

PENTAHALOPHENYLARGENTATE(I) COMPLEXES

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Summary

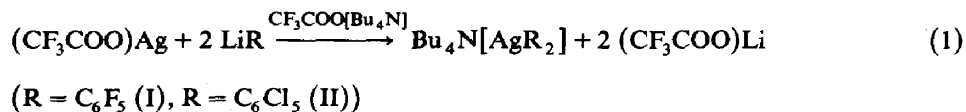
The reaction of $(\text{CF}_3\text{COO})\text{Ag}$ with LiR gives $[\text{Bu}_4\text{N}][\text{AgR}_2]$ ($\text{R} = \text{C}_6\text{F}_5$ or C_6Cl_5). The latter react with acids HX to give organoargentate(I) derivatives of the types $[\text{Bu}_4\text{N}][\text{AgRX}]$ ($\text{X} = \text{CH}_3\text{COO}$, CF_3COO or 8-oxyquinolate) or $[\text{Bu}_4\text{N}]_2[\text{Ag}(\text{C}_6\text{F}_5)_2\text{BiBzIm}]$ ($\text{BiBzIm} = \text{bibenzimidazolate}$), whilst the reaction with silver salts AgX yields $[\text{Bu}_4\text{N}][\text{Ag}(\text{C}_6\text{F}_5)_2\text{X}]$ ($\text{X} = \text{NO}_3$ or CF_3COO) or AgR ($\text{X} = \text{ClO}_4$).

Introduction

Complexes of the type $[\text{Ag}(\text{C}\equiv\text{CR})_2]^-$ [1,2] and the moisture-sensitive $\text{LiAg}(\text{C}_6\text{F}_5)_2$ [3] were the only previously known organosilver derivatives. Recently we reported the preparation of organoaurate-(I) and -(III) complexes, isolated as salts of bulky cations [4,5]. In the present paper this study is extended to anionic organosilver complexes of the types $\text{Bu}_4\text{N}[\text{AgR}_2]$ ($\text{R} = \text{C}_6\text{F}_5$, C_6Cl_5), $\text{Bu}_4\text{N}[\text{AgRX}]$ ($\text{X} = \text{CH}_3\text{COO}$, CF_3COO , 8-oxyquinolate), $\text{Bu}_4\text{N}[\text{Ag}(\text{C}_6\text{F}_5)_2\text{X}]$ ($\text{X} = \text{NO}_3$, CF_3COO) or $[\text{Bu}_4\text{N}]_2[\text{Ag}(\text{C}_6\text{F}_5)_2\text{BiBzIm}]$ ($\text{BiBzIm} = \text{bibenzimidazolate}$).

Results and discussion

$(\text{CF}_3\text{COO})\text{Ag}$ reacts with an excess of LiR [6,7] to give solutions which after addition of $\text{CF}_3\text{COO}[\text{Bu}_4\text{N}]$ yield $\text{Bu}_4\text{N}[\text{AgR}_2]$, as depicted in eq. 1.



The resulting white solids are air- and moisture-stable at room temperature. In acetone they behave as 1/1 electrolytes (Table 1). Since the anion probably has a linear structure, similar to that reported for $[\text{Au}(\text{C}_6\text{F}_5)_2]^-$ [8], complex I shows only a single band due to C_6F_5 [5] in the 800 cm^{-1} region (at 760 cm^{-1}).

The complexes I and II react with acetic acid or trifluoroacetic acid with cleavage of the $\text{Ag}-\text{R}$ bond, as in eq. 2.

TABLE I
ANALYTICAL DATA FOR COMPLEXES I-XI (Oq = 8-oxyquinolate; BiBzIm = bibenzimidazole)

Complex	Yield (%)	M.p. (°C)	Analysis (Found(calcd.)(%))			$\Delta \epsilon^a$ (ohm ⁻¹ cm ² mol ⁻¹)
			C	H	N	
(I) Bu ₄ N[Ag(C ₆ F ₅) ₂]	62	91	49.86 (49.14)	5.17 (5.30)	2.06 (2.05)	112
(II) Bu ₄ N[Ag(C ₆ Cl ₅) ₂]	62	75(dec.)	39.57 (39.61)	4.15 (4.27)	1.96 (1.65)	99
(III) Bu ₄ N[Ag(C ₆ F ₅)(CH ₃ COO)]	50	74	49.51 (50.01)	7.28 (6.82)	2.62 (2.43)	118
(IV) Bu ₄ N[Ag(C ₆ Cl ₅)(CH ₃ COO)]	86	100(dec.)	43.42 (43.76)	5.74 (5.97)	2.14 (2.13)	115
(V) Bu ₄ N[Ag(C ₆ Cl ₅)(CF ₃ COO)]	87	73(dec.)	40.21 (40.45)	5.20 (5.09)	1.88 (1.97)	118
(VI) Bu ₄ N[Ag(C ₆ F ₅)(Oq)]	57	70(dec.)	55.53 (56.28)	6.72 (6.40)	4.61 (4.23)	105
(VII) Bu ₄ N[Ag(C ₆ Cl ₅)(Oq)]	87	68(dec.)	50.32 (50.06)	5.78 (5.69)	3.95 (3.76)	108
(VIII) (Bu ₄ N) ₂ [(Ag(C ₆ F ₅) ₂)(BiBzIm)]	54	130(dec.)	54.51 (54.98)	6.39 (6.36)	6.82 (6.63)	164
(IX) Bu ₄ N[Ag(C ₆ F ₅) ₂ (CF ₃ COO)]	83	92	39.23 (39.80)	4.00 (4.01)	1.48 (1.55)	116
(X) Bu ₄ N[Ag(C ₆ F ₅) ₂ (NO ₂)]	60	104(dec.)	39.69 (39.37)	4.30 (4.25)	3.44 (3.28)	113
(XI) Ag(C ₆ Cl ₅)	67	102(dec.)	20.25 (20.18)	—	—	—

^a In acetone.



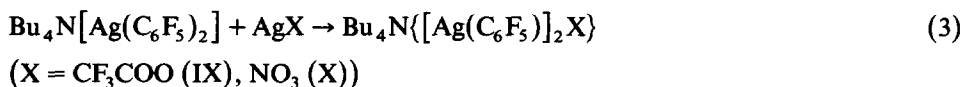
($\text{R} = \text{C}_6\text{F}_5$, $\text{X} = \text{CH}_3\text{COO}$ (III); $\text{R} = \text{C}_6\text{Cl}_5$, $\text{X} = \text{CH}_3\text{COO}$ (IV), CF_3COO (V))

Complexes III and IV are white air- and moisture-stable solids, which behave as 1/1 electrolytes in acetone. The IR spectrum of the acetato complex IV, in the solid state and in dichloromethane solution, shows two bands due to the $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ vibrations at 1580(s) and 1340(s) cm^{-1} , respectively, ($\Delta\nu = 240 \text{ cm}^{-1}$). This indicates that the acetato group is acting as a monodentate [9].

For complex III the vibration $\nu_{\text{asym}}(\text{COO})$ appears at 1575(s) cm^{-1} , but $\nu_{\text{sym}}(\text{COO})$ cannot be assigned because of overlapping with an absorption arising from C_6F_5 . In V the presence of the trifluoroacetate group is confirmed [10] by the appearance of $\nu(\text{C}-\text{F})$ bands at 1135(s), 1160(s) and 1205(s) cm^{-1} , and $\nu_{\text{sym}}(\text{COO})$ and $\nu_{\text{asym}}(\text{COO})$ bands at 1430(s) and 1675(s) cm^{-1} .

If the reaction represented in eq. 2 is carried out with $\text{HX} = 8\text{-hydroxyquinoline}$ (HOq) or 2,2'-bibenzimidazole (H_2BiBzIm), yellow mononuclear complexes of the formula $\text{Bu}_4\text{N}[\text{AgR}(\text{Oq})]$ ($\text{R} = \text{C}_6\text{F}_5$ (VI) or C_6Cl_5 (VII)) or, the green binuclear complex $[\text{Bu}_4\text{N}]_2\{[\text{Ag}(\text{C}_6\text{F}_5)_2](\mu\text{-BiBzIm})\}$ (VIII) are obtained. Complexes VI and VII are 1/1 electrolytes in acetone, and complex VIII a 1/2 electrolyte. The coordination of the 8-oxyquinolate [11,12] group in complexes VI and VII can be inferred from the $\nu(\text{CO})$ and $\nu(\text{CN})$ bands, which are located at 1330(s) and 1105(m) cm^{-1} , respectively, in both cases. The presence of the bibenzimidazolate group is revealed [13] by bands at 1350(m) (ring stretching), 1295(m), 1285(m) (in plane C-H bending) and 740(m) (out of plane C-H bending) cm^{-1} .

A new type of organoargentate(I) complex is obtained by treating I with equimolecular amounts of $(\text{CF}_3\text{COO})\text{Ag}$ or AgNO_3 , as may be seen from eq. 3



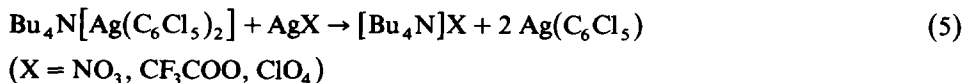
The complexes behave as 1/1 electrolytes in acetone. They are stable at room temperature. Complex IX exhibits bands at 1665(vs) ($\nu_{\text{asym}}(\text{COO})$) and 1200(s) 1170(s) and 1125(s) ($\nu(\text{C}-\text{F})$) cm^{-1} . The $\nu_{\text{sym}}(\text{COO})$ and $\nu(\text{NO}_3)$ vibrations (complex X) are masked by bands from C_6F_5 .

With AgClO_4 the reaction takes a different course, and $[\text{Bu}_4\text{N}]\text{ClO}_4$ separates (eq. 4), and AgC_6F_5 can be isolated from the solution.

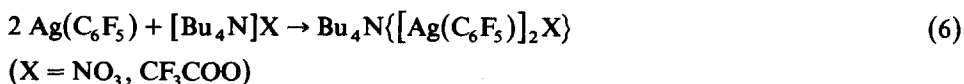


The properties of the latter were identical to those previously described [14].

The reaction of complex II with silver salts gives similar results (eq. 5).



The white $\text{Ag}(\text{C}_6\text{Cl}_5)$ is insoluble in organic solvents. At room temperature it is more stable than $\text{Ag}(\text{C}_6\text{F}_5)$. Complexes IX and X can also be prepared starting from $\text{Ag}(\text{C}_6\text{F}_5)$, as in eq. 6.



When the silver salts of the anion of the ammonium salt are not soluble ($X = \text{Cl}$, Br or SCN) the reaction takes a different course (eq. 7).



Neither of the processes 6 or 7 takes place with AgC_6Cl_5 .

Experimental

IR spectra were recorded (over the range $4000\text{--}200 \text{ cm}^{-1}$) on a Perkin–Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in $5 \times 10^{-4} \text{ M}$ acetone solutions with a Philips PW 9501/01 conductimeter. C, N and H analyses were carried out with a Perkin–Elmer 240 microanalyzer.

The yields, melting points, C, H and N analyses, and conductivities of the novel complexes are listed in Table 1.

Preparation of the complexes

$\text{Bu}_4\text{N}[\text{AgR}_2]$ ($R = \text{C}_6\text{F}_5$ (I), C_6Cl_5 (II)). To an ether solution of LiR (30 mmol) ($R = \text{C}_6\text{F}_5$ [6] at -78°C or C_6Cl_5 [7], at -20°C) was added $(\text{CF}_3\text{COO})\text{Ag}$ (2.20 g, 10 mmol) and the mixture stirred for 15 min. $[\text{Bu}_4\text{N}]\text{O}_2\text{CCF}_3$ (3.22 g, 10 mmol) was added and the mixture was stirred for 1 h at -20°C , then allowed to warm to room temperature (2 h). The precipitate was filtered off, washed with water ($2 \times 5 \text{ ml}$), and the solid was extracted with 30 ml of dichloromethane. The solution was filtered and concentrated to ca. 5 ml, and ether was added to give crystals of the white complex I or II.

$\text{Bu}_4\text{N}[\text{AgRX}]$ ($R = \text{C}_6\text{F}_5$, $X = \text{CH}_3\text{COO}$ (III) or Oq (VI); $R = \text{C}_6\text{Cl}_5$, $X = \text{CH}_3\text{COO}$ (IV), CF_3COO (V) or Oq (VII)). The appropriate acid HX (0.20 mmol) was added to a suspension of complex I or II (0.20 mmol) in 20 ml of diethyl ether and the mixture was stirred for 45 min at room temperature. Concentration to ca. 5 ml and stirring for 5 h at -20°C gave a precipitate of the white (III–V) or yellow (VI–VII) complex, which was filtered off.

$[\text{Bu}_4\text{N}]_2\{[\text{Ag}(\text{C}_6\text{F}_5)]_2\text{BiBzIm}\}$ (VIII). A suspension of complex I (0.150 g, 0.22 mmol) and 2,2'-bibenzimidazol (0.026 g, 0.11 mmol) in 20 ml of diethyl ether was stirred for 1 h at room temperature. The green VIII was separated by filtration.

$[\text{Bu}_4\text{N}]\{[\text{Ag}(\text{C}_6\text{F}_5)]_2\text{X}\}$ ($X = \text{CF}_3\text{COO}$ (IX) or NO_3 (X)). (a) The appropriate AgX (0.29 mmol) was added to a solution of complex I (0.20 g, 0.29 mmol) in 20 ml of acetone and the mixture was stirred for 3 h at room temperature. Evaporation to dryness gave IX or X, which was recrystallized from dichloromethane/diethyl ether.

(b) The salt $[\text{Bu}_4\text{N}]\text{X}$ (0.5 mmol) was added to a solution of AgC_6F_5 (0.275 g, 1 mmol) in 25 ml of diethyl ether and the mixture was stirred for 1 h at room temperature. Evaporation to ca. 5 ml and filtration gave the white IX (46% yield) or X (45% yield).

$\text{Ag}(\text{C}_6\text{F}_5)$. A mixture of complex I (0.342 g, 0.5 mmol) and AgClO_4 (0.104 g, 0.5 mmol) in 20 ml of diethyl ether was stirred for 45 min under nitrogen at room temperature. The white $[\text{Bu}_4\text{N}]\text{ClO}_4$ was filtered off and the filtrate was evaporated to dryness. The resulting white solid, AgC_6F_5 , was washed with hexane and stored under nitrogen (85% yield).

$\text{Ag}(\text{C}_6\text{Cl}_5)$ (XI). A mixture of CF_3COOAg (0.20 g, 0.90 mmol) and a solution of

complex II (0.80 g, 0.9 mmol) in 20 ml of dichloromethane was stirred for 1 h at room temperature. Complex XI separated as a white insoluble solid.

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