ELSEVIER

Journal of Organometallic Chemistry 571 (1998) 115–121

Journal of Organometallic Chemistry

Mono- and polynuclear complexes from the reaction of palladium acetate with α-substituted thioethers and thiols

Marino Basato *, Diego Tommasi, Marco Zecca

Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, CNR, Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Padova, via Marzolo 1, I-35131 Padova, Italy

Received 18 June 1998

Abstract

Palladium acetate reacts with α-substituted thioethers (RSCH(R′)Z; Z = ester, ketone, sulphone, substituted methyl) and the thiol $HSCH_2C(O)Me$ to give complexes whose composition and nuclearity depend mainly on the electronic properties of the sulphur ligand. If it contains sufficiently acidic hydrogen atoms, the acetato group is partially or totally removed as acetic acid to give complexes of the type $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}RSCR'Z)_3]$ and $[Pd(SCH_2C(O)Me)_2]_6$. The stability of the trimers decreases with the steric hindrance of the substituents at the sulphur and at the methine carbon atoms. Stable mixed sphere complexes are obtained also with carboxylato ligands different from acetato as $PhCOO^-$ and $MeSCH_2COO^-$. When the substituted thioether has poor electronwithdrawing groups, its reaction with palladium acetate affords complexes of the type $[Pd(\eta^1\text{-}OAc)_2(RSCH_2Z)_2]$, in which the sulphur donor atom has simply replaced one oxygen atom of the acetato ligand. © 1998 Elsevier Science S.A. All rights reserved.

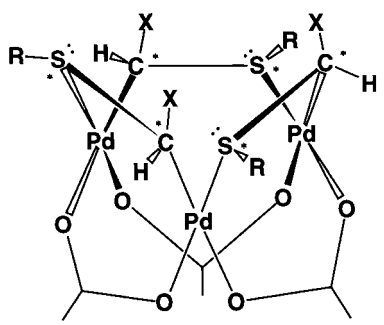
Keywords: Palladium complexes; Sulphur ligand; β-Oxothioethers; Thiolate

1. Introduction

Hybrid ligands based on substituted carbonyls are well known; in most cases the additional donor group is a phosphine, which combines the soft character of its phosphorus atom with the hard character of the keto oxygen [1]. Nickel and palladium complexes based on these O,P ligands are very numerous and some of them find interesting applications in the activation of carbon dioxide and as catalysts in the oligomerization of olefins (SHOP process) [2]. The simple idea at the beginning of this research was to extend this type of chemistry to a different donor atom like sulphur and the first ligand investigated was $MeSCH_2C(O)OEt$.

Its reaction with palladium acetate in ethanol afforded the mixed-sphere palladium complex illustrated below, which represents the first example of the coordination compound of Pd(II) maintaining the trimeric structure of the starting salt (R = Me; X = C(O)OEt) [3,4] (Scheme 1).

The formation of $[Pd_3(\mu\text{-}OAc)_3(\mu\text{-}MeSCHC(O)OEt)_3]$ has several interesting aspects: (i) the sulphur ligand is able to protonate the acetato in the exchange



Scheme 1.

* Corresponding author. Fax: +39 49 8275223; e-mail: basato@chim02.unipd.it

PII S0022-328X(98)00910-3

reaction despite its lower acidity (pK_a ca. 23); (ii) only half of the acetato groups are substituted; (iii) the anionic sulphur ligand is coordinated through the carbon and sulphur atoms and not as an O,S chelate; (iv) the carbon and sulphur atoms of the three bridging ligands have the same configuration and define R,R,R,R,R,R or S,S,S,S,S,S surfaces.

It seemed interesting to verify how the nature of the substituents (both at the sulphur atom and at the methylene group) and the type of bridging carboxylato would affect the synthesis and the stability of the mixed-sphere trinuclear complexes. Therefore, we report here on: (i) the reaction of palladium acetate with a series of α-substituted thioethers of the type $RSCH(R')Z$ (R = Me, Et, ^{t}Bu; R′ = H, Me; Z = C(O)OMenthyl(-), C(O)Me, $S(O)_2Ph$, $CH_2C(O)OMe$, $CH(OMe)_2$) and with the thiol $HSCH_2C(O)Me$; (ii) the synthesis of trinuclear mixed-sphere palladium complexes $[Pd_3(\mu\text{-}O_2CR)_3(\mu\text{-}MeSCHC(O)OR')_3]$ (R = Ph, CH_2SMe) with bridging carboxylato groups different from acetato.

2. Experimental

2.1. Reagents and apparatus

The reagents (Aldrich-Chemie) were high purity products and generally used as received. Solvents were dried before use and the reaction apparatus carefully deoxygenated. Reactions were performed under argon at room temperature and all operations were carried out under an inert atmosphere. The solution ^{1}H- and $^{13}C\{^1H\}$-NMR spectra were recorded on a Jeol FX90Q or on a Bruker AM 250 spectrometer using tetramethylsilane as an internal standard. ^{13}C CP/MAS measurements were performed on the Bruker instrument (operating at 62.89 MHz for ^{13}C), according to the procedure described previously [4]. Crystalline polyethylene was used as an 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. The FT-IR spectra were recorded on a Biorad FT S7 PC spectrophotometer at 2 cm^{-1} resolution in KBr disks. Molecular weight measurements were carried out with a Knauer Vapour Pressure Osmometer and XPS analyses with a Perkin Elmer Φ 5600ci instrument.

2.2. Synthesis of the ligands

2.2.1. $MeSCH_2C(O)Me$, $EtSCH_2C(O)Me$, $(Me)_3CSCH_2C(O)Me$

They were prepared by reaction in ethanol of $ClCH_2C(O)Me$ with the sodium salt RSNa, either commercially available or prepared in situ from the thiol and sodium ethoxyde [5]. $HSCH_2C(O)Me$ was obtained from NaHS and $ClCH_2C(O)Me$ in water at 0°C and stored at a low temperature [6].

2.2.2. $MeSCH_2C(O)OMenthyl(-)$

This new chiral ester was synthesised by reacting (**1***R*,**2***S*,**5***R*)-(-)-menthol with $MeSCH_2C(O)Cl$. To a solution of $MeSCH_2C(O)OH$ (3.50 cm^3, 4.27 g, 40.2 mmol) in 20 cm^3 of benzene, $(COCl)_2$ (3.44 cm^3, 5.00 g, 39.4 mmol) was added dropwise. The mixture was kept at reflux for 3 h and treated directly, at 0 °C, with menthol (6.14 g, 39.3 mmol) and pyridine (5 cm^3, 4.89 g, 61.8 mmol). A white precipitate of pyridinium chloride was filtered off and the product was obtained as a pale yellow oil which distillates at 80°C and 0.3 mmHg. The infrared spectrum is characterised by the strong absorption at 1710 cm^{-1} of the carbonyl stretching. ^{1}H-NMR (in $CDCl_3$, menthyl = $CH^{(1)}CH^{(2)}[CH^{(3)}(CH_3)_2^{(4,5)}]CH_2^{(6)}CH_2^{(7)}CH^{(8)}(CH_3^{(9)})CH_2^{(10)}$): δ = (predominant keto form, ca. 85%) 0.73, 0.81, 0.86, 0.94, 1.1-2.0, 2.20 (s, 3H, CH_3S), 3.18 (s, 2H, CH_2S), 4.70, 4.74 (2t, 1H, (1)); (minor enolic form, ca. 15%) menthyl group + 2.22 (s, CH_3S), 3.22 (s, CHS), 5.92 (s, OH). ^{13}C-NMR (in $CDCl_3$): δ = (predominant keto form) 16.2 (4 and CH_3S), 20.7 (5), 22.0 (9), 23.3 (6), 26.1 (3), 31.4 (8), 34.2 (7), 36.0 (CH_2S), 40.8 (10), 47.0 (2), 75.2 (1), 169.9 (C(O)); (minor enolic form) menthyl group + 35.5 (CHS), 75.7, 77.1 and 78.6 (1), 174.2 (COH).

2.3. Synthesis of the complexes

2.3.1. Synthesis of the mixed sphere acetato complexes $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHZ)_3]$ **1**–**6**

Complexes **1**–**6** were obtained by reaction of palladium acetate (typically 1 mmol) with the appropriate thioether in a 1/1 molar ratio, in ethanol (20 cm^3).

2.3.1.1. $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OMenthyl)_3]$ **1**.

After 5 h, traces of palladium metal were filtered off, the solution was reduced to a small volume and treated with hexane + ether. The solid was recovered upon filtration and washed with hexane (0.15 g, yield 30%). Elemental analysis, Calc. for $C_{15}H_{25}O_4PdS$ (F_w = 408.85): C, 44.18; H, 6.18; S, 7.86; found: C, 44.56; H, 6.36; S, 8.74. The sample always contains small amounts of free ester. ^{1}H-NMR (in $CDCl_3$): δ = 0.70–1.03 (protons of the menthyl group), 1.91 and 2.02 (s, 3H, $CH_3C(O)O$), 2.39 and 2.45 (s, 3H, CH_3S), 3.97 and 4.01 (s, 1H, CH). ^{13}C-NMR (in $CDCl_3$): δ = 15.8 and 16.6 (4), 20.9 and 21.1 (5), 22.7 (9), 23.5, 23.7, 23.9 and 24.1 ($CH_3C(O)O$ and CH_3S), 24.8 and 25.2 (CH), 25.7 and 26.4 (3), 31.4 (8), 34.0 (7), 41.1 and 41.3 (10), 47.4 and 48.1 (2), 74.2 and 74.6 (1), 170.6 and 171.0 (C(O)OMenthyl), 182.7 and 183.0 (MeC(O)O). FT-IR:

1701 cm^{-1} (C=O stretching, ester), 1551 and 1418 cm^{-1} (acetate).

*2.3.1.2. [$Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)Me)_3$] **2**.* After 24 h, traces of palladium metal were filtered off, the solution was reduced to a small volume and treated with ether. The yellow solid was recovered upon filtration and dried under vacuum (0.20 g, yield 68%). Elemental analysis, Calc. for $C_{18}H_{30}O_9Pd_3S_3$ (M_w = 805.81, determined in DCE at 50°C = 787): C, 26.83; H, 3.75; S, 11.94; found: C, 26.21; H, 3.74; S, 11.59. ^{1}H-NMR (in $CDCl_3$): δ = 2.03 and 2.18 (2s, 3H + 3H, CH_3S and CH_3C(O)O), 2.31 (s, 3H, CH_3C(O)), 4.00 (s, 1H, C*H*). ^{13}C-NMR (in $CDCl_3$): δ = 23.4 and 24.1 (*C*H_3C(O)O and *C*H_3S), 30.2 (*C*H_3C(O)), 36.7 (*C*H), 181.6 (Me*C*(O)O), 200.6 (Me*C*(O)). FT-IR: 1665 cm^{-1} (C=O stretching, carbonyl), 1557 and 1414 cm^{-1} (acetate).

*2.3.1.3. [$Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}EtSCHC(O)Me)_3$] **3**.* After 24 h, traces of palladium metal were filtered off, the solution was reduced to a small volume and treated with ether. The yellow–brown solid was recovered upon filtration and washed with ether (0.36 g, yield 87%). Elemental analysis, Calc. for $C_7H_{12}O_3PdS$ (F_w = 280.89): C, 29.75; H, 4.30; S, 11.34; found: C, 29.15; H, 4.21; S, 11.34. ^{1}H-NMR (in $CDCl_3$): δ = 1.23 (t, 3H, CH_3CH$_2$), 2.17 (s, 3H, CH_3C(O)O), 2.31 (s, 3H, CH_3C(O)), 2.33 (q, 2H, CH_2), 4.04 (s, 1H, C*H*). ^{13}C-NMR (in $CDCl_3$): δ = 13.3 (*C*H_3CH$_2$), 24.1 (*C*H_3C(O)O), 29.9 (*C*H_3C(O)), 33.3 (*C*H_2), 34.3 (*C*H), 181.3 (Me*C*(O)O), 200.8 (Me*C*(O)). FT-IR: 1671 cm^{-1} (C=O stretching, carbonyl), 1554 and 1414 cm^{-1} (acetate).

*2.3.1.4. [$Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}(Me)_3CSCHC(O)Me)_3$] **4**.* After 6 h, traces of palladium metal were filtered off, the solution was reduced to a small volume, treated with ether and cooled in an ice bath. The orange solid was filtered rapidly and washed with cold ether (0.20 g, yield 58%). Elemental analysis, Calc. for $C_9H_{16}O_3PdS$ (F_w = 311.06): C, 34.79; H, 5.19; S, 10.32; found: C, 35.79; H, 5.37; S, 10.93. ^{1}H-NMR (in $CDCl_3$): δ (most significant peaks) = 1.57 (s, CH_3C), 2.01 and ca. 2.2 (2s, CH_3C(O) and CH_3C(O)O), ca. 4.5 (s, C*H*). ^{13}C-NMR (in $CDCl_3$): δ = 23.3, 23.8, 23.9 (*C*H_3C(O)O), 29.1, 30.0, 30.8, 31.5 (*C*H_3C and *C*H_3C(O)), ca. 35 (*C*H), 51.7 (Me$_3$*C*), 180.4 (Me*C*(O)O), 199.1, 202.9, 205.6 (Me*C*(O)). FT-IR: 1681 cm^{-1} (C = O stretching, carbonyl), 1552 and 1401 cm^{-1} (acetate).

*2.3.1.5. [$Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHS(O)_2Ph)_3$] **5**.* After 35 min, the red solid was filtered and washed with ethanol (0.40 g, yield 91%). Elemental analysis, Calc. for $C_{10}H_{12}O_4PdS_2$ (F_w = 367.76): C, 32.75; H, 3.29; S, 17.48; found: C, 32.15; H, 3.10; S, 19.70. The compound is rather unstable and prolonged reaction times afforded solids containing remarkable amounts of nitrogen. One sample had: C, 22.93; H, 2.19; N, 1.49; S, 13.72 and molar ratios, determined by XPS: Pd(II) 1; Pd(0) 0.28; S, 1.48; N, 0.28. ^{13}C-NMR (solid state): δ = 25.0 (*C*H_3S, *C*H_3C(O)O, *C*H), 130.1 (Ph), 184.0 (Me*C*(O)O). FT-IR: 1552 and 1401 cm^{-1} (acetate), 1298 and 1151 cm^{-1} (O=S=O).

*2.3.1.6. [$Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSC(Me)C(O)Me)_3$] **6**.* After 30 min palladium metal was filtered off, the solution was reduced to a small volume and treated with ether. The brown solid was filtered and washed with ether (0.33 g, yield 90%). Elemental analysis, Calc. for $C_7H_{12}O_3PdS$ (F_w = 272.89): C, 29.74; H, 4.28; S, 11.34; found: C, 30.32; H, 4.33; S, 13.18. Also in this case samples were often contaminated by the presence of nitrogen and of palladium(0). ^{13}C-NMR (solid state): δ = 13.3 and 16.0 (C(*C*H_3)), 25.8 (*C*H_3S, *C*H_3C(O)O), 37.5 (*C*H_3C(O)), 42.3 and 48.7 (*C*Me), 181.8 (Me*C*(O)O), 205.6 (Me*C*(O)). FT-IR: 1688 cm^{-1} (C=O stretching, carbonyl), 1559 and 1428 cm^{-1} (acetate).

2.3.2. Synthesis of the carboxylato complexes [$Pd_3(\mu\text{-}O_2CR)_3(\mu\text{-}MeSCHC(O)OR')_3$]

*2.3.2.1. [$Pd_3(\mu\text{-}O_2CPh)_3(\mu\text{-}MeSCHC(O)OEt)_3$] **7**.* To a suspension of palladium benzoate [7] (0.23 g, 0.66 mmol) in 15 cm^3 of ethanol, $MeSCH_2C(O)OEt$ (0.11 cm^3, 0.11 g, 0.80 mmol) was added. After 2 h the yellow complex was filtered and dried under vacuum (0.18 g, yield 76%). Elemental analysis, Calc. for $C_{36}H_{42}O_{12}Pd_3S_3$ (M_w = 1082.16, determined in DCE at 50°C = 1040): C, 39.42; H, 3.90; S, 8.90; found: C, 40.31; H, 3.88; S, 9.18. ^{1}H-NMR (in $CDCl_3$): δ = 1.26 (t, 3H, CH_3CH$_2$), 2.23 (s, 3H, CH_3S), 3.87 (s, 1H, C*H*), 4.1 (cm, 2H, CH$_3$CH_2), 7.2–8.1 (Ph). ^{13}C-NMR (in $CDCl_3$): δ = 14.4 (*C*H_3CH$_2$), 24.6 (*C*H_3S), 25.8 (*C*H), 61.4 (CH$_3$*C*H$_2$), 127.6–134.2 (Ph), 172.3 (*C*(O)OEt) and 180.9 (Ph*C*(O)O). FT-IR: 1707 cm^{-1} (C=O stretching, ester), 1543 and 1397 cm^{-1} (benzoate).

*2.3.2.2. [$Pd_3(\mu\text{-}O_2CCH_2SMe)_3(\mu\text{-}MeSCHC(O)OMe)_3$] **8**.* [$Pd_3(\mu$-$O_2CMe)_3(\mu$-MeSCHC(O)OMe)$_3$] (0.25 g, 0.29 mmol) [8] was suspended in 15 cm^3 of ethanol and treated with $MeSCH_2COOH$ (80 μl, 0.92 mmol). After 1 h the yellow–greenish precipitate was filtered and recrystallised from dichloromethane + ether (0.23 g, yield 80%). Elemental analysis, Calc. for $C_7H_{12}O_4PdS_2$ (F_w = 330.69): C, 25.42; H, 3.66; S, 19.39; found: C, 25.09; H, 3.58; S, 19.04. ^{1}H-NMR (in $CDCl_3$): δ = 2.31 and 2.45 (s, ca. 3H, CH_3SCH$_2$), 2.66 (s, 3H, CH_3S), 3.44 and ca. 3.60 (s, ca. 2H, CH$_3$SCH_2), 3.75 (s, 4H, CH_3O and C*H*). ^{13}C-NMR (in $CDCl_3$): δ = 21.1, 22.4, 24.5, 26.4 and 26.7 (*C*H_3SCH$_2$, *C*H and *C*H_3S), 41.2, 42.2, 42.9 (CH$_3$S*C*H$_2$), 52.4 (*C*H$_3$O), 171.9, 172.9, 173.2

(*C*(O)OMe) and 175.7, 176.1, 176.6 ($CH_2C(O)O$). FT-IR: 1697 cm^{-1} (C=O stretching, ester), 1614 and 1429 cm^{-1} (carboxylate).

2.3.3. Synthesis of the complexes $[Pd(O_2CMe)_2(MeSCH_2Z)_2]$

2.3.3.1. $[Pd(O_2CMe)_2(MeSCH_2CH_2C(O)OMe)_2]$ **9**. To a suspension of palladium acetate (0.31 g, 1.4 mmol) in 20 cm^3 of ethanol, $MeSCH_2CH_2C(O)OMe$ (0.35 cm^3, 0.38 g, 2.8 mmol) was added slowly. After 24 h traces of palladium were filtered off, the solution reduced of volume and treated with ether. The resulting light brown solid was filtered and washed with ether (0.56 g, yield 82%). Elemental analysis, Calc. for $C_{14}H_{26}O_8PdS_2$ ($M_w = 491.25$): C, 34.11; H, 5.31; S, 13.01; found: C, 34.08; H, 5.32; S, 13.42. ^{1}H-NMR (in $CDCl_3$): $\delta = 1.87$ (s, 3H, $CH_3C(O)O$), 2.20 (s, 3H, CH_3S), 2.85 (s broad, 4H, CH_2CH_2), 3.66 (s, 3H, CH_3O). ^{13}C-NMR (in $CDCl_3$): $\delta = 18.7$ ($CH_3C(O)O$), 22.5 (CH_3S), 31.9 (CH_2CH_2), 51.6 (CH_3O), 170.9 (*C*(O)OMe) and 177.3 (Me*C*(O)O). FT-IR: 1736 cm^{-1} (C=O stretching, ester), 1574 and 1408 cm^{-1} (acetate).

2.3.3.2. $[Pd(O_2CMe)_2(MeSCH_2CH(OMe)_2)_2]$ ***10***. To a suspension of palladium acetate (0.40 g, 1.8 mmol) in 20 cm^3 of ethanol, $MeSCH_2CH(OMe)_2$ (0.48 cm^3, 0.49 g, 3.6 mmol) was added slowly. After 4 h traces of palladium were filtered off, the solution was reduced to a small volume and treated with ether + hexane. The resulting brown solid was filtered and dried under vacuum (0.63 g, yield 70%). Elemental analysis, Calc. for $C_{14}H_{30}O_8PdS_2$ ($M_w = 496.85$): C, 33.84; H, 6.09; S, 12.90; found: C, 31.53; H, 5.52; S, 12.21. ^{1}H-NMR (in $CDCl_3$): $\delta = 1.79$ (s, 3H, $CH_3C(O)O$), 2.16 (s, 3H, CH_3S), 2.75 (d, 2H, CH_2), 3.28 (s, 6H, CH_3O), 4.67 (t, 1H, C*H*). ^{13}C-NMR (in $CDCl_3$): $\delta = 19.8$ ($CH_3C(O)O$), 22.8 (CH_3S), 39.0 (CH_2), 54.1 (CH_3O), 102.6 (*C*H) and 177.7 (Me*C*(O)O). FT-IR: 1568 and 1408 cm^{-1} (acetate).

2.3.4. Synthesis of $[Pd(\mu\text{-}SCH_2C(O)Me)_2]_6$ **11**

To a suspension of palladium acetate (0.29 g, 1.3 mmol) in 20 cm^3 of ethanol, thermostatted at 0°C, $HSCH_2C(O)Me$ (0.30 g, 2.6 mmol) was added slowly. After 1 h the yellow precipitate was filtered, washed with ethanol and dried under vacuum (0.34 g, yield 92%). Elemental analysis, Calc. for $C_{36}H_{60}O_{12}Pd_6S_{12}$ ($M_w = 1707.96$, determined in DCE at 50°C = 1553): C, 25.32; H, 3.54; S, 22.52; found: C, 25.18; H, 3.33; S, 22.66. ^{1}H-NMR (in $CDCl_3$): $\delta = 2.12$, 2.16, 2.18, 2.52 (4s, 3H, CH_3), 3.24, 3.28, 3.40, 3.48 (4s, 2H, CH_2). ^{13}C-NMR (in $CDCl_3$): $\delta = 29.0$, 29.1, 29.6 (CH_3), 39.6, 40.1, 44.3 (CH_2), 202.7, 203.0, 203.4, 203.8 (*C*(O)Me). ^{13}C-NMR (solid state): $\delta = 30.4$ (CH_3), 44.6 (CH_2), 205.0 (*C*(O)Me). FTIR: 1712 cm^{-1} (C=O stretching).

3. Results and discussion

The type of palladium complexes resulting from the reaction of palladium acetate with α-substituted thioethers $RSCH_2Z$ mainly depends on the presence of acidic sites, on their relative strength and on the electronwithdrawing properties of Z.

The reaction with thioethers having in α one ester, ketonic or sulphonyl substituent proceeds with exchange of half of the acetate ligands, according to Eq. (1).

$$[Pd_3(\mu\text{-OAc})_6] + 3RSCH_2Z \rightarrow [Pd_3(\mu\text{-OAc})_3(\mu\text{-RSCHZ})_3]\ (\mathbf{1}\text{–}\mathbf{5}) + 3HOAc \quad (1)$$

1: R = Me, Z = C(O)OMenthyl(-); **2**: R = Me, Z = C(O)Me; **3**: R = Et, Z = C(O)Me; **4**: R = Me_3C, Z = C(O)Me; **5**: R = Me, Z = $S(O)_2Ph$.

The same type of complex is obtained when a methylene hydrogen is substituted by a methyl group ($[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-MeSCMeC(O)Me})_3]$ (**6**)).

In all cases the FT-IR spectroscopic data indicate that the carbonyl or sulphonyl group is not directly bonded to the metal atom (the stretching bands of such groups present only slight shifts in wavenumbers with respect to the free ligands, if any) and disclose the presence of the acetato ligands (asymmetric and symmetric stretching at 1551–1559 and 1412–1428 cm^{-1}, respectively).

The trimeric nature of complexes **1**–**6** is suggested by the close analogy of their physico-chemical properties with those of $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-MeSCHC(O)OEt})_3]$, whose structure was determined by X-ray analysis, and for **2** also by osmometric measurement of the molecular weight [3].

The yield and stability of the isolated complexes markedly depend on the nature of the ligand and generally increase in the order α-sulphonylthioether (Z = $S(O)_2Ph$) < β-ketothioether (Z = C(O)Me) < α-alkylcarboxythioether (Z = C(O)OEt). In the β-ketothioether complexes, both the carbon (34.3–36.7 ppm) and proton (4.00–4.50 ppm) resonances of the coordinated methine moiety are observed downfield with respect to the more stable products (24.8–25.2 (^{13}C) and 3.62–4.01 (^{1}H) ppm). This is probably due to a lower p character of the carbon orbitals employed in the Pd–C bond which consequently results to be weaker. Also, increasing bulkiness of the sulphur ligand decreases the stability of the complex. Thus, complexes **1** (Z = C(O)OMenthyl(-)), **4** (R = Me_3C) and **6** do not seem particularly stable and tend to evolve in solution.

The menthyl substituent is a very hindering lipophilic group which makes the complex $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-MeSCHC(O)OMenthyl})_3]$ very difficult to purify, because of its extremely high solubility and of some tendency to release $MeSCH_2C(O)OMenthyl(-)$. As a

matter of fact, the solution NMR spectra of **1** always indicates the presence of free sulphur ligand. The structure of the complex is, however, well supported by the presence of two distinct sets of ^{1}H and ^{13}C signals. In particular, the methyl and methine proton nuclei resonate at 1.91, 2.02 ($MeCO_2$), 2.39, 2.45 (MeS) and 3.97, 4.01 (CH) ppm and, in correspondence, three couples of signals (23.51, 23.69, 23.90, 24.14 and 24.81, 25.25 ppm) are observed in the ^{13}C spectrum. These data clearly indicate that the use of the optically pure $MeSCH_2C(O)OMenthyl(-)$ produces two diastereoisomers in a 1/1 molar ratio, which differ for the configuration of the six S and C donor atoms (S,S,S,S,S,S or R,R,R,R,R,R).

Complexes **4**–**6** are rather unstable and give by-products containing palladium(0) and nitrogen. The presence of this last element has been verified by both elemental analysis and XPS spectroscopy. It has been observed that the nitrogen is positively charged (BE 1s 403.8 eV) and is always accompanied by palladium(0) (BE $3d_{5/2}$ 336.0 eV) in an approximate 1/1 ratio. If one considers that the synthesis and purification of these products do not involve nitrogen containing chemicals, it seems possible that these complexes or their evolution products (palladium colloids?) are able to adsorb and activate molecular nitrogen from the air, to which they are exposed during the physico-chemical characterization.

Reaction of palladium benzoate, instead of acetate, with $MeSCH_2C(O)OEt$ also occurs according to Eq. (1), to give the mixed sphere trimer $[Pd_3(\mu\text{-}O_2CPh)_3(\mu\text{-}MeSCHC(O)OEt)_3]$ (**7**). The stability and nuclearity of the complex has been checked by molecular weight determination in 1,2-dichloroethane at 50°C and the infrared and NMR data are very similar to those of the acetato analogue. This strongly suggests that the nature of the bridging carboxylato ligands scarcely affects the type of coordination of the sulphur ligands (C,S).

The large scope of the employable carboxylato groups and the good coordinating properties of anionic α-alkylcarboxythioethers is well illustrated by the reaction of $[Pd_3(\mu\text{-}O_2CMe)_3(\mu\text{-}MeSCHC(O)OMe)_3]$ with $MeSCH_2COOH$. The exchange reaction involves only the acetato group to give again a mixed-sphere complex, $[Pd_3(\mu\text{-}O_2CCH_2SMe)_3(\mu\text{-}MeSCHC(O)OMe)_3]$ (**8**). The ^{1}H- and ^{13}C-NMR spectra show multiple resonances for some functional groups, thus suggesting a non symmetric molecular structure. This can arise from the presence of a S donor atom in the carboxylato ligand, which can compete with one O atom in coordination to the palladium centre.

A second type of complexes is obtained from the reaction of palladium acetate with dimethyl sulphides bearing poor electron-withdrawing substituents, like 1,1-dimethoxy-2-(methylthio)ethane and methyl 3-(methylthio)propionate. The sulphur donor atom simply replaces one bite of the bridging acetato, which becomes coordinated η^1 to the palladium (Eq. (2)).

$$1/3[Pd_3(\mu\text{-}OAc)_6] + 2MeSCH_2Z \rightarrow [Pd(OAc)_2(MeSCH_2Z)_2]\ (\mathbf{9}, \mathbf{10}) \quad (2)$$

9: $Z = CH_2C(O)OMe$; **10**: $Z = CH(OMe)_2$

In this case, the methylene group is apparently not acid enough to allow the intramolecular proton exchange with the adjacent acetato. The ^{1}H- and ^{13}C-NMR spectra of the complexes are simple and coherent with the proposed nature of the products, as well as their FT-IR spectra. In particular, the monohapto acetato in complex **9** shows the asymmetric and symmetric stretchings at 1574 and 1408 cm^{-1} (1568 and 1408 cm^{-1}, **10**) and NMR resonances at 1.87 ppm (CH_3), 18.7 (CH_3) and 177.3 ppm (CO_2^-) (1.79, 19.8 and 177.7 ppm, **10**).

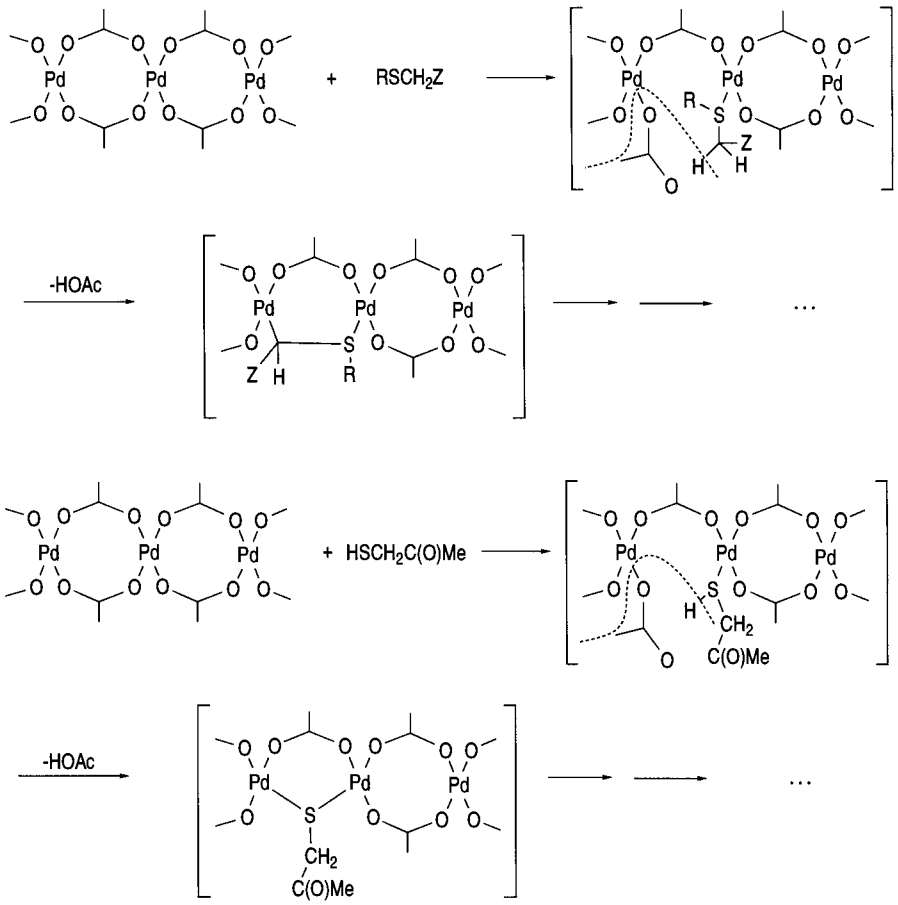
Under the same experimental conditions the replacement of an alkylthio by a thiol group in the ligand favours the exchange of all acetates with formation of the homoleptic complex **11** (Eq. (3)).

$$2[Pd_3(\mu\text{-}OAc)_6] + 12HSCH_2C(O)Me \rightarrow [Pd(SCH_2C(O)Me)_2]_6\ (\mathbf{11}) + 12HOAc \quad (3)$$

Its infrared spectrum clearly indicates that the carbonyl oxygen is not bonded to the metal centre [ν(CO) 1712 cm^{-1}] and also shows the absence of acetato ligands. The ^{1}H-NMR is characterized by the presence of four distinct resonances for the methylene and methyl protons. The intensities of the signals of the same set are different and in the case of CH_2 two singlets have an intensity double with respect to the others. This high number of signals is maintained in the ^{13}C solution spectrum, so supporting the polynuclear molecular structure determined by osmometric measurements. Similar values for the chemical shifts, but very large single signals are instead observed in the ^{13}C CP/MAS solid state spectrum: 30.4 (CH_3), 44.6 (CH_2) and 205.0 (C(O)Me) ppm. With these data, it seems reasonable to propose a coordination, in which the sulphur atom bridges two palladium centres in a cyclic toroidal structure, as found in other metal thiolato complexes [9].

It may be concluded that the nature of the products obtained in the reaction of palladium acetate with substituted thioethers or thiols depends on the properties of the sulphur ligand employed. If it does not possess any acidic hydrogen atom, a simple addition reaction takes place. The affinity of the soft sulphur atoms towards palladium(II), a soft metal centre, forces the acetato ligands to change their hapticity for allowing the coordination of two additional ligands.

When the thioethers $RSCH_2Z$ are substituted with electron-withdrawing groups ($Z = C(O)R'$, $C(O)OR'$, $S(O)_2Ph$), the sulphur bonded methylene protons are



Scheme 2.

activated. In spite of the relatively low acidity of these compounds with respect to acetic acid [10], the latter is displaced and mixed sphere complexes, in which half of the acetato ligands are replaced by anionic sulphur ligands, are formed. In this case, precoordination of the neutral thioether via the sulphur atom and change of the acetato hapticity are likely to occur. In this way, the acidic methylene protons are brought close to one acetato oxygen and this circumstance could lead to an intermediate (or transition state) in which the proton transfer from the methylene to the acetato is accompanied by the formation of the Pd–CH bond. In general, all these mixed sphere complexes exhibit the same formula and nuclearity.

Finally, when the thiol is reacted with palladium acetate, the homoleptic thiolate complex $[Pd(SCH_2C(O)Me)_2]_6$ is formed. In this case, the acidity of the HS group and the bridging coordination mode of the resulting S^- donor allow the quantitative displacement of acetic acid. The stoichiometry of these complexes implies that the thiolate ligands behave as bridging ligands and that the products are cyclic oligomers or infinite linear polymers. The former hypothesis is supported by the literature data, in that 'toroidal' structures containing four, six or eight '$M(SR)_2$' units are already known for the Ni(II) and Pd(II) complexes [9].

This synthetic evidence supports a mechanism, which implies for all reactions the preliminary coordination of the neutral ligand via its sulphur atom (Scheme 2).

In the absence of acidic sites a second neutral sulphur ligand enters the coordination sphere of the palladium centre (Eq. (2)), otherwise a proton exchange reaction takes place with the methylene (Eq. (1)) or thiol (Eq. (3)) groups. Upon coordination, the sulphur and carbon donors become stereogenic. The stereochemistry of the reaction seems governed by the configuration of the sulphur atom which gets attached first to the trimeric molecule of $[Pd_3(OAc)_6]$. In fact, the carbon atom of the adjacent methine group assumes the same configuration, as well as the donor atoms of the two further ligands. The observation that only half of the acetato group are substituted in Eq. (1) can be explained on the basis of the X-ray structure of $[Pd_3(\mu\text{-}OAc)_3(\mu\text{-}MeSCHC(O)OEt)_3]$. In fact, the OCO angle and OO distance of the residual acetate are slightly smaller than in the starting salt [3,11], which would make substitution by a CS bridge sterically unfavourable.

The formation of these mixed-sphere palladium trimers does not depend on the synthetic procedure employed; in fact, treatment of the neutral complexes $[PdCl_2(RSCH_2C(O)R')_2]$ with silver acetate gives in one step $[Pd_3(\mu\text{-}OAc)_3(\mu\text{-}RSCHC(O)R')_3]$, without any evidence of the formation of intermediates or by-products, such as O,S chelates or homoleptic thioether complexes [12]. It is remarkable that this monomer–trimer process is regio- and stereoselective and this clearly underlines the particular stability of the complexes with this mixed CSOO set of donor atoms. This is further confirmed by the easy synthesis of analogous trimers with different carboxylato ligands as $PhCOO^-$ and $MeSCH_2COO^-$.

Acknowledgements

We thank Antonio Ravazzolo for his skilled technical assistance and Progetto Strategico 'Tecnologie Chimiche Innovative', CNR, for partial financial support of this research.

References

[1] A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27.
[2] W. Keim, Angew. Chem. Int. Ed. Engl. 29 (1990) 235.
[3] M. Basato, A. Grassi, G. Valle, Organometallics 14 (1995) 4439.
[4] M. Basato, C. Bertani, B. Sesto, M. Zecca, A. Grassi, G. Valle, J. Organomet. Chem. 552 (1998) 277.
[5] C.K. Bradsher, F.C. Brown, R.J. Grantham, J. Am. Chem. Soc. 5 (1954) 114.
[6] R.F.X. Klein, V. Horak, J. Org. Chem. 51 (1986) 4644.
[7] T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer, G. Wilkinson, J. Chem. Soc. (1965) 3632.
[8] M. Basato, C. Bertani, M. Zecca, A. Grassi, G. Valle, J. Organomet. Chem. (in press).
[9] I.G. Dance, Polyhedron 5 (1986) 1037.
[10] F.G. Bordwell, Acc. Chem. Res. 21 (1988) 456.
[11] A.C. Skapski, M.L. Smart, J. Chem. Soc., Chem. Commun. (1970) 658.
[12] M. Basato, A. Cardinale, M. Zecca, G. Valle, Inorg. Chim. Acta (submitted for publication).