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The coordination ability of the organometallic sulfur ligand $[Pd_3(\mu\text{-OAc})_3(\mu\text{-MeSCHCO}_2\text{Et-}C,S)_3]$ and the XRD structure of its palladium(II) complex $[Pd_4(\mu\text{-OAc})_3(\mu\text{-MeSCHCO}_2\text{Et-}C,S)(\mu_3\text{-MeSCHCO}_2\text{Et-}C,\kappa^2 S)_2(\eta^2\text{-MeSCHCO}_2\text{Et-}C,S)]BF_4$

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Abstract

The trimetric mixed sphere complex of palladium(II) $[Pd_3(\mu\text{-OAc})_3(\mu\text{-MeSCHCO}_2\text{Et-}C,S)_3]$(**1**) affords $[Pd_4(\mu\text{-OAc})_3(\mu\text{-MeSCHCO}_2\text{Et-}C,S)(\mu_3\text{-MeSCHCO}_2\text{Et-}C,\kappa^2 S)_2(\eta^2\text{-MeSCHCO}_2\text{Et-}C,S)]BF_4$ (**2**) by reaction with the equimolar amount of HBF_4 in CH_2Cl_2. The solvato complex **2**-Me_2CO crystallizes as monoclinic, space group $P2_1/n$, $a = 13.315(2)$, $b = 24.138(2)$, $c = 15.049(2)$ Å, $\beta = 105.4(1)°$, $U = 4663(3)$ Å^3, $Z = 4$. Its structure ($R_w = 0.049$) is characterized by the presence of four (ethoxycarbonyl)(methylthio)methanide ligands, with chiral methine carbon and sulfur atoms. The latter display three different coordination modes: κ^1 in a three membered chelate ring and μ_2 bridges and κ^2 in μ_3 bridges. The tetranuclear cation formally stems from the addition of the chelate cationic fragment $[Pd(\text{MeSCHCO}_2\text{Et-}C,S)]^+$ to a molecule of the starting compound. The formation of **2** highlights the coordination ability of **1** through its sulfur atoms, which is confirmed by the successful synthesis of $[Pd\{[Pd_3(\mu\text{-OAc})_3(\mu\text{-MeSCHCO}_2\text{Et-}C,S)(\mu_3\text{-MeSCHCO}_2\text{Et-}C,\kappa^2 S)_2]\}_2](BF_4)_2$ (**3**) and of $[Cu\{[Pd_3(\mu\text{-OAc})_3(\mu\text{-MeSCHCO}_2\text{Et-}C,S)(\mu_3\text{-MeSCHCO}_2\text{Et-}C,\kappa^2 S)_2]\}_2]PF_6$ (**4**), by simple addition of **1** to the tetrakis acetonitrile complexes of palladium(II) and copper(I), respectively. © 1998 Elsevier Science S.A.

Keywords: Palladium; Sulfur ligands; Tetranuclear cation

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1. Introduction

The coordination chemistry of sulfur ligands is a very wide branch of inorganic chemistry. However, in contrast to the plenty of research carried out on metal complexes of neutral dialkylsulfide and anionic thiolate ligands [1,2], relatively little attention has been paid to the coordination chemistry of anionic ligands stemming from formal deprotonation of dialkylsulfides [3]. We have recently shown that the substituted dimethylsulfide $\text{MeSCH}_2\text{CO}_2\text{Et}$ reacts with palladium acetate to give the trimetric mixed sphere complex $[Pd_3(\mu\text{-OAc})_3(\mu\text{-MeSCHCO}_2\text{Et-}C,S)_3]$ (**1**), which maintains the same nuclearity and structure of the starting palladium salt [4]. All three thioether ligands are in the semi-half space generated by the plane of the three palladium atoms, to which they are bound by means of C–S bridges. The same coordination mode has been later reported for a tetranuclear palladium(II) complex, obtained from the rearrangement of a metal chelate monomeric species [5]. Noteworthy, the six bridging atoms in each molecule of **1** are practically equiplanar and exhibit the same configuration. As a matter of fact, the elementary cell contains two couples of trimers, with the stereogenic atoms in *R*,

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R, *R*, *R*, *R*, *R* and *S*, *S*, *S*, *S*, *S*, *S* configurations, respectively.

Palladium(II) complexes are well known and widespread catalysts or catalyst precursors for a huge number of reactions and industrial chemical processes [6–8]. Complex **1** appears to be very interesting under this point of view, because it contains only bidentate ligands and this circumstance can favour the formation of reactive subcoordinated species upon the opening of ligand bite. Thus, we have started an extensive investigation on the reactivity of **1** towards a number of nucleophiles and electrophiles and we report herein on the results of its reactions with the acidic species HBF_4, $[Pd(NCMe)_4](BF_4)_2$ and $[Cu(NCMe)_4]PF_6$.

2. Experimental

2.1. Reagents and apparatus

All reagent grade reactants and solvents (stored under argon) were purchased from Aldrich and used as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Jeol FX90Q spectrometer (89.55 MHz for ^1H and 22.63 MHz for ^{13}C) or on a Bruker AM 250 spectrometer (250.19 for ^1H and 62.89 for ^{13}C). The solution spectra were recorded at room temperature dissolving the samples in acetone-d_6 or $CDCl_3$. The chemical shifts are reported versus tetramethylsilane and were determined by reference to the residual solvent peaks. ^{13}C CP/MAS measurements were performed on a Bruker AM 250 spectrometer. The setting of the magic angle was monitored by recording the ^{79}Br NMR spectrum of KBr. Cross polarization (CP) was obtained according to conventional procedures. Samples (ca. 250 mg) were introduced into a double-bearing zirconia rotor (o.d. = 7 mm) and spun at the magic angle with a frequency of 4.2 KHz. ^{13}C CP/MAS spectra were recorded with the pulse sequence reported by Dixon et al. [9] for the suppression of spinning, using 2 ms contact time and a repetition delay of 3 s between the scans over 2000 transients. Crystalline polyethylene was used as external reference and the chemical shifts were determined with reference to tetramethylsilane, assuming the methylene carbon atoms of polyethylene to resonate at 33.6 ppm. All the chemical shifts are expressed in ppm relative to the resonance of tetramethylsilane. The FT IR spectra were recorded on a Bruker IFS 66 FT or on a Biorad FT S7 PC spectrophotometer, at 1 or 2 cm^{-1} resolution, in KBr disks.

2.2. Synthesis of $[Pd_4(\mu\text{-}OAc)_3(\mu\text{-}MeSCHCO_2Et\text{-}C,S)(\mu_3\text{-}MeSCHCO_2Et\text{-}C,\kappa^2S)_2(\eta^2\text{-}MeSCHCO_2Et\text{-}C,S)]BF_4$ (**2**)

Fifty milligrams of HBF_4 (78 μl of a diethyl ether solution 54% w/w, 0.56 mmol) in CH_2Cl_2 (5 cm^3) were added dropwise to a CH_2Cl_2(10 cm^3) solution of **1** (0.50 g, 0.56 mmol) under Ar, at 0°C. After one day, traces of a greenish product were filtered off and the orange solution evaporated to small volume. Addition of diethyl ether afforded complex **2** as a yellow solid, which was recrystallized from acetone–ether, 0.29 g, 57% yield. P.f. = 163–164°C (under vacuum, dec.). $C_{26}H_{45}BF_4O_{14}Pd_4S_4$: calc. C, 25.55; H, 3.71; S, 10.49. Found C, 25.80; H, 3.63; S, 10.84%. ^1H NMR (acetone-d_6, δ ppm, 25°C): 1.28 and 1.33 (2t, 12H, CH_3CH_2), 2.01 and 2.08 (2s, 9H, CH_3COO), 2.62 and 2.81 (2s, 12H, CH_3S), 4.14 and 4.28 (2q, CH_3CH_2); (in $CDCl_3$): 3.78 and 3.89 (2s, 4H, CH). ^{13}C NMR (acetone-d_6, δ ppm): 14.94 and 15.30 (CH_3CH_2), 24.47, 27.47 and 30.74 (CH_3COO, CH_3S, and CH_3SCH), 63.57 and 64.06 (CH_2CH_3), 167.26 and 173.63 (COOEt), 183.36 (CH_3COO). ^{13}C CP MAS NMR (δ ppm): 12.1 (CH_2CH_3), 20–30 (overlapped signals for CH_3S, CH_3COO, CH), 61.2 (broad, CH_2CH_3), 163.2 and 170.6(C(O)OEt), 180.9 (CH_3COO). In addition to the bands characteristic of **1**, the FTIR spectrum presents three bands at 1084, 1060 and 1034 cm^{-1}, attributed to the tetrafluoborate anion. A single carbonyl stretching band is observed at 1700 cm^{-1}.

2.3. Synthesis of $\{[Pd(MeSCH_2CO_2(EtOH)]BF_4\}_n$

When, under the otherwise the same experimental conditions as above, a triple quantity of HBF_4 (0.15 g, 1.70 mmol, Pd/H^+ 1/1) was added dropwise to a solution of **1**, a greenish precipitate was obtained after 2 h, which was left under stirring for one day and then filtered. Recrystallization from acetone–dichloromethane afforded pure $\{[Pd(MeSCH_2CO_2)(EtOH)]BF_4\}_n$ as a yellow solid, 0.33 g, 57% yield. $C_5H_{11}BF_4O_3PdS$: calc. C, 17.44; H, 3.22; S, 9.31. Found C, 17.60; H, 3.06; S, 9.35. ^1H NMR (acetone-d_6, δ ppm): 1.21 (t, 3H, CH_3CH_2), 2.60 (s, 3H, CH_3S), 3.90 (s, 2H, CH_3SCH_2), 4.11 (q, 2H, CH_3CH_2), 4.74 (s, 1H, OH). ^{13}C NMR (acetone-d_6, δ ppm): 14.94 (CH_3CH_2), 24.92 (CH_3S), 51.03 (CH_3SCH_2), 63.32 (CH_2CH_3), 168.84 (CH_2COO).

2.4. Synthesis of $[Pd\{[Pd_3(\mu\text{-}OAc)_3(\mu\text{-}MeSCHCO_2Et\text{-}C,S)(\mu_3\text{-}MeSCHCO_2Et\text{-}C,\kappa^2S)_2]\}_2](BF_4)_2$ (**3**)

A solution of **1** (0.34 g, 0.38 mmol) and $[Pd(NCMe)_4](BF_4)_2$ (85 mg, 0.19 mmol) in anhydrous dichloromethane (20 cm^3) was prepared in a three-necked round bottom flask, under inert atmosphere (N_2). The reaction mixture, red and clean at the start, darkened within 1 h. After about 6 h, the solution was reduced to small volume and the obtained oil was treated with ethyl ether to yield a brick-red solid (**3**, 0.34 g, 86%). The crude product was recrystallized from acetone–ethyl ether. Elemental analysis (weight%) calculated for $C_{42}H_{72}B_2F_8O_{24}Pd_7S_6$ (MW = 2071.78): C, 24.35; H, 3.50; S, 9.28. Found C, 23.80; H, 3.36; S, 9.06. ^{1}H NMR (in $CDCl_3$, δ ppm): 1.27 and 1.35 (2t, 9H, CH_3CH_2), 1.96 (s broad, 3H, CH_3COO), 2.17 (s, 6H, CH_3COO), 2.54 (s, 6H, CH_3S), 2.75 (s broad, 3H, CH_3S), 3.49 (m, 1H, CH_3SCH), 3.91 (s, 2H, CH_3SCH), 4.17 (cm, 6H, CH_3CH_2). In addition to the characteristic bands of **1**, the infrared spectrum presents very intense bands at 1094 e 1030 cm^{-1}, which are attributed to the tetrafluoborate anion.

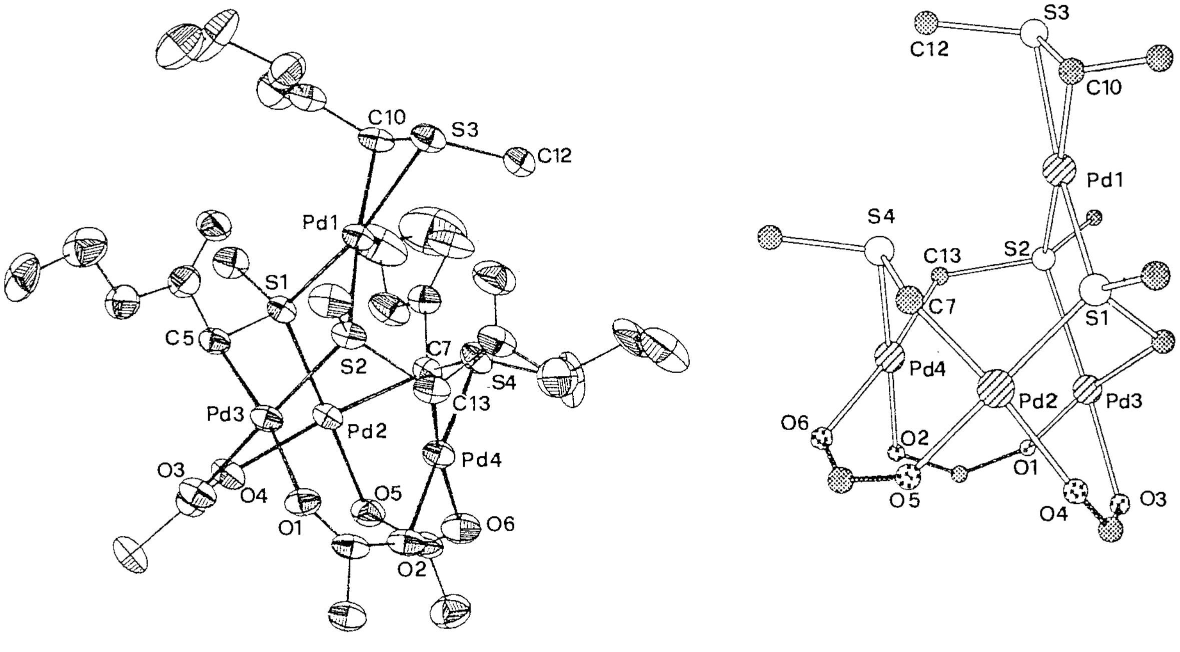
2.5. Synthesis of [Cu{[Pd_3(μ-OAc)$_3$(μ-MeSCHCO$_2$Et-C,S)(μ_3-MeSCHCO$_2$Et-C,κ^2S)$_2$]}$_2$]PF_6 (4)

A solution of **1** (0.18 g, 0.20 mmol) and $[Cu(NCMe)_4]PF_6$ (37 mg, 0.10 mmol) in anhydrous dichloromethane (20 cm^3) was prepared in a three necked round bottom flask, under inert atmosphere (N_2). After about 6 h the still clean reaction mixture, green–brown at the start, was reduced to small volume. Upon addition of ethyl ether a brown solid precipitated. The crude product (0.21 g) was recovered by filtration. Elemental analysis (wt.%) calculated for $C_{42}H_{72}CuF_6O_{24}PPd_6S_6$ (MW = 2000.26): C, 25.22; H, 3.63; S, 9.62. Found C, 24.28; H, 3.41; S, 9.36. ^{1}H NMR (in $CDCl_3$, δ ppm): 1.30 (t, CH_3CH_2), 1.68 (broad s, CH_3COO), 2.14 (s, CH_3COO), 2.52 (s, CH_3S), 3.70 (broad s, CH_3SCH), 4.20 (m, CH_3CH_2). $^{13}C\{^1H\}$ NMR (in $CDCl_3$, δ ppm): 14.3 (CH_3CH_2), 23.9, 25.4 and 26.5 (CH_3S, CH_3COO and CH), 61.4 and 62.2 (CH_3CH_2), 172.0 (CH_3COO) 181.4 and 181.9 ($COOEt$).

In addition to the characteristic bands of **1**, the infrared spectrum presents very intense bands at 845 and 558 cm^{-1}, which are attributed to the hexafluorofosfate anion.

*2.6. XRD analysis of complex **2**-Me$_2$CO*

Suitable crystals for X-ray analysis were obtained by slow diffusion of diethyl ether into an acetone solution of **2**. $C_{29}H_{51}BF_4O_{15}S_4Pd_4$: calc. C, 27.20; H, 4.01; S, 10.02. Found C, 27.43; H, 3.81; S, 10.23. The amount of acetone was checked by gas chromatography. $M = 1280.36$, monoclinic, space group $P2_1/n$, $a = 13.315(2)$, $b = 24.138(2)$, $c = 15.049(2)$ Å, $\beta = 105.4(1)°$, $U = 4663(3)$ Å^3, $Z = 4$, $D_c = 1.82$ g cm^{-3}, $\lambda = 0.71069$ Å, $\mu = 17.394$ cm^{-1}, $F(000) = 2514$, $T = 293$ K, crystal size $0.3 \times 0.3 \times 0.4$ mm. The intensities were collected with a Philips PW 1100 diffractometer with ϑ-2ϑ technique using graphite monochromatized Mo–Kα radiation. A total of 6897 independent reflections were measured up to $\vartheta = 25°$, 4707 of which had $F > 3\sigma(F)$. The structure was solved by direct method (SHELXS 86) and refined by least squares cycles (SHELX 76) using anisotropic thermal parameters for the C, S, O, Pd and F atoms, excluding the solvent molecule. The hydrogen atoms were partially found and refined in the final cycles. The disordered solvent molecule is around the point (0, 0, 0.25) of the elementary cell. An extensive disorder also involves the carbon



1a 1b

Fig. 1. Solid state structure of [Pd_4(μ-OAc)$_3$(μ-MeSCHCO$_2$Et-C,S)(μ_3-MeSCHCO$_2$Et-C,κ^2S)$_2$(η^2-MeSCHCO$_2$Et-C,S)]BF_4 · Me_2CO (**2**).

atoms of the four ethoxy groups and, where possible, the atoms were located at the positions of higher occupancies. Final residual indices $R = 0.045$, $R_w = 0.049$, where $R_w = \Sigma[w \times (F_o - F_c)]^{1/2}/\Sigma[w \times F_o]^{1/2}$ with $w = 1/[\sigma^2(F) + 0.002983\ F^2]$.

3. Results and discussion

With the aim of producing coordinatively unsaturated cationic palladium complexes, we studied the protonolysis of **1** with the equimolar amount of tetrafluoboric acid. The following reaction takes place:

$$4/3[\mathrm{Pd_3}(\mu-\mathrm{OAc})_3(\mu-\mathrm{MeSCHCO_2Et})_3] + \mathrm{HBF_4} \rightarrow [\mathrm{Pd_4}(\mu-\mathrm{OAc})_3(\mathrm{MeSCHCO_2Et})_4]\mathrm{BF_4} \times (\mathbf{2}) + \mathrm{AcOH}$$

Despite the higher basicity of $\mathrm{MeSCHCO_2Et^-}$ with respect to the acetato group, $\mathrm{HBF_4}$ preferentially protonates the latter ligand producing acetic acid. This result is not surprising, if one considers that the spontaneous reaction of $[\mathrm{Pd(OAc)_2}]_3$ with $\mathrm{MeSCH_2CO_2Et}$ produces complex **1**. Apparently, the high affinity of the $\mathrm{MeSCHCO_2Et^-}$ ligand toward palladium(II) prevents its detachment from the metal centre by acidic attack, at least as long as acetato ligands are present in its coordination sphere.

The single crystal X-ray analysis of **2** as its acetone solvate (Fig. 1a,b) shows that the sulfur atoms of the four $\mathrm{MeSCHCO_2Et^-}$ ligands behave in three different fashions, i.e., as κ^1 in a chelate ring and as κ^1 in μ_2- or κ^2 in μ_3 bridges. The molecular structure can be seen as the result of the coordination of the cationic fragment $[\mathrm{Pd(MeSCHCO_2Et}\text{-}C,S)]^+$ (**A**) to one molecule of the trimer **1** (designated hereafter as fragment **B** of the structure of tetetranuclear cation).

The formation of the triatomic ring Pd–S–C in **A** induces a great distortion of the bond angles with respect to the geometry of an ideal planar square. The value of the S(3)–Pd(1)–C(10) angle is very low [46.4(3)°] and the opposite S(1)–Pd(1)–S(2) angle is also relatively small [85.7(1)°], because of the steric constraints imposed by the trimer **B**. As the consequence, the values of the S(1)–Pd(1)–C(10) and S(2)–Pd(1)–S(3) bond angles are rather large [108.5(3)° and 119.5(1)°, respectively] and can be compared with those found in the complex $[\mathrm{PdCl}(\eta^2\text{-}\mathrm{CH_2SMe})(\mathrm{PPh_3})]$ [2]. The S–Pd–C angle is small also in this case [45.4(3)°], but the opposite P–Pd–Cl can assume a large value [99.92(8)°], so reducing the deviations of the remaining P–Pd–C [102.0(3)°] and Cl–Pd–S [112.66(9)°] angles (Table 1). The four metal-donor atom distances for the palladium atom of **A** are all different [Pd(1)–C(10) 2.078(9), Pd(1)–S(3) 2.300(3), Pd(1)–S(1) 2.367(3) and Pd(1)–S(2) 2.429(2) Å], being shorter in the Pd–S–C chelate ring. This contraction involves the C(10)–S(3) bond, which has a distance lower than the out of ring C(12)–S(3) bond [1.74(1) vs. 1.81(1) Å], thus, suggesting a partial double bond character in the first. The coordination of **A** has some effects on the remainder of the cation molecule, whose structure slightly differs from that of the starting $[\mathrm{Pd_3}(\mu\text{-}\mathrm{OAc})_3(\mu\text{-}\mathrm{MeSCHCO_2Et}\text{-}C,S)_3]$. The distance between the κ^2 sulfur atoms S(1) and S(2) is reduced to 3.262(3) Å, although the average of the three S–S distances is practically unchanged (3.51 vs. 3.48 Å). The Pd–S bond distances for the κ^2 atoms [Pd(2)–S(1) 2.278(3) and Pd(3)–S(2) 2.277(3) Å] are smaller (av. 0.12 Å) than in **A** and only slightly greater than that of the monocoordinated sulfur [Pd(4)–S(4) 2.251(2) Å]. The Pd–C bonds remain substantially unaltered, whereas the distances Pd–O are affected by the nature of the donor atom in *trans*, *C* or *S*, and by the type of coordination of *S*. It results that *r*(Pd–O, *trans* to *C*) becomes higher when the palladium atoms are bonded to the κ^2 sulfur atoms [Pd(2)–O(4) 2.123(7) and Pd(3)–O(1) 2.112(7) vs. 2.082(7) Å for Pd(4)–O(6)], whereas *r*(Pd–O, *trans* to *S*) is little affected [Pd(2)–O(5) 2.039(7), Pd(3)–O(3) 2.033(7) and Pd(4)–O(2) 2.047(6) Å]. The bond angles at palladium in **B** do not show

Table 1
Bond distances (Å) and bond angles (°) for $[\mathrm{Pd_4}(\mu\text{-}\mathrm{OAc})_3(\mu\text{-}\mathrm{MeSCHCO_2Et}\text{-}C,S)(\mu_3\text{-}\mathrm{MeSCHCO_2Et}\text{-}C,\ \kappa^2\mathrm{S})_2(\eta^2\text{-}\mathrm{MeSCHCO_2Et}\text{-}C,S)]\mathrm{BF_4}\cdot\mathrm{Me_2CO}$ (**2**)

Pd(1)–S(1)	2.367(3)	Pd(1)–S(2)	2.429(2)
Pd(1)–S(3)	2.300(3)	Pd(1)–C(10)	2.078(9)
Pd(2)–Pd(3)	3.243(1)	Pd(2)–Pd(4)	3.134(1)
Pd(2)–S(1)	2.278(3)	Pd(2)–O(4)	2.123(7)
Pd(2)–O(5)	2.039(7)	Pd(2)–C(7)	2.052(9)
Pd(3)–Pd(4)	3.290(3)	Pd(3)–S(2)	2.277(3)
Pd(3)–O(1)	2.112(7)	Pd(3)–O(3)	2.033(7)
Pd(3)–C(5)	2.028(9)	Pd(4)–S(4)	2.251(2)
Pd(4)–O(2)	2.047(6)	Pd(4)–O(6)	2.082(7)
Pd(4)–C(13)	2.05(1)	S(1)–C(5)	1.80(1)
S(2)–C(13)	1.81(1)	S(3)–C(10)	1.74(1)
S(3)–C(12)	1.81(1)	S(4)–C(7)	1.789(9)
S(3)–Pd(1)–C(10)	46.4(3)	S(2)–Pd(1)–C(10)	165.3(3)
S(2)–Pd(1)–S(3)	119.5(1)	S(1)–Pd(1)–C(10)	108.5(3)
S(1)–Pd(1)–S(3)	154.76(9)	S(1)–Pd(1)–S(2)	85.7(1)
O(5)–Pd(2)–C(7)	88.1(4)	O(4)–Pd(2)–C(7)	169.2(3)
O(4)–Pd(2)–O(5)	83.6(3)	S(1)–Pd(2)–C(7)	92.7(3)
S(1)–Pd(2)–O(5)	179.0(4)	S(1)–Pd(2)–O(4)	95.5(2)
O(3)–Pd(3)–C(5)	89.0(4)	O(1)–Pd(3)–C(5)	170.0(4)
O(1)–Pd(3)–O(3)	86.2(3)	S(2)–Pd(3)–C(5)	90.3(3)
S(2)–Pd(3)–O(3)	175.1(2)	S(2)–Pd(3)–O(1)	95.3(2)
O(6)–Pd(4)–C(13)	170.1(4)	O(2)–Pd(4)–C(13)	91.7(3)
O(2)–Pd(4)–O(6)	85.3(3)	S(4)–Pd(4)–C(13)	89.1(3)
S(4)–Pd(4)–O(6)	93.8(2)	S(4)–Pd(4)–O(2)	178.6(3)
Pd(1)–S(1)–Pd(2)	117.5(2)	Pd(2)–S(1)–C(5)	101.7(3)
Pd(1)–S(1)–C(5)	102.0(3)	Pd(1)–S(2)–Pd(3)	109.6(1)
Pd(3)–S(2)–C(13)	103.0(3)	Pd(1)–S(2)–C(13)	114.7(3)
Pd(1)–S(3)–C(12)	104.6(4)	Pd(1)–S(3)–C(10)	60.1(4)
C(10)–S(3)–C(12)	102.9(5)	Pd(4)–S(4)–C(7)	101.5(3)
Pd(3)–C(5)–S(1)	104.8(5)	Pd(2)–C(7)–S(4)	108.2(5)
Pd(1)–C(10)–S(3)	73.6(4)	Pd(4)–C(13)–S(2)	106.1(5)

great variations with respect to the original trimer, however the values of the S–Pd–C angles are higher for the two bridged units [S(1)–Pd(2)–C(7) 92.7(3) and S(2)–Pd(3)–C(5) 90.3(3) vs. 89.1(3)° for S(4)–Pd(4)–C(13)]. Finally, it can be observed that the angles at sulfur are scarcely influenced by coordination of the fragment **A**: in fact the values of Pd–S–C angles are in the two cases 101.7(3) [Pd(2)–S(1)–C(5)] and 103.0(3)° [Pd(3)–S(2)–C(13)], to be compared with the values of 101.5(3)° found for Pd(4)–S(4)–C(7). As a whole, the structural parameters of **B** are little changed with respect to the starting trimer, thus indicating a particularly lucky combination of geometric and electronic features favourable to further coordination of the sulfur atoms.

The NMR spectra of **2** in the solid state and in deuteroacetone are very similar, thus indicating that its structure determined by means of X-ray diffraction is maintained in solution. In the ^{1}H and ^{13}C solution spectra, two sets of signals for the chelate and bridging $MeSCHCO_2Et$ ligand in the fragments **A** and **B** have been respectively detected. As a matter of fact, the chelate moiety shows ^{1}H resonances at 1.28 and 4.14 for the ethoxy group, and a singlet at 2.81 for the MeS group, whereas the bridging moiety exhibits signals at 1.33, 4.28 and 2.62 for the same protons. In both cases, the signals due to MeS are shifted downfield from that observed for the MeS protons in the trimer **1** ($\delta = 2.14$). A 2D ^{1}H–^{13}C heteronuclear correlation experiment indicates that the signals due to the methine protons overlap the signals of the methylene protons at 4.28 ppm. However the methine protons can be observed as distinct resonances at 3.78 and 3.89 ppm when the sample is dissolved in $CDCl_3$. Separated sets of peaks are also observed in the ^{13}C NMR spectrum for the ethoxycarbonyl groups [14.94 (CH_3), 63.57 (CH_2) and 173.63 (C=O), **A**; 15.30, 64.06 and 167.26, **B**], whereas the MeS and methine carbon atoms shows only single signals at 27.47 and 30.74 ppm, respectively. The three acetato groups in the fragment **B** give rise to two distinct methyl proton resonances at 2.01 and 2.08 in an approximate intensity ratio 2 to 1, the last chemical shift value being attributed to the acetato ligand coordinated to the two palladium atoms bearing the κ^2 sulfur atoms. Also in this case each type of carbon nuclei show only one resonance [24.47 ($\mathit{C}H_3$) and 183.36 ppm ($\mathit{C}OO^-$)] and the chemical shift values are very close to that of the starting complex [4].

The presence of the chelate cationic fragment **A** in the structure of the tetranuclear cation suggests that the attack of HBF_4 to the acetato ligands of **1** disrupts part of the molecules of the starting trimer. This process leads to the formation of mononuclear cations in which the $MeSCHCO_2Et^-$ ligand assumes the chelate coordination mode. In this connection, it is worth mentioning that to the best of our knowledge we are not aware of examples of a different coordination mode for this kind of ligands in mononuclear species. However, the employed amount of HBF_4 is not sufficient to bring out the complete degradation of **1** and the newly formed cations are trapped by the intact molecules of the starting trimer still present in solution. This circumstance highlights the coordination ability of **1** when strong enough electrophiles are available for interaction. In this case, the Lewis acid $[Pd(MeSCHCO_2Et\text{-}C,S)]^+$ is generated in situ by the reaction of complex **1** with HBF_4. Although it is expected to be very reactive, it survives long enough to coordinate to unreacted molecules of **1** itself.

When higher molar ratios between HBF_4 and **1** are employed ($[H^+]/[Complex] = 3$–6) the complete removal of the acetato groups and the hydrolysis of ester groups are observed. Under these conditions we have isolated a complex which analyses as $[Pd(MeSCH_2CO_2)(EtOH)]BF_4$. A 1D NOE experiment shows a correlation of the alcoholic proton with the SMe protons. As a consequence, the square–planar coordination to the palladium centre should involve the ethanolic oxygen and the sulfur atom of one (methyltio)acetate ligand in mutual cis position, and the two carboxylato oxygens of a second sulfur moiety in a polynuclear molecular structure.

The donating ability towards electrophilic metal species of the sulfur atoms of **1** is confirmed by the successful synthesis of two complexes of palladium(II) and copper(I), respectively, in which two molecules of **1** are coordinated to the central metal atom and act as bidentate ligands (Fig. 2a,b).

$$2\left[Pd_3(\mu-OAc)_3(\mu-MeSCHCO_2Et)_3\right] + \left[Pd(NCMe)_4\right](BF_4)_2 \to \left[Pd\left\{\left[Pd_3(\mu-OAc)_3 \times (MeSCHCO_2Et)_3\right]\right\}_2\right](BF_4)_2\,(\mathbf{3}) + 4\,MeCN$$

$$2\left[Pd_3(\mu-OAc)_3(\mu-MeSCHCO_2Et)_3\right] + \left[Cu(NCMe)_4\right]PF_6 \to \left[Cu\left\{\left[Pd_3(\mu-OAc)_3 \times (MeSCHCO_2Et)_3\right]\right\}_2\right]PF_6\,(\mathbf{4}) + 4\,MeCN$$

For the central palladium atom in complex **3** we propose an *S*, *S*, *S*′, *S*′ coordination with the normal square planar geometry. This is supported by the available analytical (elemental analysis) and spectroscopic (^{1}H NMR) data. The infrared spectrum is of little use, in that it presents negligible differences with respect to **1**. However, no bands are detected around 2300 cm^{-1}, which demonstrates the complete displacement of the acetonitrile molecules from palladium(II) ions. The ^{1}H NMR spectrum provides evidence of the existence of two different chemical environments for the sulfur

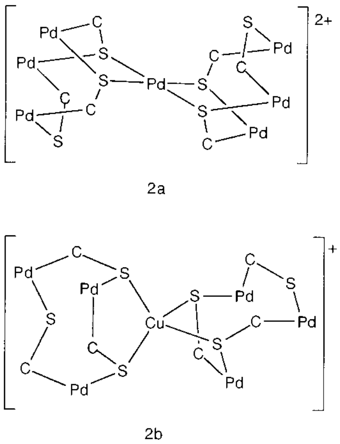


Fig. 2. Proposed coordination modes of complex **1** to Pd^{2+} and Cu^{+} in $[Pd\{[Pd_3(\mu\text{-OAc})_3(\mu\text{-MeSCHCO}_2\text{Et-}C,S)(\mu_3\text{-MeSCHCO}_2\text{Et-}C,\kappa^2S)_2]\}_2](BF_4)_2$ (**3**) and of $[Cu\{[Pd_3(\mu\text{-OAc})_3(\mu\text{-MeSCHCO}_2\text{Et-}C,S)(\mu_3\text{-MeSCHCO}_2\text{Et-}C,\kappa^2S)_2]\}_2]PF_6$ (**4**).

atoms. The assignment of the signals is made by comparison with the observed chemical shifts for the same kind of protons in **1** and **2**, whose structure has been completely elucidated both in the solid state and solution. In fact, the protons of both the methyl and methine groups bonded the sulfur atoms present a couple of signals (2.54, 2.75 and 3.91, 3.49 ppm, respectively), whose relative intensity is 2:1. The protons of the acetato ligands also show two resonances at 1.96 and 2.17 ppm, with relative intensity 2:1. As it was firmly established in the case of complex **2**, the non-equivalence of the sulfur atoms affects also the chemical shift of the protons of the coordinated acetate ions. It is apparent, from these data, that the protons of the acetato ligands are particularly sensitive to the coordination mode of the sulfur ligands. Accordingly, we can safely conclude that two out of three sulfur ligands are different from the third one and that the difference is due to the coordination of two sulfur atoms per molecule of **1** to the central palladium(II) ion.

For complex **4** we propose an *S*, *S*, *S*′, *S*′ tetracoordination for the central copper(I) atom, with tetrahedral geometry around it. In spite of the difficulties in the characterization of the complex, due to its low solubility, analytical (elemental analysis) and spectroscopic data supporting this proposal have been collected. As before, no NC-stretching bands are observed in the infrared spectrum of the complex, which fact demonstrates the complete displacement of the acetonitrile molecules from copper(I) ions. Evidence of the coordination of two molecules of **1** per copper atom are obtained from ^1H and $^{13}C\{^1H\}$ NMR. The resonance of the protons in the methyl groups bonded to the sulfur atoms gives raise to a single broad signal, which is shifted to lower fields with respect to the analogous resonance in **1** (2.52 vs. 2.10 ppm). Although this shift could itself indicate the coordination of sulfur atoms to copper(I), more sound evidence of the existence of two sets of sulfur ligands is given by the presence of two resonances for the protons of the acetato ligands (2.14 and 1.68 ppm), with relative intensity close to 2:1. As in the previous cases, the presence of two different sets of acetato ligands reflects the presence of two different sets of sulfur ligands. This is confirmed by the straightforward detection of two signals for the ^{13}C resonances of the ester carbonyls (181.9 and 181.4 ppm).

4. Conclusion

The trimeric complex $[Pd_3(\mu\text{-OAc})_3(\mu\text{-MeSCHCO}_2\text{Et-}C,S)_3]$ appears to act as a neutral bidentate ligand towards electrophilic centres of copper(I), $[Cu(NCMe)_4]^+$, and palladium(II), $[Pd(NCMe)_4]^{2+}$ and $[Pd(\text{MeSCHCO}_2\text{Et-}C,S)]^+$. The latter electrophile reagent is generated in situ by the action of the equimolar amount of HBF_4 on the molecules of **1** itself. In spite of its expected reactivity, this cationic fragment is stable enough to survive and react with the intact molecules of **1**. It also worth mentioning that the molecules of **1** contain six almost equiplanar stereogenic atoms, which lie on the side facing the central metal atom which coordinates them when complexes are formed. Thus, this peculiar and bulky organometallic ligand could be useful in creating an enantiotopic chemical environment around the central ion in relevant metal complexes.

5. Supplementary material

Full tables of bond lengths and angles, positional and thermal parameters, observed and calculated structure factors for $[Pd_4(\mu\text{-OAc})_3(\mu\text{-MeSCHCO}_2\text{Et-}C,S)(\mu_3\text{-MeSCHCO}_2\text{Et-}C,\kappa^2S)_2(\eta^2\text{-MeSCHCO}_2\text{Et-}C,S)]BF_4$ are available from one of the authors (MB).

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