Notes

Dependence of Metal–Halogen Vibrational Frequency on the Metal Co-ordination Number in some Group 1B Metal Halide Complexes $MX(PPh_3)_n$

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Metal–halogen vibrational frequencies have been assigned in the i.r. and Raman spectra of the compounds $MX(PPh_3)_n$ (n = 2, M = Au, X = Cl, Br or I; n = 3, M = Au, X = Cl; n = 2, M = Cu, X = Cl or Br) in the range 100—300 cm^{-1}. The results show that the frequencies have the expected dependence on metal co-ordination number, and confirm that the compounds $AuX(PPh_3)_2$ (X = Br or I) contain three-co-ordinate gold.

Gold(I) commonly exhibits a co-ordination number of two, but there has been considerable interest in recent years in compounds involving three- and four-co-ordination. The bis(triphenylphosphine)gold(I) halides, $AuX(PPh_3)_2$ (X = Cl, Br, or I), have been prepared by a number of workers.[1-6] Meyer and Allred [4] concluded, on the basis of conductivity and i.r. spectroscopic results, that these are best formulated as ionic compounds $[Au(PPh_3)_2]X$ involving two-co-ordinate gold. However, three-co-ordinate structures for $AuCl(PPh_3)_2\cdot 0.5C_6H_6$,[7] $AuCl(PPh_3)_2$,[8] and $AuI(PPh_3)_2$[9] were confirmed by *X*-ray crystallography, these complexes being essentially trigonal planar. A trigonal-planar geometry, with *S*-bonded thiocyanate, has also been found for $Au(SCN)(PPh_3)_2$.[10] The trigonal co-ordination environment in several $AuX(PPh_3)_2$ compounds has been investigated by Mössbauer [11,12] and *X*-ray photoelectron spectroscopy.[13]

Vibrational spectroscopy should provide a method of distinguishing between the various possible co-ordination environments in these compounds, but very few results have been reported to date, and these have been rather contradictory. Meyer and Allred [4] found no evidence of gold–chlorine stretching vibrations above 200 cm^{-1} in $AuCl(PPh_3)_2$, while McAuliffe *et al.*[6] assigned a band at 321 cm^{-1} to this mode, a value which is only 4 cm^{-1} less than ν(AuCl) in $AuCl(PPh_3)$.[6,14] This is rather surprising, because the Au–Cl bond length in $AuCl(PPh_3)_2$ (250.0 pm) [7] is significantly longer than that in $AuCl(PPh_3)$ (227.9 pm),[15] and metal–ligand vibrational frequencies in general show a marked dependence on the co-ordination number of the metal.[16] A similar situation exists for some pyrazole complexes $AuClL_n$,[17] where ν(AuCl) values for both the n = 1 and n = 2 complexes are reported to lie in the range 330—340 cm^{-1}. The only indication that ν(AuX) has the expected dependence on gold co-ordination number in these types of compound comes from a report that ν(AuI) in $AuI(PPh_3)_2$ lies at 120 cm^{-1},[9] significantly lower than the value 187 cm^{-1} for $AuI(PPh_3)$.[6,14] In order to resolve this apparent anomaly, we have examined the i.r. and Raman spectra of $AuX(PPh_3)_2$ (X = Cl, Br, or I).

Several four-co-ordinate cationic gold(I) complexes $[AuL_4]^+$ involving phosphine ligands L are known,[18] but it has only recently been demonstrated that the co-ordination sphere in gold(I) halide or pseudohalide complexes can be further expanded to give four-co-ordinate complexes $AuX(PPh_3)_3$ (X = Cl or SCN).[19,20] In order further to examine the relationship between ν(AuX) and co-ordination number, we have undertaken a study of tetrahedral gold(I) halide complexes of this type also.

The related copper(I) compounds $CuX(PPh_3)_n$ (n = 2; X = Cl or Br; n = 3, X = Cl, Br, or I) are known.[21-29] The compounds $CuX(PPh_3)_2\cdot 0.5C_6H_6$ (X = Cl or Br) have been examined by *X*-ray diffraction [26] and n.q.r. spectroscopy,[27,28] and have three-co-ordinate, trigonal-planar geometry at the copper atom. No vibrational results have been reported for these compounds, so these were obtained in the present study for comparison with the results for the corresponding gold(I) compounds, and with previously reported results for $MX(PPh_3)_3$ (M = Cu or Ag; X = Cl, Br, or I).[21]

Experimental

Preparation of Compounds.—The compounds $AuCl(PPh_3)_2\cdot 0.5C_6H_6$ (m.p. 195—200 °C), $AuBr(PPh_3)_2$ (m.p. 216—218 °C), and $AuI(PPh_3)_2$ (m.p. 227—230 °C) were prepared by literature methods.[4,7] Their melting points agreed well with those previously reported.[3-5] The compounds $AuCl(PPh_3)_3$ (Found: C, 63.6; H, 4.5. Calc. for $C_{54}H_{45}AuClP_3$: C, 63.9; H, 4.8%), $CuCl(PPh_3)_2\cdot 0.5C_6H_6$ (Found: C, 70.7; H, 5.0. Calc. for $C_{39}H_{33}ClCuP_2$: C, 70.8; H, 5.3%), and $CuBr(PPh_3)_2\cdot 0.5C_6H_6$ (Found: C, 66.3; H, 4.7. Calc. for $C_{39}H_{33}BrCuP_2$: C, 66.0; H, 4.9%) were prepared by literature methods.[19,26-29]

Spectroscopy.—The far-i.r. spectra of these compounds were recorded at *ca.* 298 K and *ca.* 125 K as petroleum jelly mulls between Polythene plates on a Grubb-Parsons MkII cube interferometer interfaced to a CBM PET microcomputer, and were calibrated against the spectrum of water vapour.

The Raman spectra were obtained on a Jasco R300 Raman spectrometer and were excited with a Coherent CR4 argon-ion laser (514.5 or 488.0 nm lines) with powers between 20 and 50 mW. The spectra were run on polycrystalline samples in glass capillary tubes.

Microanalyses were carried out by Professor A. D. Campbell at the University of Otago, Dunedin, New Zealand.

Results and Discussion

Attempts to prepare the compounds $AuX(PPh_3)_3$ (X = Br or I) by a method analogous to that used for the corresponding chloro-compound were unsuccessful, resulting only in the 2 : 1 compounds $AuX(PPh_3)_2$. Attempts to prepare $CuI(PPh_3)_2$ were likewise unsuccessful. The compounds $Cu_2I_2(PPh_3)_2$[24] and $CuI(PPh_3)_3$[21] are known, and attempts to prepare the 2 : 1 compound resulted in compounds with properties

Table. Metal–ligand bands involving the halogen atom in $MX(PPh_3)_n$

Compound	Wavenumber/cm^{-1}			
	i.r. (125 K)	i.r. (298 K)	Raman (298 K)	Assignment
$AuCl(PPh_3)_2 \cdot 0.5C_6H_6$	200vs	218vs	225(sh) 211s	ν(AuCl)
	92m	84m		δ(PAuCl)
	83m	70(sh)	66s	
	76m			
$AuBr(PPh_3)_2$	139s	139ms	140ms	ν(AuBr)
	78mw		91w	δ(PAuBr)
	48mw	45w	66vs	
$AuI(PPh_3)_2$	119s	118ms	120s	ν(AuI)
	76mw		78m	δ(PAuI)
	44mw	43m	51m	
$AuCl(PPh_3)_3$	167vs	163s	160vw	ν(AuCl)
	98ms	94ms	88vw	δ(PAuCl)
	75w	65w	62vs	
$CuCl(PPh_3)_2 \cdot 0.5C_6H_6$	293vs, br	298vs, br	288vw	ν(CuCl)
	123m	122m	122(sh)	δ(PCuCl)
	105vs	102vs		
	82s	77ms	71vs	
	73(sh)	63(sh)		
$CuBr(PPh_3)_2 \cdot 0.5C_6H_6$	228(sh)	227(sh)	228w	ν(CuBr)
	220vs	218s	220w	
	213(sh)	210(sh)		
	83m	83w	70vs	δ(PCuBr)
	67m	67m	57m	
	60vw	55w	46(sh)	

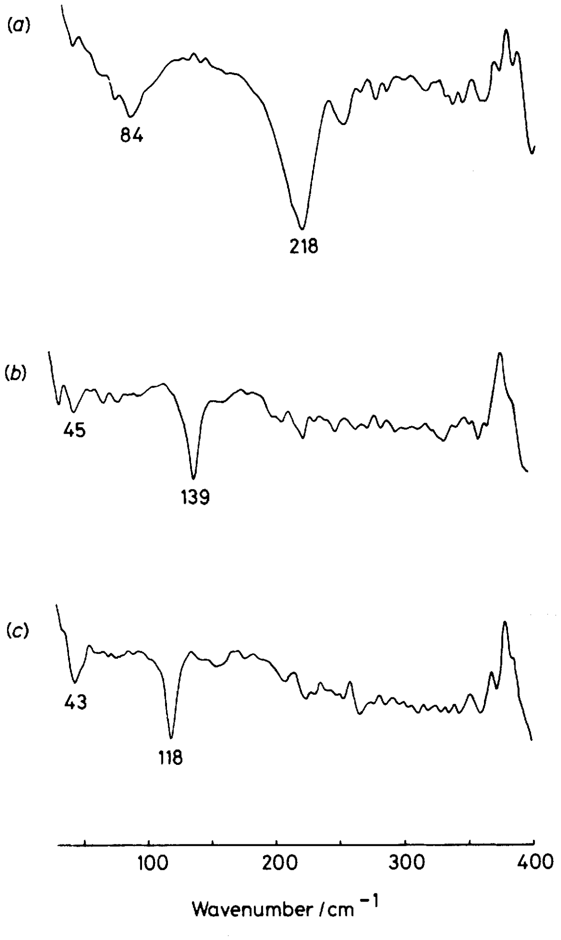

Figure 1. Far-i.r. spectra (at *ca.* 298 K) of (*a*) $AuCl(PPh_3)_2$, (*b*) $AuBr(PPh_3)_2$, and (*c*) $AuI(PPh_3)_2$

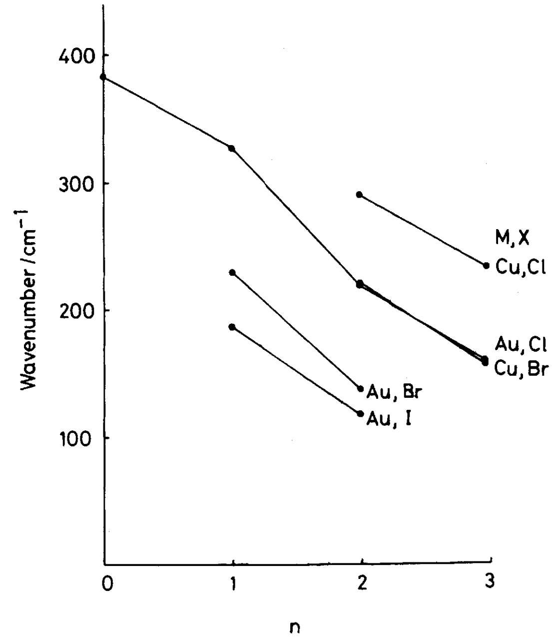

Figure 2. Dependence of ν(MX) on the number of co-ordinated PPh_3 ligands in $MX(PPh_3)_n$. Average ν(MX) values from data in the Table: $AuCl(PPh_3)_2$, 221; $AuBr(PPh_3)_2$, 139; $AuI(PPh_3)_2$, 119; $AuCl(PPh_3)_3$, 163; $CuCl(PPh_3)_2$, 293; and $CuBr(PPh_3)_2$, 221 cm^{-1}. Other data from refs. 6, 14, 21, and 30

different from these, but which did not analyse satisfactorily as $CuI(PPh_3)_2$ or any reasonable solvate.

The metal–ligand vibrational bands and their assignments for the compounds of the present study are given in the Table, and the far-i.r. spectra for the $AuX(PPh_3)_2$ series are shown in Figure 1. For the compounds $AuX(PPh_3)_2$ (Figure 1) the assignment of ν(AuX) is quite unambiguous. Strong halogen-sensitive bands in the range 120—220 cm^{-1} are observed, and no band is observed for $AuCl(PPh_3)_2$ at 321 cm^{-1}, the wavenumber previously assigned [6] as ν(AuCl) for this compound. Substantial decreases (100 cm^{-1} for X = Cl to 60 cm^{-1} for X = I) in ν(AuX) relative to the values for the 1 : 1 complexes $AuX(PPh_3)$ are observed, as expected (see Introduction). The spectra also show weaker halogen-sensitive bands at lower frequencies, which are assigned as δ(PAuX) bending modes (Table).

The far-i.r. spectrum of $AuCl(PPh_3)_3$ shows essentially two strong bands at 163 and 94 cm^{-1}. Although the corresponding bromo- and iodo-complexes are not available in this case, there can be little doubt that these should be assigned as ν(AuCl) and δ(PAuCl) respectively. Perhaps surprisingly, ν(AuCl) decreases by only 55 cm^{-1} in going from the three- to the four-co-ordinate complex, compared with a decrease of 100 cm^{-1} from the two- to the three-co-ordinate case. The dependence of ν(AuCl) in $AuCl(PPh_3)_n$ on n is shown graphically in Figure 2, which includes the $n = 0$ value obtained from the electronic spectrum of AuCl in the vapour phase.[30] Since there is an essentially linear increase in the bond length d(AuCl) with n in $AuCl(PPh_3)_n$ (n = 1—3),[19] Figure 2 effectively shows the variation in ν(AuCl) with d(AuCl) for these compounds.

The metal–halide stretching bands in the i.r. spectra of $CuX(PPh_3)_2 \cdot 0.5C_6H_6$ (X = Cl or Br) are rather broad and, particularly in the case of the bromo-complex, show evidence of some splitting, which is probably due to factor-group effects. Strong bending modes are observed in the lower-frequency region, and these too show considerable splitting. The ν(MX) assignments in this case are supported by the relationship between these and the values for the other $MX(PPh_3)_n$ compounds (Figure 2). In particular, the decrease in frequency from the $n = 2$ to $n = 3$ copper compounds (ca. 60 cm^{-1}) is the same as for the corresponding gold compounds.

Thus, it is clear that these series of compounds show a normal dependence of metal–halogen vibrational frequency on the co-ordination number of the metal.

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