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Reactivity of $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OR)_3]$ (R = Me, Et) towards bidentate nucleophiles: X-ray structure of $[Pd_2(acac)_2(\mu\text{-}MeSCHC(O)OEt)_2]$

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Abstract

$[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OEt\text{-}C,S)_3]$ (**1**) and $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OMe\text{-}C,S)_3]$ (**2**) react with acetylacetone (Hacac) and benzolylacetone (Hbzac) to give the polynuclear complexes $[Pd_2(acac)_2(MeSCHC(O)OR)_2]$ and $[Pd_3(bzac)_3(MeSCHC(O)OR)_3]$ (R = Et, Me), stemming from the exchange of the acetato ligands. The acetylacetonato derivative $[Pd_2(acac)_2(\mu\text{-}MeSCHC(O)OEt\text{-}C,S)_2]$ (**3**) is a centrosymmetric dimer with chelate $acac^-$ ligands and bridging *C*,*S* sulfur ligands, which crystallizes in the space group $P\bar{1}$, with $Z = 1$ in an elementary cell whose dimensions are $a = 10.322(2)$, $b = 11.460(2)$, $c = 6.249(1)$ Å and $\alpha = 99.1(1)$, $\beta = 96.9(1)$, $\gamma = 115.7(1)°$. The structure has been resolved on the basis of 2115 reflections with final $R = 0.022$ ($R_w = 0.024$). When **1** and **2** react with bipyridine, a comproportionation of the ligands takes place and in both cases the main reaction product is $[Pd(O_2CMe)_2(dipy)]$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Sulfur ligands; β-Dicarbonyl complexes; Bidentate nucleophiles

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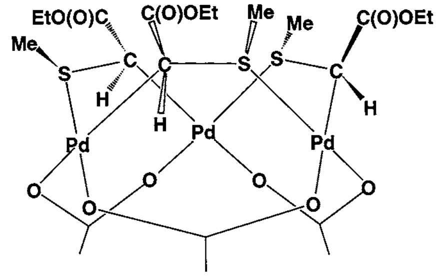
1. Introduction

We have recently reported on the synthesis and characterization of the trimeric palladium complex $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OEt\text{-}C,S)_3]$ (**1**) [1], obtained upon spontaneous metalation of ethyl (methylthio)acetate, $MeSCH_2C(O)OEt$, with $[Pd(OAc)_2]$. This complex presents several interesting features: to the best of our knowledge this is the first example of a mixed-sphere palladium complex isostructural to palladium acetate [2]. However, in spite of the presence of the potential oxygen donor of the ester function, the anionic ligand $MeSCHC(O)OEt^-$ is coordinated to the palladium atoms through the sulfur and the methine carbon atom.



In fact, its behavior is similar to that observed in carbanionic ligands $(RSCHR')^-$ (R = Me, Ph; R′ = H, $CH_2C_6F_5$) [3,4] rather than in other related bidentate ligands stemming from β-dicarbonyls, β-ketophosphines or β-ketoamines [5–7]. It is also worth mentioning that in the system $[Pd(OAc)_2]/MeSCH_2C(O)OEt$ an exchange reaction takes place, in which the weaker sulfur

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carbon acid displaces the stronger acetic acid. This circumstance highlights the great affinity of $MeSCHC(O)OEt^-$ for the palladium(II) center. We are now investigating on the chemistry of complex **1** and of related compounds synthesized in our laboratories. It has been already shown that in the presence of electrophilic reagents $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OEt\text{-}C,S)_3]$ behaves, under proper conditions, as an organometallic ligand, coordinated through the sulfur atoms [8]. We report herein on the results obtained in the reactions of $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OR\text{-}C,S)_3]$ (R = Et, **1**; Me, **2**) with the bidentate nucleophiles acetylacetone, benzoylacetone and bipyridine. This investigation was undertaken in order to ascertain (i) whether the acetato or sulfur ligand was displaced by the nucleophile and (ii) whether the reaction products retained or not the trimeric structure and the coordination mode of the sulfur ligand found in the starting complexes. In general we have observed that the protic β-diketones give an exchange reaction with the metal coordinated acetato ligand. By contrast the neutral bipyridine displaces the thioether ligand to give as the main product $[Pd(OAc)_2(dipy)]$. The same complex was also obtained from the reaction of bipyridine with palladium acetate [9,10].

2. Experimental

2.1. Reagents and apparatus

All manipulations and reactions were carried out under an inert atmosphere. The reagents were high purity products and used as received. Solvents were dried before use according to standard procedures. ^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 MHz for ^1H and 62.89 MHz for ^{13}C). The solution spectra were recorded at room temperature (r.t.) dissolving the samples in $CDCl_3$. The chemical shifts are reported versus TMS and were determined by reference to the residual solvent peaks. ^{13}C CP/MAS measurements were performed on a Bruker AM 250 spectrometer. 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. A contact time of 2 ms and a repetition delay of 3 s between the scans over 2000 transients were used. 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. IR spectra were recorded on a Perkin Elmer 418 IR spectrophotometer and the FTIR spectra on a Bruker IFS 66 FT or on a Biorad FT S7 PC spectrophotometer, at 1 or 2 cm^{-1} resolution, in KBr pellets, unless otherwise stated. The molecular weights were measured by means of a Knauer vapor pressure osmometer, in 1,2 dichloroethane or chloroform at 50°C.

2.2. Synthesis of $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OEt)_3]$ (1)

The synthesis of **1** by reaction of $[Pd(OAc)_2]$ with a double molar amount of ethyl(methylthio)acetate has already been reported [1]. However, the same product can be conveniently obtained in the presence of the equimolar amount of the sulfur ligand. Thus, the typical synthetic procedure was as follows: a solution of ethyl(methylthio)acetate (0.94 g, 7 mmol) in 10 ml of ethanol was added dropwise to a mixture of $[Pd(OAc)_2]$ (1.35 g, 6 mmol) suspended in ethanol (20 ml). The reaction mixture was kept under stirring for 3 days at r.t. Then, a yellow–greenish solid (1.61 g, yield 90%) was recovered upon filtration and washed with ethanol (10 ml). $C_{21}H_{36}O_{12}Pd_3S_3$, $F_W = 895.89$: Calc. C, 28.15; H, 4.05; S, 10.74. Found: C, 28.30; H, 4.22; S, 10.75. The NMR and IR features of the obtained product were the same as reported by Basato et al. [1].

2.3. Synthesis of $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OMe)_3]$ (2)

Methyl(methylthio)acetate (0.16 g, 1.3 mmol) was slowly added to $[Pd(OAc)_2]$ (0.29 g, 1.3 mmol) in ethanol (20 ml). A yellow precipitate formed just after the addition of the ligand. After 5 hours, the solid was recovered upon filtration and recrystallized from acetone/ethyl ether (0.31 g, yield 84%). $C_{18}H_{30}O_{12}Pd_3S_3$, $M_W = 856.74$: Calc. C, 25.23; H, 3.88; S, 11.23. Found: C, 25.85; H, 3.47; S, 11.49. M_W in 1,2-dichloroethane at 50°C: 886. ^1H-NMR (in $CDCl_3$): $\delta = 2.12$ (s, 3H, CH_3S), 2.18 (s, 3H, CH_3CO), 3.69 (s, 4H, CH_3O and CH). ^{13}C-NMR (in $CDCl_3$): $\delta = 23.5$ ($CH_3CO_2^-$), 24.0 (CH_3S), 24.6 (CH), 51.8 (CH_3O), 172.0 ($C(O)OMe$) and 180.9 ($MeCO_2^-$). FTIR (KBr, cm^{-1}): 1711 (C=O stretching, ester), 1551 and 1415 (CO_2^-).

2.4. Synthesis of $[Pd_2(acac)_2(\mu\text{-}MeSCHC(O)OEt)_2]$ (3)

Hacac (0.20 g, 1.99 mmol in 5 ml of solvent) was added dropwise to a solution of **1** (0.50 g, 0.56 mmol in 15 ml of dichloromethane). The reaction mixture was kept 9 h under stirring at gentle reflux (bath temperature 45°C), and the solvent periodically evaporated under vacuum almost to dryness. The reaction mixture was renewed by adding dichloromethane (15 ml) and Hacac in the initial amount and this procedure was repeated two to three times until total disappearance of **1**, which was checked by IR spectroscopy. The final solution was filtered to eliminate traces of palladium metal, evaporated to dryness, treated with acetone to give the bright yellow solid **3**, which was recrystallized from dichloromethane–acetone (0.49 g, 87% yield; m.p. (dec.) 169–71°C). $C_{10}H_{16}O_4PdS$, $F_W = 338.69$: Calc. C, 35.46; H, 4.76; S, 9.46. Found: C, 35.25; H, 4.75; S, 9.50. ^{1}H-NMR (in $CDCl_3$): $\delta = 1.21$ and 1.23 (t, 3H, CH_3CH_2, $J_{HH} = 7.3$ Hz), 1.84, 1.85, 1.87, 1.94, 2.16 and 2.50 (s, 9H, 2 CH_3CO, CH_3S), 3.34 (s, 1H, CH_3SCH), 4.11 (m, 2H, CH_3CH_2), 5.24 and 5.26 (s, 1H, $CH_3C(O)CH$). ^{13}C-NMR (in $CDCl_3$): $\delta = 14.3$ (CH_3CH_2), 20.9, 25.3, 26.9, 27.2, 27.4, 29.2, 31.0 (CH_3SCH, CH_3CO and CH_3S), 60.3 and 60.6 (CH_3CH_2), 99.8 ($CH_3C(O)CH$), 173.5 and 173.8 (COOEt), 185.1, 185.3 and 186.4 (CH_3CO). ^{13}C CP/MAS-NMR: $\delta = 15.8$ (CH_3CH_2), 20.1 (CH_3S), 26.4, 27.6 and 28.9 (CH_3CO and CH_3SCH), 59.5 (CH_3CH_2), 99.5 ($CH_3C(O)CH$), 173.0 (COOEt), 185.5 and 186.5 (CH_3CO). FTIR (KBr, cm^{-1}): 1702 (C=O stretching, ester), 1577, 1545, 1513 ($C\overset{\cdots}{-}O$ and $C\overset{\cdots}{-}C$ stretching, metal chelate).

2.5. Synthesis of $[Pd_3(bzac)_3(\mu\text{-}MeSCHC(O)OEt)_3]$ (4)

A solution of **1** (0.50 g, 0.56 mmol) and benzoylacetone (0.32 g, 1.95 mmol) in 20 ml of dichloromethane was kept 20 h under stirring at gentle reflux (bath temperature 45°C). The volatiles (solvent and acetic acid) were periodically removed (ca. every 3 h, almost to dryness) under vacuum and an aliquot (ca. 20 ml) of fresh solvent added thereafter. The final solution was filtered to eliminate traces of palladium metal, reduced to ca. 10 ml and treated with an equal volume of acetone. The resulting suspension was left under stirring 12 h and filtered to give the yellow solid **4** (0.51 g, 76% yield; m.p. (dec.) 187–90°C). $C_{15}H_{18}O_4PdS$, $F_W = 400.77$: Calc. C, 44.96; H, 4.55; S, 8.00. Found: C, 45.35; H, 4.55; S, 8.14. M_W in chloroform at 50°C: 1130. ^{1}H-NMR (in $CDCl_3$): $\delta = 1.03$, 1.24 and 1.26 (t, 3H, CH_3CH_2, $J_{HH} = 7.0$ Hz), 2.01, 2.02, 2.04, 2.11, 2.15, 2.32, 2.35 and 2.60 (s, 6H, CH_3CO, CH_3S), 3.50 (s, 1H, CH_3SCH), 4.12 (cm, 2H, CH_3CH_2), 5.94 (s, 1H, $CH_3C(O)CH$), 7.35–7.78 (cm, 5H, C_6H_5). ^{13}C-NMR (in $CDCl_3$): $\delta = 14.3$ and 14.5 (CH_3CH_2), 21.0, 27.9, 28.1 and 29.6 (CH_3SCH, CH_3CO and CH_3S), 60.6 and 60.8 (CH_2CH_3), 97.2 ($CH_3C(O)CH$), 127–139 (C_6H_5), 173.8 (COOEt), 178.9, 179.6 and 180.2 (C_6H_5CO), 187.3, 187.5 and 188.5 (CH_3CO). ^{13}C CP/MAS-NMR: $\delta = 13.6$ (CH_3CH_2), 19.3 (CH_3S), 28.8 and 30.7 (CH_3CO and CH_3SCH), 59.6 (CH_2CH_3), 94.8 ($CH_3C(O)CH$), 123–137 (C_6H_5), 173.8 (COOEt), 177.5 (C_6H_5CO), 188.5 (CH_3CO). FTIR (KBr, cm^{-1}): 1700 (C=O stretching, ester), 1589, 1557, 1516, 1486 ($C\overset{\cdots}{-}O$ and $C\overset{\cdots}{-}C$ stretching, metal chelate and phenyl rings).

2.6. Synthesis of $[Pd_2(acac)_2(\mu\text{-}MeSCHC(O)OMe)_2]$ (5)

Hacac (200 µl, 0.20 g, 1.99 mmol in 5 ml of solvent) was added dropwise to a solution of **2** (0.40 g, 0.47 mmol in 15 ml of dichloromethane). The reaction mixture was kept 9 h under stirring at gentle reflux (bath temperature 45°C), and periodically evaporated under vacuum almost to dryness. The reaction mixture was renewed by adding dichloromethane (15 ml) and Hacac in the initial quantity and this procedure was repeated two to three times until total disappearance of **2**, which was checked by IR spectroscopy. The final solution was filtered to eliminate traces of palladium metal, evaporated to dryness, treated with acetone to give the bright yellow solid **5**, which was recrystallized from dichloromethane–acetone (0.28 g, 61%; m.p. (dec.) 187°C). $C_9H_{14}O_4PdS$, $F_W = 324.67$: Calc. C, 33.29; H, 4.35; S, 9.90. Found: C, 32.02; H, 3.92; S, 9.61. ^{1}H-NMR (in $CDCl_3$): $\delta = 1.92$, 1.95, 2.01, 2.11, 2.16 (s, 9H, 2 CH_3CO, CH_3S), 3.66, 3.69 (s, 3H, CH_3O), 3.74 (s, 1H, CH_3SCH), 5.32, 5.35 (s, 1H, $CH_3C(O)CH$). ^{13}C-NMR (in $CDCl_3$): $\delta = 25.4$, 27.0, 27.4 and 29.2 (CH_3SCH, CH_3CO and CH_3S), 51.6 and 52.0 (CH_3O), 100.0 ($CH_3C(O)CH$), 174.1 and 174.6 (COOMe), 185.2, 185.5 and 186.7 (CH_3CO). FTIR (KBr, cm^{-1}): 1706 (C=O stretching, ester), 1576, 1516, 1419 ($C\overset{\cdots}{-}O$ and $C\overset{\cdots}{-}C$ stretching, metal chelate).

2.7. Synthesis of $[Pd_3(bzac)_3(\mu\text{-}MeSCHC(O)OMe)_3]$ (6)

A solution of **2** (0.50 g, 0.58 mmol) and benzoylacetone (0.32 g, 2.0 mmol) in 20 ml of dichloromethane was kept 20 h under stirring at gentle reflux (bath temperature 45°C). The volatile parts (solvent and acetic acid) were periodically removed (ca. every 3 h, almost to dryness) under vacuum and an aliquot (ca. 20 ml) of fresh solvent added thereafter. The final solution was filtered to eliminate traces of palladium metal, reduced to ca. 10 ml and treated with an equal volume of acetone. The resulting suspension was left under stirring 12 h and filtered to give a light green solid, from which **6** was extracted upon treatment with 50 ml of dichloromethane for 4 days in a Soxhlet apparatus (0.34 g, 50%). $C_{14}H_{16}O_4PdS$, $F_W = 386.74$, requires: C, 43.48; H, 4.17; S, 8.29. Found: C, 43.35; H, 4.47; S, 7.80. FTIR (KBr, cm^{-1}): 1707 (C=O stretching, ester), 1587, 1557, 1514, 1486, 1449 ($C\overset{\cdots}{-}O$ and $C\overset{\cdots}{-}C$ stretching, metal chelate and phenyl rings).

*2.8. Reaction of **1** and **2** with bipyridine*

Bipyridine (0.08 g, 0.5 mmol) dissolved in 5 ml of anhydrous dichloromethane was added to a brown–yellow solution of **1** or **2** (respectively 0.30 and 0.28 g, 1 mmol Pd) in the same solvent (10 ml). The reaction mixture was kept under stirring, in the darkness, for 30 h producing a suspension, from which an olive–green solid was recovered by filtration. The solid was recrystallized from acetone and a pale yellow compound, which analyses as [Pd(OAc)$_2$(dipy)]·3H$_2$O, was obtained (0.14 and 0.12 g, from **1** and **2**, respectively, corresponding to 68 and 58% yields with respect to bipyridine). $C_{14}H_{20}N_2O_7Pd$, $F_W = 434.72$: Calc. C, 38.68; H, 4.64; N, 6.44. Found: C, 38.25; H, 4.60, N, 6.18 (from **1**); C, 38.53; H, 4.40; N, 6.28 (from **2**).

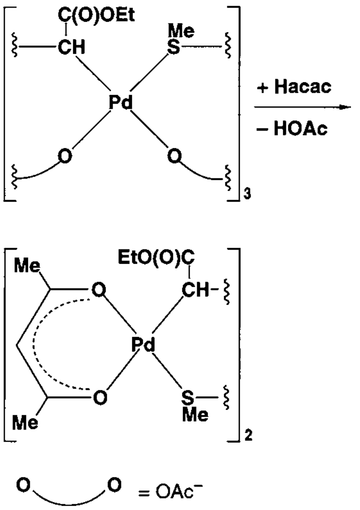
The same pattern was observed when the reaction was carried out in the presence of different amount of bipyridine (dipy/Pd = 1/1, acetone; 3/2, CH$_2$Cl$_2$). Under these conditions, [Pd(OAc)$_2$(dipy)] was again the main product and no pure compounds could be isolated from the mixtures of secondary products, but from analytical and spectroscopic data they appeared to be more rich in the aromatic ligand than in the previous case (approximate dipy/sulfur ligand molar ratio = 1/1 vs. 1/4).

2.9. *Crystal data for [Pd$_2$(acac)$_2$(μ-MeSCHC(O)OEt)$_2$] (3)*

Suitable crystals of **3** were obtained by slow crystallization from a dichloromethane–ethanol solution. Crystal data: $C_{20}H_{32}O_8Pd_2S_2$, $M_W = 677.39$, $F(000) = 340$, triclinic, space group $P\bar{1}$, $a = 10.322(2)$, $b = 11.460(2)$, $c = 6.249(1)$ Å, $\alpha = 99.1(1)$, $\beta = 96.9(1)$, $\gamma = 115.7(1)$, $V = 642.7(8)$ Å^3, $D_{calc.} = 1.75$ g cm^{-3}, $Z = 1$, $\lambda(\text{Mo–K}_\alpha) = 0.71069$ Å, $\mu = 15.76$ cm^{-1}. Intensities were measured by the $\theta - 2\theta$ method up to $\theta = 25°$ yielding 2274 unique reflections of which 2115 were significantly above background [$F > 3\sigma(F)$]. The structure was solved by direct method using the SHELXS 86 program. The positions of the C, O, S and Pd atoms were refined with cycles of least-squares using anisotropic thermal parameters. All hydrogen atoms were identified in the difference Fourier map and introduced with isotropic thermal parameters in the final refinement cycles (SHELXS 76). Convergence was reached at $R = 0.022$ and $R_w = 0.024$ ($w = 1/[\sigma^2(F) + 0.001065F^2]$).

3. Results and discussion

Complexes **1** and **2** react with all the herein investigated bidentate ligands, according to the nature of the donor atoms. In the reactions with β-diketones in dichloromethane or acetone under strictly controlled conditions, both acetylacetone and benzoylacetone give a ligand exchange reaction with the acetato group, which is liberated in solution as acetic acid. The formation of a stable six-member PdOO′ chelate allows the displacement of acetic acid, although Hacac is a weaker acid [11]. The acetylacetonato complex **3** is obtained from **1** as a dimer according to Eq. ((1)):



(1)

The reaction, however, has to be forced by keeping the reaction mixture in dichloromethane with the bath at 45°C, by removing periodically under reduced pressure the volatile parts (to eliminate the acetic acid) and by renewing the solvent and Hacac. The disappearance of **1** is checked by IR and the reaction stopped before the formation of the disubstitution product [Pd(acac)$_2$].

Single crystal X-ray analysis of **3** (Fig. 1) indicates that the substitution of the acetato by the acetylacetonato group destroys the trimeric structure of **1** to give a binuclear complex in which MeSCHC(O)OEt$^-$ maintains the preferred bridging coordination and acac$^-$ forms a chelate ring with the palladium center.

The structure is centrosymmetric and each of the two palladium atoms lies on the center of the square plane defined by the C,O,O,S set of atoms. The Pd–O bond distances (Table 1) slightly depend on the nature of the opposite donor atom, being smaller for Pd–O(1) (2.035(3), *trans* to S) than Pd-O(2) (2.058(3) Å, *trans* to C). In both cases the bond distances are ca. 0.1 Å

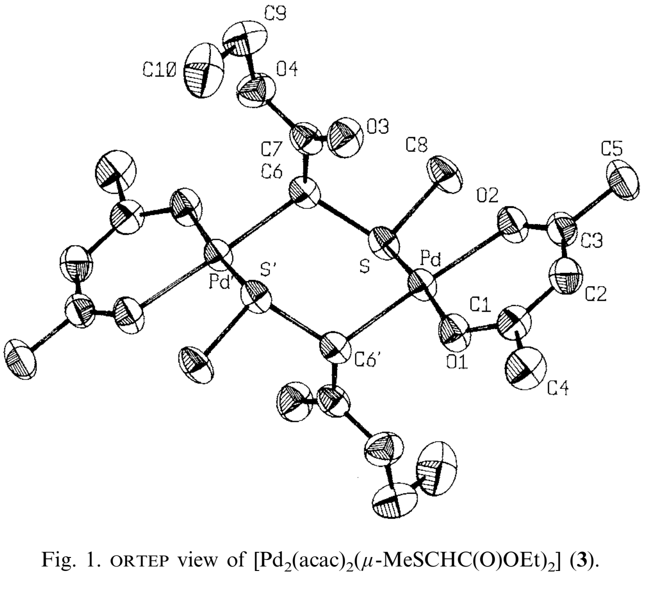


Fig. 1. ORTEP view of [Pd$_2$(acac)$_2$(μ-MeSCHC(O)OEt)$_2$] (**3**).

Table 1
Selected bond distances (Å) and angles for **3**

Bond length (Å)			
Pd–S	2.274(3)	Pd–O(1)	2.035(3)
Pd–O(2)	2.058(3)	Pd–C(6′)	2.043(3)
S–C(6)	1.798(4)	S–C(8)	1.806(4)
O(1)–C(1)	1.275(4)	O(2)–C(3)	1.276(3)
O(3)–C(7)	1.197(4)	O(4)–C(7)	1.356(3)
O(4)–C(9)	1.457(5)	C(1)–C(2)	1.388(5)
C(1)–C(4)	1.504(5)	C(2)–C(3)	1.380(5)
C(3)–C(5)	1.508(5)	C(6)–C(7)	1.499(5)
C(9)–C(10)	1.466(6)		
Bond angle (°)			
O(1)–Pd–O(2)	91.2(2)	S–Pd–O(2)	92.7(1)
O(1)–Pd–C(6′)	85.0(2)	S–Pd–C(6′)	91.0(2)
S–Pd–O(1)	173.6(2)	O(2)–Pd–C(6′)	176.2(2)
Pd–S–C(8)	106.1(2)	Pd–S–C(6)	110.8(1)
C(6)–S–C(8)	101.0(3)	Pd–O(1)–C(1)	124.5(2)
Pd–O(2)–C(3)	124.0(3)	C(7)–O(4)–C(9)	115.3(4)
O(1)–C(1)–C(4)	114.0(4)	O(1)–C(1)–C(2)	126.4(4)
C(2)–C(1)–C(4)	119.6(4)	C(1)–C(2)–C(3)	127.3(5)
O(2)–C(3)–C(2)	126.4(4)	C(2)–C(3)–C(5)	119.4(4)
O(2)–C(3)–C(5)	114.2(4)	S–C(6)–C(7)	114.9(3)
O(4)–C(7)–C(6)	108.6(4)	O(3)–C(7)–C(6)	127.5(5)
O(3)–C(7)–O(4)	123.9(4)	O(4)–C(9)–C(10)	112.2(5)

higher than those observed in [Pd(acac)$_2$] (1.974–1.985 Å) [12,13]. A similar effect was found in a series of [Pd(acac)L$_2$] complexes and has been explained on the basis of a greater *trans* influence of the carbon with respect to the oxygen. The lengthening of the Pd–O bond favors a decrease of the O-Pd-O angle, which approaches the ideal value of 90° (91.2(2) vs. 94.9(1)° in [Pd(acac)$_2$]). The remaining organic part in the Pd–acac ring does not show significant differences in the two cases. As to the interaction of the metal center with MeSCHC(O)OEt$^-$, Pd–S and Pd–C bond distances are substantially unaltered with respect to [Pd$_3$(μ-O$_2$CMe)$_3$(μ-MeSCHC(O)-OEt)$_3$] (2.274(3) and 2.043(3) Å vs. 2.268(2) and 2.040(5) Å, respectively), but removal of the steric constraints due to the trimeric structure produces important modifications on the bond angles at the coordinated atoms. In particular the angles Pd–C–S (112.5(3)°), Pd–S–C (110.8(1)°), S–Pd–C (91.0(2)°) in **3** all show higher values than in the trimer (107.1(1.2), 101.3(9) and 89.9(1.0)°, respectively).

The IR spectrum of **3** is consistent with the X-ray structure: the bands at 1558 and 1414 cm^{-1} characteristic of the acetato group are replaced by absorptions at 1577, 1545 and 1513 due to the $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretching of the chelate ring [14,15]. In addition the strong band at 1702 cm^{-1} of the –C(O)OEt group is at only -3 cm^{-1} with respect to **1**, thus indicating that the ester function is little affected by the modifications in the coordination sphere of palladium(II).

The solid state CP/MAS ^{13}C-NMR spectrum of complex **3** (see Fig. 2) is fully consistent with the above reported crystal structure. The symmetry properties of the dimer and the non equivalence of the acac$^-$ carbonyls that are *trans* to carbon and sulfur atoms, respectively, suggest the presence of ten chemically not equivalent carbon atoms in this complex. Actually ten ^{13}C resonances were detected in the CP/MAS spectrum and were attributed to the various nuclei (see Section 2) by comparison with the data reported in the literature [1] and with the ^{13}C-NMR spectrum of complex **4** (see below). The solution ^{13}C-NMR spectrum of complex **3** is complicated at r.t. by the presence of several additional resonances. Also the corresponding ^{1}H-NMR spectrum exhibits multiple broad resonances, in particular for the ethoxy groups and for the methyls. Variable temperature ^{1}H-NMR investigation of a dichloromethane-d$_2$ solution of **3** showed that these features arise from ligand exchange processes active in solution at r.t. As a matter of fact, the ^{1}H-NMR spectrum at -90°C exhibits almost sharp resonances for the ethoxy protons observed at 1.23 (CH_3CH$_2$O) and 4.11 ppm (CH$_3$CH_2O) and for the three methyls (2CH$_3$CO and 1CH$_3$S) at 1.89, 1.95 and 2.01 ppm. In addition, two sharp singlets at 3.59 and 5.39 ppm, assigned to the methine protons of MeSCHC(O)OEt$^-$ and acac$^-$ have also been detected. By increasing the temperature splitting of these ^{1}H resonances has been observed. The relative intensities and the chemical shifts of these new signals are temperature dependent. When the r.t. is reached, the ^{1}H spectrum contains the above mentioned multiple resonances. This finding indicates that the exchange process is slow in comparison with NMR time scale at low temperature and only one species is present in solution under this condition. The structure of this species can, most likely, be assumed to be similar to that determined in the solid structure by X-ray diffrattometric analysis. We suggest that a reversible detachment of the sulfur donor atoms can take place at relatively high temperature, determining a rearrangement of the ligands in the palladium coordination sphere. The count of the signals indicates that two compounds should be present in solution, so one can envisage either a (μ-*C*,*S*)$_2$–(μ-*C*,*S*)(η^1-*C*) equilibrium between double and single bridged dimers or even a dimer–monomer equilibrium, in which the MeSCHC(O)OEt$^-$ ligand changes from bridging (in [Pd$_2$(acac)$_2$(μ-MeSCHC(O)OEt)$_2$]) to chelate (in [Pd(acac)(η^2-MeSCHC(O)OEt)]). This last η^2-*C*,*S* coordination mode has been already observed in palladium(II) complexes with this [8] and other anionic R′SCHR$^-$ ligands [3,4].

The reactions of [Pd$_3$(μ-O$_2$CMe)$_3$(μ-MeSCHC(O)-OMe)$_3$] (**2**) with acetylacetone and of **1** and **2** with benzoylacetone follow the pattern already observed with acetylacetone (Eq. (2)).

$$n[\mathrm{Pd_3}(\mu\text{-}\mathrm{O_2CMe})_3(\mu\text{-}\mathrm{MeSCHC(O)OR})_3] + 3n\mathrm{Hdike} \rightarrow 3[\mathrm{Pd(dike)}(\mu\text{-}\mathrm{MeSCHC(O)OR})]_n + 3n\mathrm{MeCOOH} \quad (2)$$

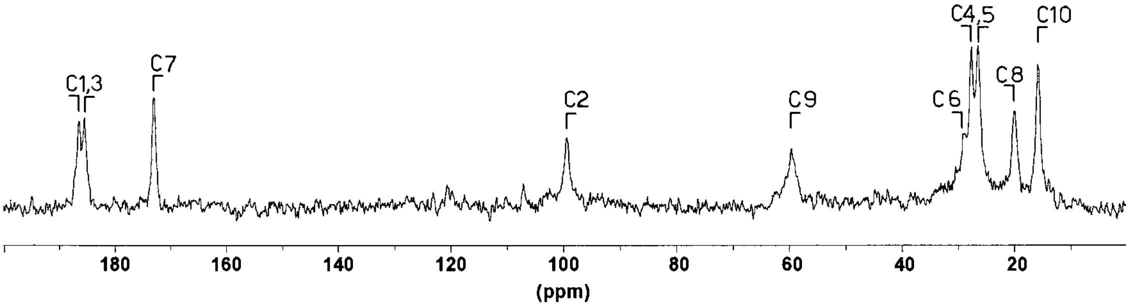


Fig. 2. ^{13}C CP/MAS-NMR spectrum of **3** (carbon atoms numbered as in Fig. 1).

(R = Et: **4**, dike = bzac, $n = 3$; R = Me: **5**, dike = acac, $n = 2$; **6**, dike = bzac, $n = 3$)

The synthesis of **4**, **5** and **6** also requires the careful control of the disappearance of **1** or **2**, in order to stop the reaction before the formation of the relevant bis-β-diketonato palladium complexes.

The solid state CP/MAS ^{13}C-NMR spectrum of complex **4** (see Fig. 3) is very similar to that of complex **3**. The main differences are the presence of the aromatic signals in the region 120–140 ppm and the upfield shift of the carbonyl of the benzoyl group observed at 177.5 ppm. From the comparison of this spectrum with that of complex **3** one can observe that one of the two ^{13}C signals at about 27 ppm (see Fig. 2), attributable to the methyls of the acac$^-$ ligand, is missing. This finding allows to tentatively assign the resonances at 13.6, 19.3, 28.8 and 30.7 ppm in the spectrum of **4** to CH$_3$CH$_2$O, CH$_3$S, CH$_3$$C$O, and CH$_3SC$H carbon atoms, respectively. In the same manner, the five signals observed at 15.8, 20.1, 26.4 and 27.6, 28.9 ppm in the solid state CP/MAS ^{13}C-NMR spectrum of **3** can be assigned to CH$_3$CH$_2$O, CH$_3$S, two CH$_3$CO, and CH$_3$SCH carbon atoms, respectively. The inspection of the ^{1}H- and ^{13}C-NMR spectra of complex **4** in dichloromethane-d$_2$ solution suggests that the same ligand exchange process observed for complex **3** is active also in this case at r.t. This fluxional behavior of the ligands coordinated to palladium centers is not 'frozen' at low temperature. In fact, the ^{1}H-NMR spectrum at −90°C exhibits, in particular, splitting of the signals for the methine proton of bzac$^-$ (three resonances observed at 6.05, 6.08 and 6.10 ppm) and of MeSCHC(O)OEt$^-$ (two resonances at 3.78 and 3.83 ppm). The presence of three methine proton resonances is consistent with the nuclearity of the complex determined by molecular weight measurements in chloroform at 50°C. The different steric hindrance of the methyl and phenyl substituent might be responsible of the difference in nuclearity between the acac (**3**) and the bzac (**4**) complexes.

The IR spectrum of **4** is consistent with its composition. In fact it shows the stretching bands of the ester C=O bond (at 1700 cm^{-1}), and of the bonds in the chelate and aromatic rings (PhC⋯O, MeC⋯O, C⋯C at 1589, 1557, 1516, 1486 cm^{-1}). As in the case of **3**, the position of the ν_{CO} band of the ester group of the sulfur ligand is only slightly shifted in comparison with the spectrum of the free ligand, which means that this moiety is not involved in metal coordination.

The IR spectrum of **5** is closely related to that of **3**. The C=O stretching band of the ester function of the sulfur ligand, which again is not involved into metal coordination, appears at 1706 cm^{-1}, and bands due to the stretching of the C⋯O and C⋯C bonds of the chelate rings are observed at 1576 and 1516 cm^{-1}. The ^{1}H- and ^{13}C-NMR spectral features of **5** in CDCl$_3$ solution are very similar to those of **3**. In particular, as far as the ^{13}C-NMR spectrum is concerned, in both complexes two and three resonances are observed, respectively, for the ester carbonyl carbon atoms (173.5 and 173.8 (**3**), 174.1 and 174.6 (**5**)) and for the acac$^-$ carbonyl carbon atoms (185.1, 185.3 and 186.4 (**3**), 185.2, 185.5 and 186.7 (**5**)). Moreover, two resonances arise from methoxy carbon atoms in **5** as well as from the methylene carbon atoms of the ethoxy group in **3**. The values of the chemical shift for all remaining signals are also strictly comparable in the two complexes.

The IR spectrum of complex **6** is quite similar to that of **4**. The same band pattern is observed from 4000 down to about 1000 cm^{-1}. Only slight shifts, if any, are observed for the stretching bands of the ester C=O bond and of the bonds in the chelate and aromatic rings with respect to the spectrum of **4** (1707 vs. 1700 cm^{-1}, C=O; 1587, 1557, 1514, 1486 vs. 1589, 1557, 1516, 1486 cm^{-1}, PhC⋯O, MeC⋯O, C⋯C). Due to the extremely low solubility of this complex, the solution ^{1}H- and ^{13}C-NMR spectra were not recorded.

The reaction of **1** and **2** with bipyridine shows a different behavior with respect to that with β-diketones. In all experimental conditions (dichloromethane, dipy/Pd molar ratio = 1/2 or 3/2; acetone, dipy/Pd 1/1) the main reaction product is [Pd(OAc)$_2$(dipy)] [9,10], which precipitates from the reaction mixture with a variable amount of crystallization water. Mixtures of palladium(II) complexes can be obtained as side prod-

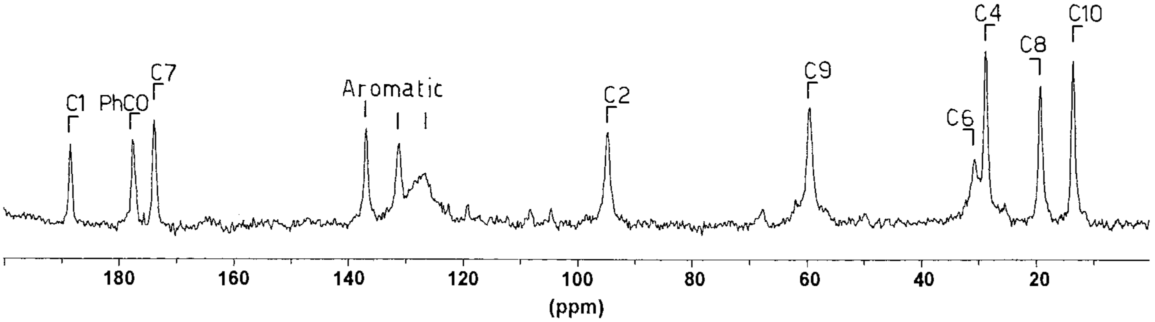


Fig. 3. ^{13}C CP/MAS-NMR spectrum of **4** (carbon atoms are numbered as those of the same nature in Fig. 2).

ucts from the solutions recovered upon separation of $[Pd(OAc)_2(dipy)]$. If the comproportionation of the ligands is active, the reaction scheme should be the following (Eq. (3)):

$$2[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OR)_3] + 3dipy \rightarrow 3[Pd(O_2CMe)_2(dipy)] + 3[Pd(MeSCHC(O)OR)_2] \quad (3)$$

However, bipyridine is never quantitatively incorporated into $[Pd(OAc)_2(dipy)]$, even when it is in defect with respect to the metal and nitrogen is always detected in the elemental analysis of side products. The absorptions due to the aromatic rings are always present in both the FTIR (the bands around 1600 cm^{-1}, at 1450 and at 755 cm^{-1}) and ^1H-NMR (complex multiplets in the 7.3–9.2 ppm range) spectra. The acetato ligand is also present in the secondary products, as shown by the characteristic bands at 1560 and 1415 cm^{-1} in the IR spectra. Thus, the reaction described by Eq. (3) is not quantitative and must be accompanied by other ones. The side products are either relatively unstable and do not withstand the recrystallization conditions, or form a complex mixture from which no pure species can be separated in sensible amount. In fact, these circumstances prevent us from drawing sound conclusions about the nature of the side-reactions and the fate of the sulfur ligand.

4. Conclusions

The trimeric mixed-sphere complexes of palladium(II) $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OEt\text{-}C,S)_3]$ and $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OMe\text{-}C,S)_3]$ react with acetylacetone and benzoylacetone and yield complexes in which the chelate β-diketonato ligands have replaced the bridging acetates. These results clearly indicate the relatively high coordinating ability of (alkoxycarbonyl)(methylthio)methanide ligands towards palladium(II). $[Pd_2(acac)_2(\mu\text{-}MeSCHC(O)OEt\text{-}C,S)_2]$ has been shown to be a dimer in the solid state by means of XRD single crystal analysis. Although the coordination of $MeSCHC(O)OEt^-$ as either a C,S or O,S chelating ligand is possible, it maintains the same mode of coordination via C,S bridges as in the starting trimer. All the other complexes present spectroscopic features (^1H and ^{13}C solution NMR, ^{13}C CP/MAS-NMR, FTIR) quite similar to those of $[Pd_2(acac)_2(\mu\text{-}MeSCHC(O)OEt\text{-}C,S)_2]$. Therefore, their structure should be basically the same, although the nuclearity of the molecular units can be different (two or three). The reaction with bipyridine is not as simple. The main reaction product is $[Pd(O_2CMe)_2(dipy)]$, which results from the comproportionation of the acetato and sulfur ligands, promoted by bipyridine. However, the expected co-product $[Pd(MeSCHC(O)OEt)_2]$ is not isolated, as it evolves to mixtures of ill-defined side-products. The results obtained on the coordination properties of these monoanionic β-ketothioether ligands can be compared with those of the related β-ketophosphine enolates [6]. The sulfur ligands do not show any evidence of oxygen coordination and preferentially engage the carbon atom in α to S, both in bridging and chelate modes. Apparently the presence of an electron lone pair on the coordinated sulfur atom not only makes it capable of further coordination to acid metal centers [8], but it may also induce delocalization of electron density on the adjacent carbon atom so increasing its nucleophilicity. This effect is absent in the phosphine derivatives, which form generally five-member O,P metal chelates [6]. It is worth mentioning, however, that the $Ph_2PCHC(O)OEt^-$ ligand gives, in addition, palladium complexes in which it acts as bidentate μ_2 via the P donor atom and the C in α [16], or even as tridentate μ_3 via a P,C,O donor set [17].

5. Supplementary material

Full tables of bond lengths and angles, positional and thermal parameters, observed and calculated structure factors for $[Pd_2(acac)_2(\mu\text{-}MeSCHC(O)OEt)_2]$ (**3**) are available from the corresponding author upon request.

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