Metal Complexes of Group 1B. Part 1. Triphenylphosphinesilver(I) Carboxylates

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An investigation has been made into the mode of co-ordination of carboxylic acids with Ag^I. From a study of the ^1H n.m.r. and i.r. spectra and solution molecular weights the silver atoms in the complexes are all four-co-ordinate but the stoicheiometry depends on the pK_a of the acid. All the acids studied form complexes of stoicheiometry $[Ag(O_2CR)(PPh_3)_2]$ (R = Me, CH_2Cl, $CHCl_2$, Ph, C_6H_4Me-*o*, C_6H_4Me-*m*, or C_6H_4OH-*o*). In addition, for acids having $pK_a > 3.9$ (*i.e.* R = Me, Ph, C_6H_4Me-*o*, or C_6H_4Me-*m*) chelation of the acid to the silver results in a complex of stoicheiometry $[Ag(O_2CR)(PPh_3)_2]$. The two dibasic acids studied, adipic and malonic, show a similar pK_a dependence.

CARBOXYLIC ACIDS have a formidable history as ligands towards most metals in the Periodic Table.[1] Acetic acid in particular, and carboxylates in general, are versatile ligands and a number of interesting stereochemical arrangements are known. However, although silver carboxylates find extensive use as catalysts in the manufacture of urethane polymer, with the exception of the perfluorobutyrato-complex,[2] little is known of their structure or chemistry. This is in part due to the frequent insoluble and light-sensitive nature of the complexes, making chemical characterisation difficult. We report here the use of triphenylphosphine as a ligand capable of solubilising and making light-stable many silver carboxylates. Two types of monocarboxylatosilver complexes were studied, one containing three triphenylphosphine molecules together with a unidentate carboxylate group, and a second containing two triphenylphosphines and a bidentate carboxylate group. The behaviour of the carboxylate ligand appears to be pK_a-dependent and this is confirmed by studies on silver complexes of dibasic carboxylic acids.

EXPERIMENTAL

Tris Complexes.—Tris(triphenylphosphine)silver carboxylates were prepared by dissolving the silver(I) carboxylate (0.01 mol) in benzene (50 cm^3) containing triphenylphosphine (0.035 mol). Addition of pentane (150 cm^3) gave a white product which was filtered off, washed with pentane, and dried *in vacuo*. The complexes of dibasic carboxylic acids were prepared by an analogous procedure from the disilver(I) carboxylates.

The triphenylphosphinecopper complex of malonic acid was prepared by the method of Hammond *et al.*[3]

Bis Complexes.—Bis(triphenylphosphine)silver carboxylates were prepared by heating the tris complex (0.01 mol) under reflux in chloroform (100 cm^3). The product obtained by removal of the solvent was filtered off, washed with diethyl ether, and dried *in vacuo*.

Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer using caesium iodide plates with Nujol and hexachlorobutadiene mulls. N.m.r. spectra were obtained on a Varian A-60A analytical n.m.r. spectrometer. Analyses were made at the Microanalytical Laboratory, Manchester, and are shown in Table 1.

DISCUSSION

(*a*) *Monobasic Carboxylic Acids.*—(*i*) *Solution data.* The osmometric molecular-weight and ^1H n.m.r. data for the complexes of the monobasic acids studied in the present work are given in Table 2. Confirmation of the analytical data for the $[Ag(O_2CR)(PPh_3)_3]$ series of complexes was obtained from intensity measurements of the ^1H n.m.r. data. All these complexes dissociate in chloroform, with their apparent molecular weight corresponding to half their formula weight. Failure to detect carboxylate ions in solution, when combined with the n.m.r. data, strongly suggests that this dissociation is due to loss of triphenylphosphine. Confirmation of this for some, but not all, of the carboxylic acids studied was obtained from the isolation, from refluxing chloroform solution, of new complexes containing only two triphenylphosphine ligands. These new complexes $[Ag(O_2CR)(PPh_3)_2]$ (Table 2) show no dissociation in chloroform solution, the observed molecular weight corresponding to the formula weight. Thus, in chloroform solution, reaction (1) takes place for acids where R = Me, Ph, C_6H_4Me-*o*, or C_6H_4Me-*m*.

TABLE 1

Analytical data (%)

	Calc.		Found	
Complex	C	H	C	H
$[Ag(O_2CMe)(PPh_3)_3]$	70.5	5.0	69.1	4.9
$[Ag(O_2CCH_2Cl)(PPh_3)_3]$	68.8	4.8	68.1	4.8
$[Ag(O_2CCHCl_2)(PPh_3)_3]$	65.6	4.5	65.7	4.7
$[Ag(O_2CCCl_3)(PPh_3)_3]$	63.6	4.3	63.1	4.1
$[Ag(O_2CPh)(PPh_3)_3]$	70.9	4.9	71.6	4.9
$[Ag_2(O_2CMe)(PPh_3)_2]$	66.0	4.8	66.0	4.8
$[Ag(O_2CPh)(PPh_3)_2]$	68.5	4.6	67.8	4.7
$[Ag(O_2CC_6H_4Me\text{-}m)(PPh_3)_3]$	72.3	5.1	72.5	5.1
$[Ag(O_2CC_6H_4Me\text{-}o)(PPh_3)_3]$	72.3	5.1	72.8	4.9
$[Ag(O_2CC_6H_4OH\text{-}o)(PPh_3)_3]$	72.2	4.8	72.0	4.8
$[Ag(O_2CC_6H_4Me\text{-}m)(PPh_3)_2]$	68.8	4.8	68.7	5.1
$[Ag(O_2CC_6H_4Me\text{-}o)(PPh_3)_2]$	68.8	4.8	68.6	4.8
$[(Ph_3P)_2Ag\{O_2C(CH_2)_4CO_2\}Ag(PPh_3)_2]$	66.8	4.7	67.0	4.6
$[(Ph_3P)_3Ag(O_2CCH_2CO_2)Ag(PPh_3)_2]$	68.6	4.7	67.1	4.6

$$[Ag(O_2CR)(PPh_3)_3] \longrightarrow [Ag(O_2CR)(PPh_3)_2] + PPh_3 \quad (1)$$

(*ii*) *I.r. data.* The effect of different modes of co-ordination on the i.r. spectrum of the acetate group has

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[1] C. Oldham, *Progr. Inorg. Chem.*, 1968, **10**, 223.

[2] A. E. Blakelese and J. L. Hoard, *J. Amer. Chem. Soc.*, 1956, **78**, 3029.

[3] B. Hammond, F. H. Jardine, and A. G. Vohra, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1017.

been reviewed.[4] The most useful diagnostic frequencies are those corresponding approximately to the C=O and C–O groups (ν_8 and ν_3 using the assignments of Itoh and Bernstein[5] and Nakamura[6]). Table 3 lists these two frequencies for both the 3 : 1 and 2 : 1 complexes. From the Table it can be seen that the separation between ν_8 and ν_3 ($\Delta\nu$) is always greater for the tris(triphenylphosphine) compared to the analogous bis(triphenylphosphine) series. When compared to $\Delta\nu$ for the corresponding anhydrous sodium carboxylates Grigor'ev[7] concluded that for bidentate carboxylate co-ordination $\Delta\nu$(complex) $\approx$ $\Delta\nu$(sodium salt) but for unidentate carboxylate complexes $\Delta\nu$(complex) $\gg$ $\Delta\nu$(sodium salt). Thus for all the silver(I) complexes studied the metal atom maintains a co-ordination number of four. It is noteworthy that the $[Ag(O_2CR)(PPh_3)_2]$ complexes represent one of the few where chelation to silver occurs with two oxygen donor atoms.

TABLE 2

Molecular-weight and ^{1}H n.m.r. data for silver carboxylates

Complex	^{1}H N.m.r.[a] Shift[b]	Intensity	Assignment	M[c]
$[Ag(O_2CMe)(PPh_3)_3]$	1.95	3	CH_3	461 (953)
	7.30	47	$(C_6H_5)_9$	
$[Ag(O_2CCH_2Cl)(PPh_3)_3]$	3.95	2	CH_2Cl	488 (987)
	7.30	49	$(C_6H_5)_9$	
$[Ag(O_2CCHCl_2)(PPh_3)_3]$	5.90	1	$CHCl_2$	501 (1 022)
	7.30	43	$(C_6H_5)_9$	
$[Ag(O_2CCCl_3)(PPh_3)_3]$				523 (1 056)
$[Ag(O_2CPh)(PPh_3)_3]$				509 (1 015)
$[Ag(O_2CC_6H_4Me\text{-}m)(PPh_3)_3]$	2.30	3	CH_3	530 (1 029)
	7.30	50	C_6H_4 and $(C_6H_5)_9$	
$[Ag(O_2CC_6H_4OH\text{-}o)(PPh_3)_3]$				528 (1 031)
$[Ag(O_2CC_6H_4Me\text{-}o)(PPh_3)_3]$	2.60	3	CH_3	511 (1 029)
	7.30	51	C_6H_4 and $(C_6H_5)_9$	
$[Ag(O_2CMe)(PPh_3)_2]$	1.90	3	CH_3	688 (691)
	7.30	31	$(C_6H_5)_6$	
$[Ag(O_2CPh)(PPh_3)_2]$				767 (753)
$[Ag(O_2CC_6H_4Me\text{-}m)(PPh_3)_2]$	2.30	3	CH_3	760 (767)
	7.30	37	C_6H_4 and $(C_6H_5)_6$	
$[Ag(O_2CC_6H_4Me\text{-}o)(PPh_3)_2]$	2.60	3	CH_3	775 (767)
	7.30	38	C_6H_4 and $(C_6H_5)_6$	

[a] In $CDCl_3$ solution. [b] In p.p.m. from $SiMe_4$. [c] In $CHCl_3$ solution. Values in parentheses were calculated for the monomeric formulae.

TABLE 3

Infrared COO^- stretching data (cm^{-1}) for silver carboxylates

Complex	ν_8	ν_3	$\Delta\nu = \nu_8 - \nu_3$	$\Delta\nu$ (sodium salt)	Mode of co-ordination *	pK_a of parent acid
$[Ag(O_2CMe)(PPh_3)_3]$	1 570	1 380	190	164	uni	4.76
$[Ag(O_2CMe)(PPh_3)_2]$	1 530	1 390	140	164	bi	4.76
$[Ag(O_2CPh)(PPh_3)_3]$	1 525	1 360	165	140	uni	4.18
$[Ag(O_2CPh)(PPh_3)_2]$	1 530	1 400	130	140	bi	4.18
$[Ag(O_2CC_6H_4Me\text{-}m)(PPh_3)_3]$	1 530	1 360	170	150	uni	4.27
$[Ag(O_2CC_6H_4Me\text{-}m)(PPh_3)_2]$	1 480	1 360	120	150	bi	4.27
$[Ag(O_2CC_6H_4Me\text{-}o)(PPh_3)_3]$	1 550	1 360	190	145	uni	3.91
$[Ag(O_2CC_6H_4Me\text{-}o)(PPh_3)_2]$	1 510	1 355	155	145	bi	3.91
$[Ag(O_2CCH_2Cl)(PPh_3)_3]$	1 600	1 340	260	185	uni	2.87
$[Ag(O_2CCHCl_2)(PPh_3)_3]$	1 625	1 320	305	235	uni	1.48
$[Ag(O_2CCCl_3)(PPh_3)_3]$	1 660	1 295	365	295	uni	0.70
$[Ag(O_2CC_6H_4OH\text{-}o)(PPh_3)_3]$	1 590	1 405	185	160	uni	3.00

* Uni- or bi-dentate.

However, not all the carboxylate complexes show this *OO'* chelating behaviour, only those having pK_a > 3.90 (Table 3). A similar observation was made by Hammond[3] for a series of copper(I) carboxylates where the critical pK_a value was 3.50. In order to further investigate this chelating tendency of Ag^I to potential *OO'* ligands we examined two complexes of dibasic carboxylic acids with pK_a values which span the critical value: adipic (pK_a 4.43 and 4.41) and malonic acid (pK_a 5.69 and 2.83).

(*b*) *Dibasic Acids.*—(*i*) *Adipic acid.* For convenience, ethanol was used as the medium in which to prepare the silver complexes. This resulted in a complex

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[4] N. W. Alcock, V. M. Tracy, and T. C. Waddington, *J.C.S. Dalton*, 1976, 2243.

[5] K. Itoh and H. J. Bernstein, *Canad. J. Chem.*, 1956, **34**, 170.

[6] K. Nakamura, *J. Chem. Soc. Japan*, 1958, **79**, 1411, 1420.

[7] A. I. Grigor'ev, *Russ. J. Inorg. Chem.*, 1963, **8**, 409.

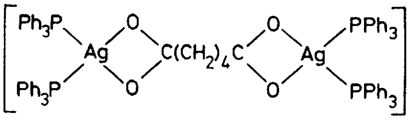
TABLE 4

Spectral data for complexes of dibasic acids

Complex	Data	Conclusion or assignment
$[(Ph_3P)_2Ag\{O_2C(CH_2)_4CO_2\}Ag(PPh_3)_2]$	ν_8 at 1 555, ν_3 at 1 370 cm^{-1}; $\Delta\nu$ 185 cm^{-1}	$\Delta\nu$ (sodium salt) 195 cm^{-1}; two bidentate carboxylate groups
$[(Ph_3P)_2Ag(O_2CCH_2CO_2)Ag(PPh_3)_3]$	ν_8 at 1 580 and 1 720, ν_3 at 1 335 and 1 310 cm^{-1}; $\Delta\nu$ 405 and 245 cm^{-1}	$\Delta\nu$ (sodium salt) 280 cm^{-1}; both bi- and uni-dentate carboxylate groups
	^{1}H N.m.r.:[a] Shift[b] 3.0, Intensity 2	CH_2
	Shift 7.3, Intensity 70	5 Ph_3
$[(Ph_3P)_2Cu(O_2CCH_2CO_2)Cu(PPh_3)_3]$	ν_8 at 1 585 and 1 705, ν_3 at *ca.* 1 350br cm^{-1}; $\Delta\nu$ 355 and 235 cm^{-1}	Both bi- and uni-dentate carboxylate groups
	^{1}H N.m.r.: Shift,[b] Intensity 2	CH_2
	Shift 7.3, Intensity 65	5 Ph_3
	M:[c] Found 741	
	Formula weight 1 539	PPh_3 dissociation

[a] In $CDCl_3$ solution. [b] In p.p.m. from $SiMe_4$. [c] In $CHCl_3$ solution.

containing two molecules of ethanol of crystallisation which were removed in a drying pistol at 80 °C. Infrared measurements of ν_8 and ν_3 before and after heating showed no changes. Unfortunately, the ethanol-free product was insoluble in most common organic solvents but i.r. data (Table 4) showed $\Delta\nu$ to be similar to that for disodium adipate and hence, as predicted by the pK_a correlation for the monobasic acids, the complex formed contains bidentate carboxylate as in (1).



(1)

(*ii*) *Malonic acid.* The silver complex, prepared in an analogous way to the complexes of the monobasic acids, had an analysis which suggested two silver atoms per dibasic acid. Infrared spectra in the COO stretching region are complex showing four strong absorptions which are consistent with both uni- and bi-dentate co-ordination of the malonate ligand (Table 4). Hydrogen-1 n.m.r. intensity data in chloroform solution favour a stoicheiometry of $[(Ph_3P)_3Ag(acid)Ag(PPh_3)_2]$ (calc. intensity for triphenylphosphine: methylene protons, 75 : 2) rather than $[(Ph_3P)_3Ag(acid)Ag(PPh_3)_3]$ (90 : 2) or $[(Ph_3P)_2Ag(acid)Ag(PPh_3)_2]$ (60 : 2).

Most significant for this complex is the molecular-weight data which in chloroform give an apparent molecular weight of 805. This corresponds to a species $[(Ph_3P)_3Ag(O_2CCH_2CO_2)Ag(PPh_3)_2]$ with a formula weight of 1 628, but like all other $(PPh_3)_3$ species this would be expected to dissociate in solution to give an apparent molecular weight of 814. The complexes $[(Ph_3P)_3Ag(O_2CCH_2CO_2)Ag(PPh_3)_3]$ and $[(Ph_3P)_2Ag(O_2CCH_2CO_2)Ag(PPh_3)_2]$ would be anticipated to have apparent molecular weights of 630 and 1 366 respectively. An analogous, and soluble, copper(I) malonate complex can be prepared. The i.r. and ^{1}H n.m.r. spectra and molecular-weight data, from chloroform solutions (Table 4), show this to be of the same form as the corresponding silver(I) complex, *i.e.* $[(Ph_3P)_3Cu(O_2CCH_2CO_2)Cu(PPh_3)_2]$. Thus a dibasic acid which has pK_a values both above and below the critical value appears to give copper and silver complexes containing both uni- and bi-dentate oxygen co-ordination of the same ligand. The extent of this pK_a dependency for dibasic acids will be the subject of a future publication.

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