Dimeric Silver(I) Complexes with Trimethylphosphine and Aliphatic Perfluorinated Carboxylates

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Silver(I) complexes with trimethylphosphine and perfluorinated carboxylates of general formula $[\{Ag(PMe_3)_2\}_2(\mu\text{-}OOCR)_2]$, where R = CF_3, C_2F_5, C_3F_7, C_4F_9, C_7F_{15}, have been prepared and characterized with IR, ^1H, ^{13}C, ^{19}F, ^{31}P NMR. Spectral analysis suggests four coordinated Ag(I) with two monodentate trimethylphosphine and bidentate carboxylates forming bridges between silver(I) ions. Thermal decomposition process was studied between 293–973 K in nitrogen. Decomposition proceeds in one exothermic stage corresponding to the elimination of perfluorinated carboxylate and trimethylphos- phine. The final product was a mixture of metallic silver and carbon, formed between 473–633 K.

Key words: Ag(I) complexes, trimethylphosphine, perfluorinated carboxylate, thermal analysis, IR and NMR

Silver(I) complexes with tertiary phosphines and perfluorinated carboxylates are attractive objects due to the interesting structures, which can be formed and possible applications as precursors for Chemical Vapour Deposition (CVD) of metals [1–5]. Volatility of Ag^I, Au^I and Au^{III} complexes with oxygen bonded ligands [6–11] prompted us to study analogous silver(I) carboxylates complexes stabilized with tertiary phosphines. Carboxylate anions are able to bind in mono- or bidentate (chelating or bridging) mode, hence one may expect mono or multinuclear complexes. Reported X-ray structures confirmed the presence of the bridging carboxylates in many Ag(I) complexes [12–15]. However, monodentately bonded formate was found in $[Ag(OOCH)(PPh_3)_2]$ [16] and $[Ag(OOCCF_3)\{P(C_6H_4CH_2NMe_2\text{-}2)_3\}]$ [17], whereas in $[Ag\{OOC(CH_2)_{16}CH_3\}(PPh_3)_2]$ [18] a symmetrically chelate was detected. Presented differences in carboxylates binding prompted us to study the influence of the chain length and the effect of electronegative fluorine atoms on the way of coordination and thermal stability of the Ag–O bond. In order to stabilize the Ag(I) coordination sphere, trimethylphosphine as a π-acceptor, σ-donor ligand was chosen.

In the present paper analysis of the thermal decomposition processes and spectral characteristics of $[\{Ag(PMe_3)_2\}_2(\mu\text{-}OOCR)_2]$ complexes (where R = CF_3, C_2F_5, C_3F_7, C_4F_9, C_7F_{15}) will be described.

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EXPERIMENTAL

Chemicals: Perfluorinated carboxylic acids (98–99%) and PMe_3 (99%, 1M solution in THF) were purchased from Aldrich, whereas $AgNO_3$ analytical grade was obtained from POCh Gliwice (Poland).

Instrumentation: IR spectra were measured with a Perkin-Elmer Spectrum 2000 FTIR spectrometer, using KBr (400–4000 cm^{-1}) and polyethylene discs (100–400 cm^{-1}). NMR spectra were recorded on a Varian Gem 200 MHz spectrometer. ^{13}C spectra were recorded at 50 MHz, ^{19}F at 188 MHz and ^{31}P at 81 MHz in 300 K at ambient temperature in $CDCl_3$ solution. References were TMS for ^{13}C, CCl_3F for ^{19}F and 85% H_3PO_4 for ^{31}P. Thermal studies were performed on a MOM OD-102 Derivatograph, Paulik and Paulik (Hungary). Samples (50 mg) were run under nitrogen, heating up to 973 K, at a rate 3,5 K·min^{-1}, TG sensitivity 50 mg; the reference material was Al_2O_3. Powder X-ray diffraction data were obtained with a Dron 1 diffractometer using CuKα radiation.

Preparation of complexes: All reactions were carried out under argon in Schlenk glassware. Solvents were purified and dried by standard methods. Complexes were obtained in the reaction of $[Ag_2(\mu\text{-OOCR})_2]$, where R = CF_3, C_2F_5, C_3F_7, C_4F_9, C_7F_{15} with PMe_3 in molar ratio M:L=1:2. PMe_3 (0.008 mol) in tetrahydrofuran was mixed and suspension of $[Ag_2(\mu\text{-OOCR})_2]$ (0.002 mol) in ethanol stirred in the dark until the reaction mixture became clear. After solvent evaporation under vacuum colourless crystals were found. Complexes of Ag(I) were recrystallized from dichloromethane. Silver was determined by the argentometric method, after mineralization. Carbon and hydrogen were determined by elemental semi-microanalysis. The elemental analyses confirmed the compositions.

RESULTS AND DISCUSSION

Thermal analysis: Results of the thermal analysis in nitrogen are listed in Table 1. DTA curves exhibited one exotherm, which is splitted in two processes. The first effect, which is also connected with the mass loss on TG, can be assigned to the detachment of carboxylate. However, this effect overlaps with the beginning of PMe_3 dissociation. Similar decomposition mechanism was observed for Ag(I) [19] and Au(I) [20] complexes with perfluorinated carboxylates and trimethylphosphine in molar ratio M:L=1:1. Observed exotherm corresponds to the mass loss on TG, what can be correlated almost quantitatively with the detachment of perfluorinated acid residues and trimethylphosphine. Decomposition processes of complexes started between 373–403 K, depending on the carboxylate. Observed onset temperatures of the exotherm can be used in Ag–O bond strength estimation. The lowest onset temperature in the examined series of complexes was found for $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCC}_4F_9)_2]$ (373 K), whereas the highest for $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCC}_2F_5)_2]$ (403 K), which is *ca.* 25 K lower than for the analogous silver(I) complex with PMe_3 in molar ratio M:L=1:1 [19]. The Ag–O bond strength is also affected by the type of tertiary phosphine, because the onset temperatures are significantly lower in comparison to PPh_3 and PEt_3 complexes (*ca.* 75 K and 30 K respectively) [21,22]. This can be explained by the weaker σ-donor properties of PMe_3, in relation to PEt_3 and PPh_3. Thermal decomposition of studied complexes resulted in a mixture of metallic silver and carbon, what is evident from the TG calculations and X-ray powder diffraction studies (except $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCC}_4F_9)_2]$, where pure metallic silver was obtained). Observed diffractograms lines (0.2352, 0.2026, 0.1179, 0.1444, 0.1233 nm) correspond to metallic silver (Powder Diffraction File [23]). Final products were formed between

693–783 K for the series studied. Detected temperatures for **(1)**–**(5)** are 270 K lower than for the respective silver complexes with monodentate trimethylphosphine and bidentately bonded perfluorinated aliphatic carboxylates [19]. The lowest temperature of silver formation was found for $[\{Ag(PMe_3)_2\}_2(\mu\text{-}OOCC_4F_9)_2]$ (693 K), but this temperature is too high for hot wall CVD.

Table 1. Results of thermal analysis in nitrogen.

Complex	Heat effect	Temperature [K]			Weight loss in (%)		Detached groups
		T_i	T_m	T_f	exp.	calc.	
(1) $[\{Ag(PMe_3)_2\}_2(\mu\text{-}OOCCF_3)_2]$	exo	393	453	753	67.3	67.7	$C_2F_6O_4$; 4PMe$_3$
(2) $[\{Ag(PMe_3)_2\}_2(\mu\text{-}OOCC_2F_5)_2]$	exo	403	448	733	70.0	70.2	$C_3F_{10}O_4$; 4PMe$_3$
(3) $[\{Ag(PMe_3)_2\}_2(\mu\text{-}OOCC_3F_7)_2]$	exo	403	418	733	70.3	70.7	$C_3F_{14}O_4$; 4PMe$_3$
(4) $[\{Ag(PMe_3)_2\}_2(\mu\text{-}OOCC_4F_9)_2]$	exo	373	418	693	79.0	79.4	$C_{10}F_{18}O_4$; 4PMe$_3$
(5) $[\{Ag(PMe_3)_2\}_2(\mu\text{-}OOCC_7F_{15})_2]$	exo	388	433	783	80.3	80.4	$C_{12}F_{30}O_4$; 4PMe$_3$

T_i – initial temperature, T_m – maximum temperature, T_f – final temperature.

NMR spectra analysis: ^{13}C, ^{19}F and ^{31}P NMR chemical shifts of complexes **(1)**–**(5)** are listed in Table 2. ^{31}P resonance appeared as a sharp singlet in the range –37.8 – –39.6 ppm, shifted 21.7–22.5 ppm downfield in relation to free PMe$_3$ (Table 2), what is in favour of PMe$_3$ coordination. The ^{13}C resonances of COO carbon for **(1)**–**(5)** were observed as weak signals shifted upfield (*ca*. 0.9–2.1 ppm) in comparison to uncoordinated acid (Table 2), except **(5)** (where downfield shift was noted). These bands are splitted into triplets, due to the spin-spin coupling ^2J(C-F) = 23.4–25.4 Hz except **(1)**, where the singlet was observed. The coordination shifts are similar to that one observed for Ag(I) complexes with trimethylphosphines and bidentately bonded carboxylates in molar ratio M:L=1:1 [19]. The upfield COO coordination shift can be explained by the stronger π-acceptor properties of two PMe$_3$ molecules, resulting in deshielding of COO carbon. However, the magnitude of COO coordination shift suggests that carboxylates are weakly bonded as it was also proposed by Griffin [12] and observed by us in similar systems [19–22]. We have noted no straightforward relation between the COO chemical shift and the number of CF$_2$ groups in the aliphatic chain. Observed fluorine resonances are also affected by the Ag–O bond formation and the most pronounced effects were observed on the resonances of $C_\alpha F_2$ fluorine. Recorded ^{19}F NMR signals of **(1)**–**(5)** revealed $C_\alpha F_2$ signals shifted downfield upon coordination (Table 2). Coordination shift of $C_\alpha F_2$ signals is an additional evidence of the carboxylate linkage with the central ion in solution, although the data obtained do not allow a correlation with the mode of carboxylates binding. The downfield coordination shift of $C_\alpha F_2$ can be referred to the electron deficit in the perfluorinated chain, caused by the π-acceptor ligand such as trimethylphosphine. Analogous effects were observed in ^{19}F NMR spectra of Cu(I) [24], Ag(I) [19,22] and Au(I) [20] complexes with perfluorinated carboxylates and tertiary phosphines.

Table 2. ^{13}C, ^{19}F and ^{31}P chemical shifts (δ) of silver(I) complexes in ppm (coordination shifts in parentheses).

Complex	^{13}C		^{19}F		^{31}P
	δCOO	$^2J_{C\text{-}F}$	$\delta C_\alpha F_2$	δCF_3	δ
(1) $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCCF}_3)_2]$	161.2 (−0.9)	*	−	1.7 (+1.3)	−38.7 (+21.6)
(2) $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCC}_2F_5)_2]$	161.2 (−2.0)	23.4	−43.3 (+1.5)	−6.7 (−1.2)	−39.6 (+20.7)
(3) $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCC}_3F_7)_2]$	161.2 (−1.0)	23.9	−40.8 (+1.7)	−4.9 (−1.6)	−38.4 (+21.7)
(4) $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCC}_4F_9)_2]$	161.0 (−1.3)	24.8	−39.9 (+1.5)	−4.9 (−1.8)	−39.2 (+21.1)
(5) $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCC}_7F_{15})_2]$	161.4 (+0.9)	25.4	−40.1 (+1.4)	−4.9 (−1.6)	−37.8 (+22.5)

*$^1J_{13C\text{-}19F}$ was not calculated.

IR spectra analysis: Carboxylates coordinate to metal ions in several ways, such as mono- or bidentate (bridging or chelating) [25–27]. As a criterion of carboxylates binding in the solid state we have applied the parameter $\Delta\nu_{COO} = \nu_{asym} - \nu_{sym}$ [27]. The estimation of the carboxylate linkage with a metal ion is based on the relation between $\Delta\nu_{COO}$, calculated for the considered complex and found in the identical sodium carboxylate [27]. In the spectra of the complexes COO absorption bands were detected: $\nu_{asym} = 1669–1693$ cm^{-1} and $\nu_{sym} = 1410–1426$ cm^{-1}. Calculated $\Delta\nu_{COO}$ parameters 248–268 cm^{-1} for the examined complexes, in relation to the $\Delta\nu_{COO}$ for the appropriate sodium carboxylates, are in favour of the bidentate coordination. The coordination number of the central ion is completed by the bridging carboxylate groups. Spectra in the range of metal–ligand vibrations should reveal bands, which can be assigned to Ag–O and Ag–P stretching vibrations. From group theory calculations, for C_{2v} coordination sphere geometry (AgO$_2$P$_2$) stretching vibrations of Ag–O should be of the A$_1$ and B$_1$ type, whereas Ag–P(PMe$_3$) type A$_1$, all IR active. The Ag–P stretching vibration bands appeared in the 223–239 cm^{-1} range, that is consistent with the reported frequencies [28]. The Ag–O asymmetric stretching vibrations bands emerged in the 328–339 cm^{-1} range, whereas the symmetric band was found at 190–198 cm^{-1} (in the spectra of **(3), (4)**) [29].

Table 3. Characteristic IR spectral frequencies (cm^{-1}).

Complex	$\nu_{as}COO$	ν_sCOO	Δ_1	Δ_2	$\nu(M\text{-}P)$	$\nu(M\text{-}O)$
(1) $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCCF}_3)_2]$	1674	1421	248	268	218	333
(2) $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCC}_2F_5)_2]$	1671	1417	254	268	220	332
(3) $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCC}_3F_7)_2]$	1688	1426	256	272	215	332,199
(4) $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCC}_4F_9)_2]$	1693	1425	268	272	225	322,198
(5) $[\{Ag(PMe_3)_2\}_2(\mu\text{-OOCC}_7F_{15})_2]$	1669	1410	259	272	223	333

$\Delta_1 = \nu_{as}COO - \nu_sCOO$ (in silver complex); $\Delta_2 = \nu_{as}COO - \nu_sCOO$ (in sodium salt).

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