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Note

Polyhalophenylsilver(I) complexes

Eduardo J. Fernández[a], Antonio Laguna[b,*], Aránzazu Mendìa[a]

[a]Departamento de Química, Universidad de La Rioja, 26001 Logroño, Spain

[b]Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, C.S.I.C., 50009 Zaragoza, Spain

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Abstract

The reaction of [AgR] (R = 2,4,6-$C_6F_3H_2$, C_6F_5 or C_6Cl_5) with neutral ligands L (L = pyridine, 3-fluoropyridine, tetrahydrothiophene or 2,2′-bipyridyl) gives [Ag_2R_2L]. The same complexes are obtained by reaction of $NBu_4[AgR_2]$ with [AgL_2]ClO_4. The ^{19}F NMR spectra suggest the presence of bridging perfluorophenyl groups and a tetranuclear structure is proposed.

Keywords: Silver complexes; Polyhaloaryl complexes

1. Introduction

Few mono- or polynuclear arylsilver(I) complexes AgR (R = Ph, C_6F_5, C_6Cl_5, MeC_6H_4, $Me_2C_6H_3$, $Me_3C_6H_2$, $(MeO)_2C_6H_3$, $(MeO)_3C_6H_2$ or $Ph_3C_6H_2$) [1–4] and $Ag(C_6F_5)$(ylide) [5] have been reported, and, to the best of our knowledge, no aryl complexes of the type Ag_2R_2L (L = neutral ligand) have been described.

In this paper we describe the synthesis of Ag_2R_2L (R = 2,4,6-$C_6F_3H_2$, C_6F_5 or C_6Cl_5; L = SC_4H_8 (tht), C_5H_5N (py), 3-F(C_5H_4N) (Fpy) or 2,2′-bipyridyl (bipy) obtained by reaction of AgR with the neutral ligand or of $NBu_4[AgR_2]$ with [AgL_2]ClO_4.

2. Experimental

^1H and ^{19}F NMR spectra were obtained on a Varian XL-200 instrument in $OC(CD_3)_2$ solution; chemical shifts are quoted relative to $SiMe_4$ (^1H) and $CFCl_3$ (external; ^{19}F). C, H and N analyses were performed with a Perkin-Elmer 240B microanalyser. Conductivities were measured in *c.* 5×10^{-4} M acetone solution with a Philips PW 9509 apparatus. Molecular weights were determined in approximately 10^{-2} M solution in $CHCl_3$ using the isopiestic method on a Knauer vapour pressure osmometer model 1100. Melting points were determined in a Büchi apparatus and are uncorrected. All the reactions were performed at room temperature and carried out under nitrogen atmosphere. Anhydrous and deoxygenated solvents were used.

The yields, melting points, C, H and N analyses, and conductivities are listed in Table 1. ^1H and ^{19}F NMR data are given in Table 2.

2.1. Preparation of the complexes

2.1.1. [$Ag_2(2,4,6\text{-}C_6F_3H_2)_2L$] (L = py (1), Fpy (2), tht (3) or bipy (4))

The following procedures were used.

(a) To a solution of $Ag(2,4,6\text{-}C_6F_3H_2)$ [6] (0.239g, 1 mmol) in diethyl ether (50 ml) was added the neutral ligand (L = py (80 μl, 1 mmol), Fpy (86 μl, 1 mmol), tht (89 μl, 1 mmol) or bipy (0.762 g, 0.5 mmol)). The solution was stirred for 45 min and the white precipitate of **4** was filtered off. Concentration of the solution to *c.* 5 ml gave complex **3**. Evaporation of the solution to *c.* 3 ml and addition of hexane (20 ml) led to **1**.

(b) To a solution of $NBu_4[Ag(2,4,6\text{-}C_6F_3H_2)_2]$ [6] (0.288g, 0.5 mmol) in dichloromethane (50 ml) was added [AgL_2]ClO_4 (L = py (0.123g, 0.5 mmol), Fpy (0.201g, 0.5 mmol), tht (0.192 g, 0.5 mmol) or L_2 = bipy (0.182 g, 0.5 mmol)) and the mixture was stirred for 1 h. The solvent was evaporated to dryness and the white solid (**1**, **2** or **3**) was treated with diethyl ether. The insoluble $(NBu_4)ClO_4$ was filtered off. Concentration of solution to *c.* 5 ml and addition of n-hexane (20 ml) led to precipitation of complexes **1–3** as white solids.

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*Corresponding author.

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Table 1
Analytical data for the complexes

Complexes	Yield[a] (%)	Analysis[b] (%)			M.p. (°C)	Λ_M[c]
		C	H	N		
$[Ag_2(C_6F_3H_2)_2(py)]$ (**1**)	78, 47	36.9 (36.65)	1.75 (1.65)	2.45 (2.55)	150 (dec.)	4
$[Ag_2(C_6F_3H_2)_2(Fpy)]$ (**2**)	74, 36	35.0 (35.55)	1.3 (1.4)	2.2 (2.45)	155 (dec.)	6
$[Ag_2(C_6F_3H_2)_2(tht)]$ (**3**)	78, 58	34.6 (33.95)	2.35 (2.15)		150 (dec.)	4
$[Ag_2(C_6F_3H_2)_2(bipy)]$ (**4**)	75, 65	42.0 (41.7)	1.85 (1.9)	4.35 (4.45)	120 (dec.)	7
$[Ag_2(C_6F_5)_2(Fpy)]$ (**5**)	86, 51	32.0 (31.6)	0.6 (0.65)	2.35 (2.2)	155 (dec.)	32
$[Ag_2(C_6F_5)_2(tht)]$ (**6**)	62, 53	30.05 (30.15)	1.25 (1.3)		190 (dec.)	24
$[Ag_2(C_6F_5)_2(bipy)]$ (**7**)	82, 83	37.15 (37.45)	1.0 (1.15)	4.05 (4.0)	150 (dec.)	23
$[Ag_2(C_6Cl_5)_2(py)]$ (**8**)	53, 77	25.6 (25.75)	0.65 (0.65)	1.6 (1.8)	95 (dec.)	[d]
$[Ag_2(C_6Cl_5)_2(tht)]$ (**9**)	64, 73	23.65 (23.95)	0.9 (1.0)		70 (dec.)	[d]
$[Ag_2(C_6Cl_5)_2(bipy)]$ (**10**)	75, 64	29.8 (30.35)	1.0 (0.95)	3.45 (3.45)	110 (dec.)	[d]

[a] According to Eq. (1) or Eq. (2).
[b] Calculated values are given in parentheses.
[c] In acetone Ω^{-1} cm^2 mol^{-1}.
[d] Insoluble.

For **4** the white solid was washed with 3×10 ml of water and the solid was dissolved in dichloromethane (20 ml). The solution was filtered through a 2 cm layer of anhydrous magnesium sulfate and evaporated to ~5 ml. Addition of diethyl ether (20 ml) gave complex **4** as a white solid.

2.1.2. $[Ag_2(C_6F_5)_2L]$ (L = Fpy (5), tht (6) or bipy (7))

The following procedures were used.

(a) To a solution of $Ag(C_6F_5)$ [2] (0.275 g, 1 mmol) in diethyl ether (50 ml) was added the neutral ligand (L = Fpy (86 μl, 1 mmol), tht (89 μl, 1 mmol) or bipy (0.762 g, 0.5 mmol)). After stirring for 30 min the solution was evaporated to ~5 ml. Addition of n-hexane afforded complexes **5**–**7** as white solids.

(b) To a solution of $NBu_4[Ag(C_6F_5)_2]$ [2] (0.342g, 0.5 mmol) in dichloromethane (50 ml) was added $[AgL_2]ClO_4$ (L = Fpy (0.201g, 0.5 mmol), tht (0.192 g, 0.5 mmol) or L_2 = bipy (0.182g, 0.5 mmol)). After stirring the mixture for 3 h, the precipitate of complex **7** was filtered off and washed with 2×3 ml of diethyl ether. For complexes **5** and **6** the solution was evaporated to dryness. The resulting solid was treated with diethyl ether (30 ml) and the precipitated $(NBu_4)ClO_4$ was filtered off. Concentration of the solution to ~5 ml and addition of n-hexane (10 ml) gave complexes **5** or **6** as white solids.

2.1.3. $[Ag_2(C_6Cl_5)_2L]$ (L = py (8), tht (9) or bipy (10))

The following procedures were used.

(a) To a suspension of $Ag(C_6Cl_5)$ [2] (0.257g, 1 mmol) in tetrahydrofuran (50 ml) was added the neutral ligand (L = py (80 μl, 1 mmol), tht (89 μl, 1 mmol) or bipy (0.762 g, 0.5 mmol)). After stirring the mixture for 4 h the precipitate of complex **10** was filtered off and washed with 2×3 ml of tetrahydrofuran. Evaporation of the solution to ~5 ml and addition of diethyl ether (20 ml) gave complexes **8** or **9** as white solids.

(b) To a solution of $NBu_4[Ag(C_6Cl_5)_2]$ [2] (0.425 g, 0.5 mmol) in dichloromethane (50 ml) or tetrahydrofuran (50 ml, L = tht) was added $[AgL_2]ClO_4$ (L = py (0.123 g, 0.5 mmol), tht (0.192 g, 0.5 mmol) or L_2 = bipy (0.182 g, 0.5 mmol)). After stirring the mixture for 3 h, the precipitate of complexes **8** or **10** was filtered off. The tetrahydrofuran solution (**9**) was evaporated to dryness and the resulting solid was washed with water (3×5 ml). The solid was dissolved in dichloro-

Table 2
^{19}F and ^{1}H NMR data for the complexes[a]

Complex	*o*-F	*p*-F	*m*-F	*m*-H
$NBu_4[Ag(C_6F_3H_2)_2]$	−75.5(dm) (*J*(AgF) 40.9)	−119(m)		6.41(dd) (2.3, 9.9)
$[Ag(C_6F_3H_2)]$	−67.4(dd)	−101.4(q) (9.8)		6.75(dd) (3.9, 9.8)
$[Au(C_6F_3H_2)(PPh_3)]$	−84.6(m)	−113.8(m)		6.70(dd) (4.8, 9.2)
$[(\mu\text{-}C_6F_3H_2)\{Au(PPh_3)\}_2]ClO_4$	−71.3(m)	−90.5(m)		6.95(m)
$[Ag_2(C_6F_3H_2)_2(py)]$ (**1**)	−71.8(m)	−107.8(q) (9.5)		6.69(dd) (3.6, 9.5)
$[Ag_2(C_6F_3H_2)_2(Fpy)]$ (**2**)	−68.5(m)	−103.0(q) (9.4)		6.76(dd) (3.9, 9.4)
$[Ag_2(C_6F_3H_2)_2(tht)]$ (**3**)	−71.5(m)	−106.5(m)		6.75(dd) (3.2, 9.3)
$[Ag_2(C_6F_3H_2)_2(bipy)]$ (**4**)	−69.0(m)	−104.1(m)		6.46(dd) (2.5, 9.6)
$NBu_4[Ag(C_6F_5)_2]$	−106.1(m)	−161.5(t) (19.5)	−162.5(m)	
$[Ag(C_6F_5)]$	−99.5(m)	−149.5(t) (18.8)	−160.0(m)	
$[Ag_2(C_6F_5)_2(Fpy)]$ (**5**)	−103.4(m)	−155.6(t) (19.3)	−161.5(m)	
$[Ag_2(C_6F_5)_2(tht)]$ (**6**)	−103.3(m)	−154.9(t) (19.3)	−161.4(m)	
$[Ag_2(C_6F_5)_2(bipy)]$ (**7**)	−103.4(m)	−156.5(t) (19.2)	−161.6(m)	

[a] Coupling constants in hertz are shown in parentheses; t = triplet, q = quintuplet, m = multiplet, dd = doublet of doublets, dm = doublet of multiplets.

methane and filtered through a 2 cm layer of anhydrous magnesium sulfate. Evaporation to ~5 ml and addition of hexane gave complex **9**.

3. Results and discussion

The syntheses of $NBu_4[AgR_2]$ and AgR (R = 2,4,6-$C_6F_3H_2$, C_6F_5 or C_6Cl_5), have been described elsewhere [2,6]. The three AgR derivatives react with an excess of neutral ligand L to give Ag_2R_2L, as in Eq. (1).

$$2[AgR] + L \longrightarrow [Ag_2R_2L] \qquad (1)$$

R = 2,4,6-$C_6F_3H_2$; L = py (**1**), Fpy (**2**), tht (**3**) or bipy (**4**)
R = C_6F_5; L = Fpy (**5**), tht (**6**) or bipy (**7**)
R = C_6Cl_5; L = py (**8**), tht (**9**) or bipy (**10**)

Complexes **1**–**10** can also be obtained by reaction of $NBu_4[AgR_2]$ with $[AgL_2]ClO_4$, according to Eq. (2).

$$NBu_4[AgR_2] + [AgL_2]ClO_4 \longrightarrow [Ag_2R_2L] + (NBu_4)ClO_4 + L \qquad (2)$$

Complexes **1**–**10** are white solids, which decompose slowly at room temperature but can be preserved for months at 0 °C, protected from light. The trifluorophenyl complexes **1**–**4** are non-conducting in acetone solutions (Table 1) and the pentafluorophenyl complexes **5**–**7** are only slightly conducting, though their conductivities are much lower than expected for 1:1 electrolytes.

In the FAB^+ mass spectra of compounds **1**, **2** and **4**, the molecular cation peak ($[Ag_2(C_6F_3H_2)_2L]^+$ or $[Ag_4(C_6F_3H_2)_4L_2]^+$) does not appear, but other species containing $C_6F_3H_2$ groups and different silver atoms as $[Ag_2(C_6F_3H_2)]^+$, $[Ag_3(C_6F_3H_2)_2L]^+$, $[Ag_4(C_6F_3H_2)_3]^+$ or $[Ag_4(C_6F_3H_2)_3(bipy)]^+$ are present, which could indicate a higher nuclearity than two for these complexes. It has also been confirmed by molecular weight measurements in $CHCl_3$ solutions for complexes **2** and **7** (1285 and 1617, respectively. Calc. for $[Ag_4(C_6F_3H_2)_4(Fpy)_2]$: 1150, $[Ag_4(C_6F_5)_4(bipy)_2]$: 1412).

The ^{1}H NMR spectra of $[Ag(C_6F_3H_2)]$, $NBu_4[Ag(C_6F_5H_2)_2]$ and complexes **1**–**4** (Table 2) show a doublet of doublets (dd) for the *meta*-protons as a consequence of the coupling with *ortho*- and *para*-fluorine atoms. In the ^{19}F NMR spectra two different signals for the trifluorophenyl complexes **1**–**4** and three for the pentafluorophenyl complexes **5**–**7** appear, which indicates the presence of only one type of polyfluorophenyl ligands in these derivatives. The resonances due to the *para*-F appear as an apparent quintuplet ($J(FH) \approx J(FF)$ ~ 9.5 Hz) for $Ag(C_6F_3H_2)$ and complexes **1** or **2** and as a triplet for the pentafluorophenyl derivatives. The resonance due to the fluorine atom of 3-fluoropyridine appears as a broad singlet at δ -124.0 or -124.4 for complexes **2** or **5**, respectively. Integration of the signals confirms the proposed stoichiometry.

It has been reported in pentafluorophenyl palladium or platinum complexes [7,8] that the signals due to the *ortho*- and *para*-fluorine atoms of the bridging C_6F_5 appear at lower fields than those due to the terminal C_6F_5 groups. A similar feature is observed in the ^{19}F NMR spectrum of the bridging trifluorophenyl in $[(\mu\text{-}C_6F_3H_2)\{Au(PPh_3)\}_2]ClO_4$ [6] compared with the terminal $C_6F_3H_2$ group in $[Au(C_6F_3H_2)(PPh_3)]$ (Table 2). Also the *ortho*- and *para*-fluorine resonances of [AgR] ($R = C_6F_5$ or $C_6F_3H_2$) and complexes **1**–**7** appear at lower fields than those of $NBu_4[AgR_2]$ suggesting the presence of bridging perfluorophenyl groups in these derivatives.

The structures of the copper complexes $Cu_4(mes)_4(tht)_2$ [9], $Cu_4Ph_4(SMe_2)_2$ [10] and $Cu_4(2\text{-}MeC_6H_4)_4(SMe_2)_2$ [11] have been described and contain four copper centres bonded by four bridging aryl groups.

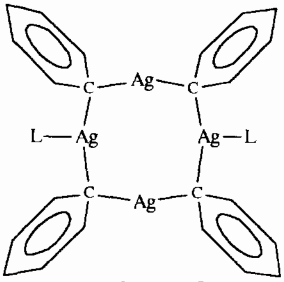

Fig. 1. Proposed structure for $[Ag_2R_2L]$.

We assume a similar structure for our silver complexes (Fig. 1). It has not been possible to grow good crystals for X-ray studies but we propose a tetranuclear structure because our complexes have the same stoichiometry as the copper complexes and ^{19}F NMR suggests the presence of only one type of polyfluorophenyl group, each one bridging two silver centres.

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