir evidence) to be impure $[(C_2H_5)_4N][C_6H_5AuI_3]$. Calcd: C, 21.40; H, 3.18; N, 1.78. Found: C, 23.7; H, 3.6; N, 2.3_5. This preparation, although unsatisfactory in that it does not yield a pure product, is interesting for comparison with that reported by Lee;[11] *viz.*, treatment of $C_6H_5TlCl_2$ or $C_6H_5TlBr_2$

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Table I. Analytical Data and Physical Properties of the Arylgold(III) Complexes

		% C		% H		% N		% X			
No.	Complex	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Description	Mp, °C
I	$[(C_2H_5)_4N][C_6H_5AuCl_3]$	32.91	33.0	4.90	4.8	2.75	2.4	20.86	20.9	Pale cream prisms	154
II	$[(n\text{-}C_4H_9)_4N][C_6H_5AuCl_3]$	42.41	42.3	6.59	6.65	2.25	2.25	17.11	17.2	Pale yellow prisms	99
III	$[(C_2H_5)_4N][C_6H_5AuBr_3]$	26.09	26.0	3.88	3.9	2.17	2.1	37.27	35.5	Yellow plates	122
IV	$[(n\text{-}C_4H_9)_4N][C_6H_5AuBr_3]$	34.92	34.9	5.42	5.35	1.85	1.8	31.75	31.8	Yellow prisms	87
V	$[(n\text{-}C_4H_9)_4N][C_6H_5AuI_3]$	29.43	30.8	4.57	4.75	1.56	1.65	42.47		Orange prisms	78–79
VI	$[(C_2H_5)_4N][p\text{-}ClC_6H_4AuCl_3]$	30.83	30.9	4.41	4.4	2.57	2.6	26.05		White plates	160
VII	$[(C_2H_5)_4N][p\text{-}BrC_6H_4AuCl_3]$	28.50	28.4	4.07	4.0	2.38	2.4			Pale yellow prisms	178
VIII	$[(C_2H_5)_4N][p\text{-}NO_2C_6H_4AuCl_3]$	30.24	30.4	4.32	4.4	5.04	5.1	19.17		Yellow needles	168

with KI results in the rapid formation of iodobenzene. Phenylthallium diiodide is thus unknown.

Tetra-*n*-butylammonium Triiodophenylaurate(III). A solution of $[(n\text{-}C_4H_9)_4N]I$ (0.166 g, 0.45 mmol) in CH_2Cl_2 (5 ml) was added dropwise at room temperature to a solution of $[(n\text{-}C_4H_9)_4N][C_6H_5AuCl_3]$ (0.093 g, 0.15 mmol) in CH_2Cl_2 (3 ml). The resulting orange solution was cooled to 0° and both orange and white crystals precipitated. These were filtered off and washed with diethyl ether. After rinsing with distilled water, the white crystals of $[(n\text{-}C_4H_9)_4N]Cl$ redissolved, leaving orange crystals of the required complex (yield 0.070 g, 52%).

Other experiments indicated that decomposition products were formed during the reaction and that triiodophenylaurate(III) complexes are far less stable than their chloro or bromo analogs. Moreover, recrystallization destroyed most of the product and afforded, among other products, the complex $[(n\text{-}C_4H_9)_4N]AuI_2$. These properties are comparable with those of $(C_2H_5)_3PAuI_3$ (which is unstable)[12] and of $[(CH_3)_2SPtI_3^-]$ (which cannot be isolated in the solid state).[13]

Tetraethylammonium Trichloro(*p*-chlorophenyl)aurate(III). Tetraethylammonium tetrachloroaurate(III) (0.50 g, 1.07 mmol) was partly dissolved in absolute ethanol (50 ml) and mixed with a suspension of *p*-chlorophenylhydrazine hydrochloride (0.10 g, 0.56 mmol) in CH_2Cl_2 (15 ml). The solution was gently heated for 20 min and then left to cool slowly and placed in a refrigerator after the addition of diethyl ether (10 ml). White plates precipitated and were filtered off, washed with diethyl ether, and dried to give $[(C_2H_5)_4N][p\text{-}ClC_6H_4AuCl_3]$ (yield 0.06 g, 21%). No attempt was made to isolate the second product of the reaction, *viz.*, $[(C_2H_5)_4N]AuCl_2$.

Tetraethylammonium Trichloro(*p*-bromophenyl)aurate(III). This complex is obtained in 17% yield by the above procedure with *p*-bromophenylhydrazine replacing *p*-chlorophenylhydrazine. The reaction was left for 40 min, thereby affording very pale yellow prisms of the required complex.

Tetraethylammonium Trichloro(*p*-nitrophenyl)aurate(III). Tetraethylammonium tetrachloroaurate(III) (0.88 g, 1.9 mmol) was dissolved in a mixture of anhydrous methanol (100 ml) and dichloromethane (50 ml) while another solution was prepared of *p*-nitrophenylhydrazine (0.15 g, 0.98 mmol) in methanol (10 ml) and dichloromethane (15 ml). The latter was slowly added to the former with agitation and the final solution was then gently heated for 15 min. Some particles of metallic gold which formed during the reaction were removed by filtration and to the resulting pale yellow solution diethyl ether (5 ml) was added and the mixture placed in a refrigerator for 24 hr. Long yellow needles of the required compound precipitated; these were filtered off, washed with diethyl ether, and dried (yield 0.16 g, 30%).

Instrumental Information. Infrared Spectra. Infrared spectra of the complexes were recorded as polyethene disks on the Polytec Fourier interferometer, FIR 30, and as paraffin wax disks on an RIIC interferometer.

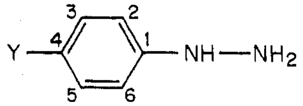
Raman Spectra. Raman spectra of the complexes in the solid state were recorded on Spex 1401 and Coderg PH1 spectrometers by use of Coherent Radiation Model 52 Kr^+ (647.1 nm) and OIP Model 181E He–Ne (632.8 nm) excitation (powers of 400 and 100 mW, respectively) and 90° collection optics. The spectra were calibrated by reference to the emission lines of neon. The spectra of compounds I, VI, VII, and VIII were recorded as capillaries and of II, III, and IV on a finger.

Nmr Spectra. Nmr spectra were recorded on a Perkin-Elmer R 12B instrument at 60 MHz with TMS as reference. The complexes were dissolved in CD_3COCD_3.

Results and Discussion

Preparation and Properties of the Complexes. The analytical data and other properties of the arylaurate(III) salts prepared in the course of this investigation are summarized in Table I. The complexes form white, yellow, or orange crystals which are air and water stable. With the exception of the two salts of the $[C_6H_5AuCl_3^-]$ ion (previously obtained from $[RAuCl_2]_2)^2$ the complexes are new.

The transfer of the phenyl group from the hydrazine to the gold(III) atom has been postulated[3] to take place *via* an *N*-nitrene intermediate. This mechanism accounts for the fact that para-substituted arylaurate(III) ions are formed from para-substituted phenylhydrazines since it involves nucleophilic attack by the carbon atom (C_1) bonded to the nitrogen atom on to the gold(III) species.



Ortho metalation[14,15] was rejected since either C_2 or C_6 would thereby become bonded to the gold(III) species; *i.e.*, this mechanism would lead to the formation of meta-substituted arylaurate(III) ions.

It was also of interest to find that the para isomers were obtained where Y is either a mesomeric electron-donating group such as Cl or Br or a mesomeric electron-withdrawing group such as NO_2. Consequently it seems certain that a free $YC_6H_4^-$ anion is not liberated during the reaction, since rearrangement would then occur according to the nature of Y. Where Y = NO_2, atoms C_2 and C_6 carry the highest electronic density in the ring and this would favor the formation of Au–C_2 or Au–C_6 bonds. Again, this mechanism would lead to the formation of a meta-substituted arylaurate(III) anion.

The position of the Y group in the anions $YC_6H_4AuCl_3^-$ is thus central to the above conclusions as to the mechanism of their formation. ^1H nmr and vibrational spectroscopies have been used to establish this feature of the stereochemistry of the anions, and the appropriate results are accordingly discussed in detail.

Spectroscopic Studies to Establish the Position of Y in the $YC_6H_4AuCl_3^-$ Ions. A. Infrared Measurements. In substituted arylaurate(III) species $YC_6H_4AuCl_3^-$ it is possible to establish the position of the Y group by ir spectroscopic studies. Indeed, it is well known that the substitution pattern of an aromatic ring may be deduced from the series of weak overtone and combination bands in the region 2000–1600

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Table II. Important Infrared-Active Vibrations of the Complexes $[Et_4N][p\text{-}YC_6H_4AuCl_3]$ (Y = H, Cl, Br, NO_2)

I $C_6H_5AuCl_3^-$	VI $p\text{-}ClC_6H_4AuCl_3^-$	VII $p\text{-}BrC_6H_4AuCl_3^-$	VIII $p\text{-}NO_2C_6H_4AuCl_3^-$	Assignment
1962 vw				Overtone and combination bands
1949 w			1942 w	
1878 w	1903 w	1903 w		
1860 w				
1813 vw			1811 w	
1798 w		1783 w		
1726 w	1656 vw		1682 w	
1635 w	1637 w	1634 w	1628 vw	
1564 s	1561 w	1544 mw	1595 s	C=C skeletal in-plane vibrations
	1551 w			
			850 vs	$\delta(NO_2)$
742 vs	819 s	815 s	836 sh	Out-of-plane C-H deformations
			745 s	$\gamma(NO_2)$
689 s		692 vw	689 w	Trigonal ϕ(CC)[17]

cm^{-1},[16] together with the frequency of the strong bands between 900 and 650 cm^{-1} due to out-of-plane CH bending vibrations.[17]

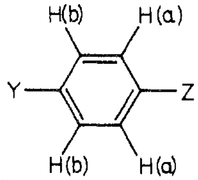
The combination bands between 2000 and 1600 cm^{-1} (Table II) in the infrared spectra of complexes I-V (see Table I for the numbering of the complexes) are characteristic of complexes containing monosubstituted benzene rings. The defining feature is a series of four bands showing slightly decreasing intensity with decreasing frequency,[16] the pattern being more important than the exact frequencies. On the other hand, the patterns of the infrared bands in this region for complexes VI-VIII are typical of para-disubstituted benzene rings.[16]

In the CH out-of-plane deformation region, five adjacent ring hydrogen atoms usually give rise to an infrared absorption between 770 and 730 cm^{-1} (vs) ("umbrella" mode).[17] In our case, complex I, for example, has a band at 742 (vs). On the other hand, if the aromatic derivative has two adjacent ring hydrogen atoms (as in the case of a para-disubstituted benzene) it is known that a very strong absorption occurs between 860 and 800 cm^{-1}; in accordance with this generalization, complexes VI and VII have very strong bands at 819 and 815 cm^{-1}, respectively. The situation is slightly different for VIII, which has a strong band at 850 cm^{-1} ($\delta(NO_2)$),[18] a shoulder at 836 cm^{-1}, and another strong band at 745 cm^{-1} ($\gamma(NO_2)$). It has often been found that a nitro substituent shifts bands due to the aromatic ring to higher frequencies. Moreover, some vibrations of the nitro group are mixed with CH modes,[18] particularly the "umbrella" γ(CH) and $\gamma(NO_2)$ modes. Thus the infrared spectrum of VIII in this spectral region is different from that of VI and VII, and it is not possible to establish by infrared measurements alone the position of the nitro group in the ring. In conclusion, the infrared data on the complexes VI-VIII in the 2000-1670-cm^{-1} region and the corresponding data for all except VIII in the 900-650-cm^{-1} region consistently indicate that the Y group is in the para position in the aurate(III) complexes.

Assignments for some other fundamentals of the complexes are included in Table II. The spectra of all the tetraethylammonium salts contain a strong band at *ca.* 785 cm^{-1} which is due to the cation.

B. Nmr Measurements. The nmr spectra of the aromatic protons are of great interest mainly for two reasons: (a) confirmation that the complexes VI-VIII are para substituted (this being particularly important in the case of VIII, for which the infrared evidence was inconclusive); (b) variation of the chemical shift with the nature of the substituents.

Table III. ^1H Nmr Spectra of



Y	Z	δ,[a] ppm
H	$NHNH_2$	6.90 (multiplet)
H	$AuCl_3$	7.03
Cl	$AuCl_3$	7.12 (singlet)
H	CH_3	7.17 (singlet)
Br	$AuCl_3$	7.17
H	H	7.37
NO_2	$AuCl_3$[b]	7.50 (H(a)) 7.97 (H(b))
NO_2	Cl	7.52 (H(a)) 8.17 (H(b))
NO_2	H(c)	7.48 (H(a)) 8.22 (H(b)) 7.60 (H(c))

[a] Reference tetramethylsilane (δ 0); values in CD_3COCD_3. [b] J_{ab} = 8.6 Hz.

The chemical shifts (δ) are given in Table III. A multiplet centered at δ 6.90 is found for phenylhydrazine and at δ 7.03 for complex I. For the latter, a value of τ 7.07 has been reported,[2] which probably should be δ 7.07.

Complex VIII gave a typical A_2B_2 spectrum[19] with two pairs of equivalent protons H(a) and H(b). The chemical shift for the H(a), in the ortho position with respect to the $-AuCl_3$ moiety, is δ 7.50 and for the H(b) is δ 7.97, with J_{ab} = 8.6 Hz. These results clearly demonstrate that the nitro group is in the para position in complex VIII.

Complexes VI and VII gave single peaks at δ 7.12 and 7.17, respectively, with accidentally equivalent chemical shifts for H(a) and H(b) in each complex. No attempt was made to record the spectra at lower than room temperature, owing to low solubilities of the complexes.

The δ values are expected to follow the order of electron-withdrawing abilities of the substituents in the ring. Bearing in mind the dangers associated with comparing δ values for anions and neutral molecules, the following order of decrease in the electron density at the carbon atom to which the proton is attached has been established: $C_6H_5NHNH_2 > C_6H_5AuCl_3^- > p\text{-}ClC_6H_4AuCl_3^- \sim C_6H_5CH_3 \sim p\text{-}BrC_6H_4AuCl_3^- > C_6H_6 > p\text{-}NO_2C_6H_4AuCl_3^- > p\text{-}NO_2C_6H_4Cl > C_6H_5NO_2$.

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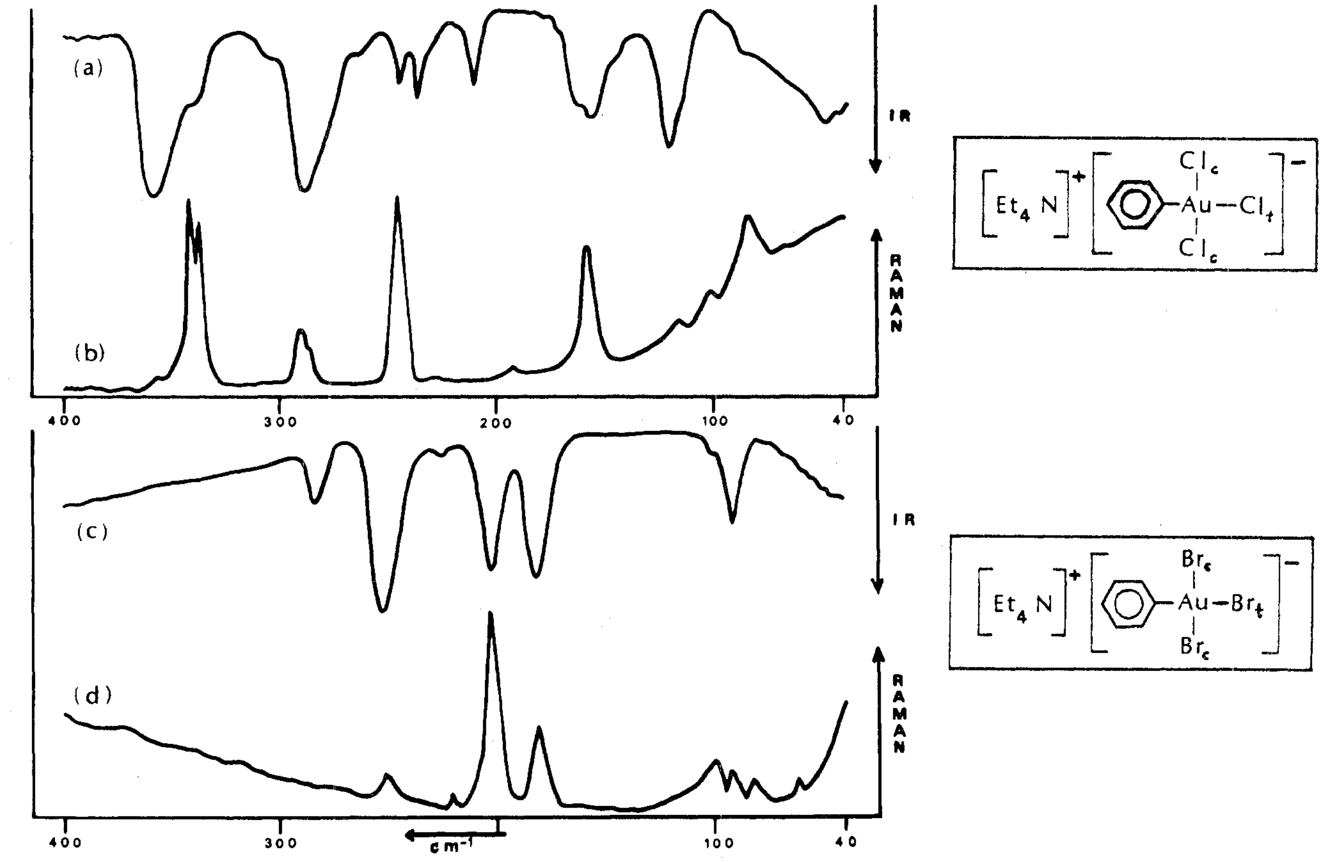

Figure 1. Infrared (a) and Raman (b) spectra of the complex $[(C_2H_5)_4N][C_6H_5AuCl_3]$ and infrared (c) and Raman (d) spectra of the complex $[(C_2H_5)_4N][C_6H_5AuBr_3]$ (region 400–40 cm^{-1}).

This order parallels the decrease in the electron-donating properties of substituents on the phenyl ring. It is interesting to draw attention to the result that, in these complexes, the $-AuCl_3$ group appears to be less electron donating than the $-NHNH_2$ group but more than Cl and H.

Vibrations of the Square-Planar Skeleton. If the phenyl group (R) is regarded as a single dynamic unit, the $RAuX_3^-$ square-planar skeleton would possess nine normal modes of vibration. These belong to the irreducible representations $4\ a_1 + 2\ b_1 + 3\ b_2$ in C_{2v} symmetry, which is the highest possible (by convention, the y axis is taken in the plane of the molecule).[20] The numbering scheme (Table IV) for ν_1-ν_9 (all of which are both infrared and Raman active) is the same as that chosen for the complex ion[21] $Pt(NH_3)Cl_3^-$. The nonequivalent X atoms in $RAuX_3^-$ will be distinguished as follows: X_t refers to the X atom trans to R, whereas X_c refers to the two symmetrically equivalent X atoms cis to R.

Compounds of the type $LAuX_3$ have previously been studied only by infrared spectroscopy,[22-24] but recently the results of an infrared and Raman study of dialkyl sulfide complexes of gold(III) have been reported.[25]

A. Complexes $C^+[C_6H_5AuX_3^-]$ ($C^+ = (C_2H_5)_4N^+$ or $(n\text{-}C_4H_9)_4N^+$; X = Cl, Br, or I). Only very slight modifications (to the relative intensities of some bands) are observed to the vibrational spectra of the $RAuX_3^-$ skeleton when the cation, C^+, is changed. Larger differences obviously occur in the lattice spectral region, as the lattice frequencies depend on the masses of the ions. In general, any vibration involving a halogen atom, X, is shifted to lower frequencies on replacing chlorine by bromine.

Table IV. Description of the Skeletal Fundamentals of the $RAuX_3^-$ Ions

ν_n	Species	Approx description[a]	ν_n	Species	Approx description[a]
ν_1	a_1	$\nu(Au\text{-}R)$	ν_6	b_1	$\pi(X_t\text{-}Au\text{-}R)$
ν_2	a_1	$\nu(Au\text{-}X_c)$	ν_7	b_2	$\nu(Au\text{-}X_c)$
ν_3	a_1	$\nu(Au\text{-}X_t)$	ν_8	b_2	$\delta(X_c\text{-}Au\text{-}R)$
ν_4	a_1	$\delta(X_c\text{-}Au\text{-}X_c)$	ν_9	b_2	$\delta(X_t\text{-}Au\text{-}X_c)$
ν_5	b_1	$\pi(X_c\text{-}Au\text{-}X_c)$			

[a] Key: ν, stretching vibration; π, bond angle deformation (out of plane); δ, bond angle deformation (in plane).

(a) Gold-Chlorine Stretching Vibrations. The infrared spectra of all the $C^+[RAuCl_3^-]$ complexes (Figure 1) show similar features in the 400-280-cm^{-1} range, *viz.*, a very strong band at *ca.* 360 cm^{-1}, a medium band at *ca.* 340 cm^{-1}, and a very strong and composite band at *ca.* 285 cm^{-1} (Table V). One component of the 285-cm^{-1} band has a counterpart in the spectra of $[(C_2H_5)_4N][C_6H_5AuBr_3]$ (medium band) and of $[(n\text{-}C_4H_9)_4N][C_6H_5AuI_3]$ (very strong band).

The ~360-cm^{-1} band is assigned to the $\nu_7(b_2)$ asymmetric stretching vibration of the Cl_cAuCl_c moiety because (a) it appears to correlate with the very intense e_u fundamental of the $AuCl_4^-$ ion and thus is expected to be the strongest band in the infrared spectrum of each chloro complex[23] and (b) its frequency is nearly identical with that of the e_u funda-

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Table V. Infrared and Raman Vibrational Frequencies (400–90 cm^{-1}) in Complexes of the Type $C^+[p\text{-}YC_6H_4AuX_3^-]$

	I		II		III		IV[a]		V[b]		VI		VII		VIII	
Assignment	Ir	R	Ir	R	Ir	R	Ir	R	Ir	R	Ir	R	Ir	R	Ir	R
$\nu_{asym}(Au\text{–}X_c)$, $\nu_7(b_2)$	359 vs	356 w	359 vs	357 w	253 vs	252 w	256 vs		183 s		361 vs	358 w	360 vs	360 w	359 vs	358 vw
$\nu_{sym}(Au\text{–}X_c)$, $\nu_2(a_1)$	341 m 337 sh	341 vs 336 m	336 m	334 vs	204 s	203 vs	206 m	207 vs	153 w		339 m	342 vs 337 s	339 m	340 vs 336 sh	338 m	340 vs 336 s
$\nu(Au\text{–}X_t)$, $\nu_3(a_1)$	289 vs	291 wm	287 vs	284 m	182 s	182 s	180 s	179 s	162 w		278 vs	283 ms	280 vs	282 ms	289 vs	290 ms
$\nu(Au\text{–}R)$, $\nu_1(a_1)$	*c*	*c*	*c*	*c*	284 m				286 vs				*c*	*c*		
											326 m		326 sh			
											305 s	305 w	299 w	301 w	295 sh	297 w
Y sensitive[e]	243 m	246 vs	240 ms	245 vs							197 m?	204 s	176 m	176 m		200 s
	236 m		221 w	212 w	226 vw	222 vw	226 m		224 w		228 w				240 w	
	209 ms	193 w		193 w			201 m		212 mw						230 w	
							154 w				173 w		182 m		177 m	183 wm
							142 w									
δ (in-plane def)[d]	160 sh 155 ms	159 s	148 w	148 s	104 w	98 m	105 w?	103 m 100 m			161 m 153 m	158 s	153 w 140 w	156 vs 150 sh	154 vs	158 s 152 s
π (out-of-plane def)[d]	120 vs	118 w 105 m, sh?	128 s	125 wm	91 m	91 mw	92 w	113 w			121 s	109 s 105 s	120 vs	120 m 103 m	132 m 96 ms	97 s

[a] The spectrum of this compound also contains medium bands at 342 and 335 cm^{-1} assigned to the cation. [b] Assignments uncertain; the spectrum of this compound also contains cation bands at 353 (m) and 325 (m) cm^{-1} and unassigned bands at 129 (w) and 117 (w) cm^{-1}. [c] Masked by ν_3; see text for discussion of this and an alternative assignment. [d] Suggested assignments; see text. [e] Y is the para substituent in the phenyl ring.

mental of the $AuCl_4^-$ ion (356 cm^{-1})[26] consistent with the idea that the vibration of a trans XAuX moiety would give rise to a good group frequency.[10,27]

The ~340-cm^{-1} band is assigned to the $\nu_2(a_1)$ fundamental (symmetric Cl_cAuCl_c stretch); this is very close to the frequency of the $\nu_1(a_{1g})$ fundamental of the $AuCl_4^-$ ion (347 cm^{-1}).[26] One component of the band at *ca.* 285 cm^{-1} arises from the $\nu_3(a_1)$ fundamental vibration of the $AuCl_t$ group; the marked frequency difference between ν_2 and ν_3 illustrates the high trans influence of a phenyl group.[28] Similar assignments have been made for a different series of $LMCl_3^-$ ions (M = Pt or Pd; L = SR_2, PR_3, AsR_3, C_2H_4, or CO) which are isoelectronic with $RAuCl_3^-$ ions. It is noteworthy that $\nu(M\text{–}Cl_t)$ for these ions does not follow the order expected on the basis of the trans effect as distinct from the trans influence.[13,29]

(b) Gold-Bromine Stretching Frequencies. The infrared spectra of the $C^+[C_6H_5AuBr_3^-]$ complexes possess three bands which are not present in the spectra of the analogous chloro complexes, *viz.*, 255, 205, and 180 cm^{-1} (by coincidence, a band also occurs at *ca.* 180 cm^{-1} in the iodo complex) (Figure 1). The most intense infrared-active band (weak in the Raman spectrum) is that at *ca.* 255 cm^{-1} (*cf.* the e_u fundamental of the $AuBr_4^-$ ion which occurs at 252 cm^{-1});[30] this band is logically assigned to the asymmetric Br_cAuBr_c stretching vibration, $\nu_7(b_2)$.

The band at *ca.* 205 cm^{-1}, which is strong in the infrared spectrum and very strong in the Raman spectrum, is attributed to the symmetric Br_cAuBr_c stretching vibration, $\nu_2(a_1)$. It is closely similar to the $\nu_1(a_{1g})$ vibrational frequency (212 cm^{-1})[30] of the $AuBr_4^-$ ion, in accordance with this assignment. The band at *ca.* 180 cm^{-1} is assigned to the $\nu_3(a_1)$ fundamental $\nu(AuBr_t)$. Comparison of the present results on $\nu(AuX_t)$ with those on the dialkyl sulfide complexes[31] $(CH_3)_2SAuX_3$ (X = Cl or Br) indicates that dialkyl sulfide has a lower trans influence than the phenyl group.

(c) Gold-Iodine Stretching Frequencies. The assignment of the gold-iodine stretching frequencies is not as certain as for the other gold-halogen frequencies, partly owing to the fact that no Raman data could be obtained on account of the decomposition of the complex $[(n\text{-}C_4H_9)_4N][C_6H_5AuI_3]$ in the laser beam. Four bands occur in the general region where AuI stretching fundamentals are expected, *viz.*, 212, 183, 162, and 153 cm^{-1}

One possibility is to assign the 212-cm^{-1} bands to the $\nu_7(b_2)$ fundamental (asymmetric I_cAuI_c vibration) and the 162-cm^{-1} band to the corresponding symmetric stretching vibration $\nu_2(a_1)$. The $\nu_3(a_1)$ vibration may then give rise to the weak band at 153 cm^{-1}. The strong band at 183 cm^{-1} (which is too strong and is at too high a frequency to be ν_3) remains unassigned. An alternative and preferable possibility is to assign the 212-cm^{-1} band to a ring mode (*cf.* the 201-cm^{-1} band in IV and 209-cm^{-1} band in I) and the bands at 183, 162, and 153 cm^{-1} to ν_7, ν_3, and ν_2, respectively. For the AuI_4^- ion, the e_u and a_{1g} fundamentals occur at 192 and

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148 cm^{-1}, respectively.[32] The AuX_4^- ion data provide strong support for the second assignment, which also is analogous to that made for the $(CH_3)_3PPtI_3^-$ ion;[33] in this case ν_7, ν_3, and ν_2 occur at 185, 156, and 141 cm^{-1}, respectively.

(d) **Gold-Halogen Deformation Modes.** According to Table IV, three bending modes ($a_1 + 2\ b_2$) correlating with in-plane vibrations of the AuX_4^- ion and two bending modes ($2\ b_1$) correlating with out-of-plane vibrations of the AuX_4^- ion are active in both the infrared and the Raman spectra. Proposed assignments, based on previous related work on the AuX_4^- ions as well as on gold(III) complexes,[25,33] are made in Table V.

(e) **Gold-Phenyl Stretching Modes.** Many assignments have been made for metal-aryl stretching frequencies,[34-40] where the metal atom is Si, Ge, Sn, Pb, As, Sb, or Tl; there are several contradictions in these assignments. The ν(AuC) stretching vibration of the complex $[(C_2H_5)_4N][C_6H_5AuCl_3]$ has been assigned[2,5] to a band occurring in the infrared spectrum at 490 cm^{-1}. However, in the light of previous work this seems far too high, and it is much more probable that the 490-cm^{-1} band arises from the well-known y-mode deformation[41] of the aromatic ring.

In the infrared and/or Raman spectra of most of the complexes a medium band occurs at *ca.* 285 cm^{-1} (most obviously in the infrared spectra of III and V; in some cases it is masked by $\nu_3(a_1)$). This fundamental is not sensitive to change in the halogen atom and has tentatively been assigned (Table V) to the $\nu_1(a_1)$ fundamental, *i.e.*, the AuR stretching frequency (t-mode in Whiffen's nomenclature).[41] An alternative candidate for the AuR stretching fundamental is the band in the spectra of all the complexes at 220-235 cm^{-1} which, like the ~285-cm^{-1} band, is little affected by changing the halogen atom. Such an assignment would be more consistent with that of Green[42] for compounds PhHgX (X = Cl, Br, or I), 216-242 cm^{-1}, and of Smith[34] for the compound $PhSnCl_3$, 253 cm^{-1}. The distinction between these alternatives cannot be made with the data available at present.

B. Complexes $[(C_2H_5)_4N^+][p\text{-}YC_6H_4AuCl_3^-]$ (Y = Cl, Br, or NO_2). The gold-chlorine stretching frequencies of the para-substituted arylaurate(III) ions are similar to those of the $C_6H_5AuCl_3^-$ ion and are not very dependent on the substituent. These and other assignments are included in Table V. One fundamental (possibly a deformation mode of the ring) is very dependent on the substituent, occurring at 246 cm^{-1} for $p\text{-}ClC_6H_4AuCl_3^-$, at 200 cm^{-1} for $p\text{-}NO_2C_6H_4AuCl_3^-$, and at 176 cm^{-1} for $p\text{-}BrC_6H_4AuCl_3^-$.

Conclusion

The new preparative route involving the use of para-substituted phenylhydrazines leads in all cases to the formation of stable complex ions of the sort $YC_6H_4AuCl_3^-$ in which Y remains in the para position.[43] The gold-halogen stretching frequencies lie in the ranges 361-278 (AuCl), 256-180 (AuBr), and 183-153 (?) (AuI) cm^{-1}.

Extensions of this work to the study of the reactions of other metallic halides with substituted phenylhydrazines are in progress.[44] Preliminary results show that phenylhydrazines react with the $PtCl_4^{2-}$ ion to form complexes of the type $[Pt(phenylhydrazine)_2Cl_2]$ with no further migration of the phenyl group to Pt(II) as outlined above for Au(III).

Acknowledgment. P. B. thanks the Royal Society and the CNRS for financial support.

Registry No. I, 51567-46-5; II, 35798-01-7; III, 51567-42-1; IV, 51567-42-2; V, 51567-45-4; VI, 51567-48-7; VII, 51567-50-1; VIII, 51567-52-3; $[Et_4N][AuBr_4]$, 25504-27-2; phenylhydrazinium hydrochloride, 21740-08-5; $[(n\text{-}C_4H_9)_4N]I$, 311-28-4; $[Et_4N][AuCl_4]$, 25478-67-5; *p*-chlorophenylhydrazine hydrochloride, 1073-70-7; *p*-nitrophenylhydrazine, 100-16-3.

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