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PENTAHALOPHENYLARGENTATE(I) COMPLEXES

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Summary

The reaction of $(CF_3COO)Ag$ with LiR gives $[Bu_4N][AgR_2]$ ($R = C_6F_5$ or C_6Cl_5). The latter react with acids HX to give organoargentate(I) derivatives of the types $[Bu_4N][AgRX]$ ($X = CH_3COO$, CF_3COO or 8-oxyquinolate) or $[Bu_4N]_2\{[Ag(C_6F_5)]_2BiBzIm\}$ (BiBzIm = bibenzimidazolate), whilst the reaction with silver salts AgX yields $[Bu_4N]\{[Ag(C_6F_5)]_2X\}$ ($X = NO_3$ or CF_3COO) or AgR ($X = ClO_4$).

Introduction

Complexes of the type $[Ag(C{\equiv}CR)_2]^-$ [1,2] and the moisture-sensitive $LiAg(C_6F_5)_2$ [3] were the only previously known anionic 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 $Bu_4N[AgR_2]$ ($R = C_6F_5$, C_6Cl_5), $Bu_4N[AgRX]$ ($X = CH_3COO$, CF_3COO, 8-oxyquinolate), $Bu_4N\{[Ag(C_6F_5)]_2X\}$ ($X = NO_3$, CF_3COO) or $[Bu_4N]_2\{[Ag(C_6F_5)]_2BiBzIm\}$ (BiBzIm = bibenzimidazolate).

Results and discussion

$(CF_3COO)Ag$ reacts with an excess of LiR [6,7] to give solutions which after addition of $CF_3COO[Bu_4N]$ yield $Bu_4N[AgR_2]$, as depicted in eq. 1.

$$(CF_3COO)Ag + 2\,LiR \xrightarrow{CF_3COO[Bu_4N]} Bu_4N[AgR_2] + 2\,(CF_3COO)Li \qquad (1)$$

$$(R = C_6F_5\ (I),\ R = C_6Cl_5\ (II))$$

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 $[Au(C_6F_5)_2]^-$ [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 Ag–R bond, as in eq. 2.

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TABLE 1

ANALYTICAL DATA FOR COMPLEXES I–XI (Oq = 8-oxyquinolate; BiBzIm = bibenzimidazolate)

Complex	Yield (%)	M.p. (°C)	Analysis (Found(calcd.)(%))			Λ_M [a] (ohm^{-1} cm^2 mol^{-1})
			C	H	N	
(I) $Bu_4N[Ag(C_6F_5)_2]$	62	91	49.86 (49.14)	5.17 (5.30)	2.06 (2.05)	112
(II) $Bu_4N[Ag(C_6Cl_5)_2]$	62	75(dec.)	39.57 (39.61)	4.15 (4.27)	1.96 (1.65)	99
(III) $Bu_4N[Ag(C_6F_5)(CH_3COO)]$	50	74	49.51 (50.01)	7.28 (6.82)	2.62 (2.43)	118
(IV) $Bu_4N[Ag(C_6Cl_5)(CH_3COO)]$	86	100(dec.)	43.42 (43.76)	5.74 (5.97)	2.14 (2.13)	115
(V) $Bu_4N[Ag(C_6Cl_5)(CF_3COO)]$	87	73(dec.)	40.21 (40.45)	5.20 (5.09)	1.88 (1.97)	118
(VI) $Bu_4N[Ag(C_6F_5)(Oq)]$	57	70(dec.)	55.53 (56.28)	6.72 (6.40)	4.61 (4.23)	105
(VII) $Bu_4N[Ag(C_6Cl_5)(Oq)]$	87	68(dec.)	50.32 (50.06)	5.78 (5.69)	3.95 (3.76)	108
(VIII) $(Bu_4N)_2\{[Ag(C_6F_5)]_2(BiBzIm)\}$	54	130(dec.)	54.51 (54.98)	6.39 (6.36)	6.82 (6.63)	164
(IX) $Bu_4N\{[Ag(C_6F_5)]_2(CF_3COO)\}$	83	92	39.23 (39.80)	4.00 (4.01)	1.48 (1.55)	116
(X) $Bu_4N\{[Ag(C_6F_5)]_2(NO_3)\}$	60	104(dec.)	39.69 (39.37)	4.30 (4.25)	3.44 (3.28)	113
(XI) $Ag(C_6Cl_5)$	67	102(dec.)	20.25 (20.18)	–	–	–

[a] In acetone.

$$Bu_4N[AgR_2] + XH \rightarrow Bu_4N[AgRX] + RH \quad (2)$$

$(R = C_6F_5, X = CH_3COO \text{ (III)}; R = C_6Cl_5, X = CH_3COO \text{ (IV)}, CF_3COO \text{ (V)})$

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 ν_{asym}(COO) and ν_{sym}(COO) vibrations at 1580(s) and 1340(s) cm^{-1}, respectively, ($\Delta\nu = 240$ cm^{-1}). This indicates that the acetato group is acting as a monodentate [9].

For complex III the vibration ν_{asym}(COO) appears at 1575(s) cm^{-1}, but ν_{sym}(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 ν(C–F) bands at 1135(s), 1160(s) and 1205(s) cm^{-1}, and ν_{sym}(COO) and ν_{asym}(COO) bands at 1430(s) and 1675(s) cm^{-1}.

If the reaction represented in eq. 2 is carried out with HX = 8-hydroxiquinoline (HOq) or 2,2′-bibenzimidazole (H_2BiBzIm), yellow mononuclear complexes of the formula $Bu_4N[AgR(Oq)]$ ($R = C_6F_5$ (VI) or C_6Cl_5 (VII)) or, the green binuclear complex $[Bu_4N]_2\{[Ag(C_6F_5)]_2(\mu\text{-BiBzIm})\}$ (VIII) are obtained. Complexes VI and VII are 1/1 electrolytes in acetone, and complex VII a 1/2 electrolyte. The coordination of the 8-oxyquinolate [11,12] group in complexes VI and VII can be inferred from the ν(CO) and ν(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 $(CF_3COO)Ag$ or $AgNO_3$, as may be seen from eq. 3

$$Bu_4N[Ag(C_6F_5)_2] + AgX \rightarrow Bu_4N\{[Ag(C_6F_5)]_2X\} \quad (3)$$

$(X = CF_3COO \text{ (IX)}, NO_3 \text{ (X)})$

The complexes behave as 1/1 electrolytes in acetone. They are stable at room temperature. Complex IX exhibits bands at 1665(vs) (ν_{asym}(COO)) and 1200(s) 1170(s) and 1125(s) (ν(C–F)) cm^{-1}. The ν_{sym}(COO) and $\nu(NO_3)$ vibrations (complex X) are masked by bands from C_6F_5.

With $AgClO_4$ the reaction takes a different course, and $[Bu_4N]ClO_4$ separates (eq. 4), and AgC_6F_5 can be isolated from the solution.

$$Bu_4N[Ag(C_6F_5)_2] + AgClO_4 \xrightarrow{\text{ether}} [Bu_4N]ClO_4 + 2\,Ag(C_6F_5) \quad (4)$$

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).

$$Bu_4N[Ag(C_6Cl_5)_2] + AgX \rightarrow [Bu_4N]X + 2\,Ag(C_6Cl_5) \quad (5)$$

$(X = NO_3, CF_3COO, ClO_4)$

The white $Ag(C_6Cl_5)$ is insoluble in organic solvents. At room temperature it is more stable than $Ag(C_6F_5)$. Complexes IX and X can also be prepared starting from $Ag(C_6F_5)$, as in eq. 6.

$$2\,Ag(C_6F_5) + [Bu_4N]X \rightarrow Bu_4N\{[Ag(C_6F_5)]_2X\} \quad (6)$$

$(X = NO_3, CF_3COO)$

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

$$2\,Ag(C_6F_5) + [Bu_4N]X \rightarrow AgX + Bu_4N[Ag(C_6F_5)_2] \qquad (7)$$

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

Experimental

IR spectra were recorded (over the range 4000–200 cm^{-1}) on a Perkin–Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in 5×10^{-4} *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

$Bu_4N[AgR_2]$ (R = C_6F_5 (I), C_6Cl_5 (II)). To an ether solution of LiR (30 mmol) (R = C_6F_5 [6] at −78°C or C_6Cl_5 [7], at −20°C) was added $(CF_3COO)Ag$ (2.20 g, 10 mmol) and the mixture stirred for 15 min. $[Bu_4N]O_2CCF_3$ (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 × 5 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.

$Bu_4N[AgRX]$ (R = C_6F_5, X = CH_3COO (III) or Oq (VI); R = C_6Cl_5, X = CH_3COO (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.

$[Bu_4N]_2\{[Ag(C_6F_5)]_2BiBzIm\}$ (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.

$[Bu_4N]\{[Ag(C_6F_5)]_2X\}$ (X = CF_3COO (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 $[Bu_4N]X$ (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).

$Ag(C_6F_5)$. 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 $[Bu_4N]ClO_4$ 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).

$Ag(C_6Cl_5)$ (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.

References

1 R. Nast and H. Schindell, Z. Anorg. Allg. Chem., 326 (1963) 201.

2 P.W.R. Corfiedd and H.M.M. Shearer, Acta Cryst., 21 (1966) 957.

3 V.B. Smith and A.G. Massey, J. Organometal. Chem., 23 (1970) C9.

4 R. Usón, A. Laguna and J. Vicente, J. Chem. Soc., Chem. Commun., (1976) 353; J. Organometal. Chem., 131 (1977) 471.

5 R. Usón, A. Laguna, J. García and M. Laguna, Inorg. Chim. Acta, 37 (1979) 201.

6 P.L. Coe and R. Stephens, J. Chem. Soc. A, (1962) 3227.

7 M.D. Rausch, F.E. Tibbetts and H.B. Gordon, J. Organometal. Chem., 5 (1966) 493.

8 R. Usón, A. Laguna, J. Vicente, J. Carcía, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1981) 655.

9 K. Nakamoto. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edit., John Wiley and Sons, New York, 1978, p. 232.

10 M.J. Baillie, D.H. Brown, K.C. Moss and D.A. Sharp, J. Chem. Soc., A, (1968) 3110.

11 R.G. Charles, H. Freiser, R. Friedel, L.E. Milliard and W.D. Johnston, Spectrochim. Acta, 8 (1956) 1.

12 F. Gomez-Beltran, L.A. Oro, M.P. Puebla and R. del Val, Rev. Acad. Ciencias, Zaragoza, 30 (1975) 99.

13 R. Usón, J. Gimeno, J. Forniés and F. Martínez, Inorg. Chim. Acta, 50 (1981) 173.

14 K.K. Sun and W.T. Miller, J. Am. Chem. Soc., 92 (1970) 6985.