

Reactivity of $[\text{Pd}_3(\mu\text{-OAc})_3(\mu, \eta^2\text{-MeSCHCO}_2\text{Et-C,S})_3]$ in the presence of triphenylphosphine: a model of the early steps of the Pd/PR₃-catalysed Heck reaction

Marino Basato*^{a,1}, Barbara Sesto^a, Marco Zecca*^{a,2}, Giovanni Valle^b,
Sabrina Antonello^c, Flavio Maran*^{c,3}

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

^b Centro di Studio sui Biopolimeri, C.N.R., via Marzolo 1, I-35131 Padua, Italy

^c Dipartimento di Chimica Fisica, Università di Padova, via Loredan 2, I-35131 Padua, Italy

Received 23 July 1999; accepted 17 January 2000

Abstract

The stable complex $[\text{Pd}(\eta^1\text{-OAc})(\eta^2\text{-MeSCHCO}_2\text{Et-C,S})(\text{PPh}_3)]$ (**2**) is readily formed by addition of triphenylphosphine to $[\text{Pd}_3(\mu\text{-OAc})_3(\mu, \eta^2\text{-MeSCHCO}_2\text{Et-C,S})_3]$ (1:1 P:Pd) in acetone. It crystallizes in the monoclinic space group $C2/c$, with $Z = 8$, $a = 145.08(2)$, $b = 109.82(1)$, $c = 306.33(3)$ pm and $\beta = 96.3(1)^\circ$, $R(F) = 0.026$, $R_w(F^2) = 0.0765$. The coordination of a second triphenylphosphine to the palladium atom leads to $[\text{Pd}(\eta^1\text{-OAc})\{\text{CH}(\text{SMe})\text{CO}_2\text{Et}\}(\text{PPh}_3)_2]$ (**3**). Whereas **2** appears to be remarkably stable, **3**, after a slow reductive elimination, evolves mainly to $[\text{Pd}(\eta^2\text{-MeSCHCO}_2\text{Et-C,S})(\text{PPh}_3)_2]^-$. Zero-valent palladium species can also be generated by electrochemical reduction of **3**. The rate constant for the oxidative addition of iodobenzene to the electrogenerated palladium(0) species has been estimated. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Palladium complex; β -Oxothioether ligands; Phosphines; Oxidative addition; Reductive elimination; Aryl iodides

1. Introduction

We have recently published the synthesis of the mixed-sphere trimeric complex of palladium(II), $[\text{Pd}_3(\mu\text{-OAc})_3(\mu, \eta^2\text{-MeSCHCO}_2\text{Et-C,S})_3]$ (**1**) [1]. This complex is isostructural to palladium acetate and the three bridging sulfur ligands lie on the same side of the Pd₃ plane. The coordinated sulfur atoms can bind further to electrophilic metal centres. For example, we have found that **1** reacts with either $[\text{Pd}(\text{NCMe})_4](\text{BF}_4)_2$ or $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ and behaves as an organometallic ligand towards Pd(II) and Cu(I) in the relevant adducts [2]. We have also investigated the reactivity of **1** with bidentate nucleophiles, both neutral (bipyridine) and monoanionic (acetylacetonate, benzoylacetonate) [3]. In

the reaction with bipyridine the sulfur ligand is displaced from the metal coordination sphere and $[\text{Pd}(\text{OAc})_2(\text{bipy})]$ is the main product. By contrast, the reaction with β -diketones affords dimers or trimers with bridging sulfur ligands and chelate β -diketonates are formed.

We report herein data on the reactivity of **1** with triphenylphosphine. The presence of acetato ligands in the coordination sphere of palladium(II) centres and the close structural relationship to palladium acetate make the reactivity of complex **1** towards PPh₃ very similar to that of $[\text{Pd}(\text{OAc})_2]$. The system $[\text{Pd}(\text{OAc})_2]/\text{PR}_3$ has been the subject of extensive investigation, as it is commonly used to catalyse the Heck reaction [4]. Phosphines reduce $[\text{Pd}(\text{OAc})_2]$ and the reaction affords zero-valent palladium species along with the pertinent phosphine oxide [5–7]. Electrochemical and ³¹P-NMR studies have shown that, in the presence of an excess of PPh₃, the reactive anionic complex $[\text{Pd}(\eta^1\text{-OAc})(\text{PPh}_3)_2]^-$ is in equilibrium with the coordinatively

¹*Corresponding author. Fax: +39-049-8275223; e-mail: basato@chin.unipd.it

²*Corresponding author. E-mail: mzecca@chin.unipd.it

³*Corresponding author. E-mail: f.maran@chfi.unipd.it

saturated species $[\text{Pd}(\eta^1\text{-OAc})(\text{PPh}_3)_3]^-$ and readily undergoes oxidative addition of iodobenzene [8]. These reactions account for the activation of aryl halides in the Heck reaction, according to a widely accepted mechanism [2]. We have also found that **1** is reduced by an excess amount of PPh_3 and that the ensuing zero-valent palladium species undergoes oxidative addition of iodobenzene. The reduction is a stepwise process, in which the C,S-chelate [2,9] monophosphino complex $[\text{Pd}(\eta^1\text{-OAc})(\eta^2\text{-MeSCHCO}_2\text{Et-C,S})(\text{PPh}_3)]$ (**2**) is formed first. The intermediacy of palladium(0) species was also supported by analysis of the voltammetric behaviour of the **1**/ PPh_3 system. In addition, electrochemistry provided relevant information on the effect of added PPh_3 on the reduction of **1**, the oxidation of the zero-valent palladium species and the reactivity of the latter towards iodobenzene.

2. Experimental

2.1. Reagents and apparatus

Palladium acetate (98%), ethyl (methylthio)acetate (98%) and other products were supplied by Aldrich. All of them except for triphenylphosphine, which was recrystallized from hot ethanol prior to use, were used as received. Anhydrous solvents were purchased from BDH and stored under inert atmosphere over molecular sieves. All the syntheses were carried out under inert atmosphere with standard vacuum/Schlenk line techniques. $[\text{Pd}_3(\mu\text{-OAc})_3(\mu,\eta^2\text{-MeSCHCO}_2\text{Et})_3]$ (**1**) was synthesized as described in Ref. [3]. FTIR spectra were recorded on either a Bruker IFS 66 Fourier Transformer or a Biorad FT S7 PC spectrophotometer. NMR measurements were carried out with a Jeol FX 90Q Fourier transform spectrometer. Chemical shifts were referenced to either TMS ($^1\text{H-NMR}$ and $^{13}\text{C-NMR}$) or 75% aqueous H_3PO_4 ($^{31}\text{P-NMR}$).

2.2. Synthesis of

$[\text{Pd}(\eta^1\text{-OAc})(\eta^2\text{-MeSCHCO}_2\text{Et})(\text{PPh}_3)]$ (**2**)

PPh_3 (0.26 g, 1 mmol) was added to a suspension of **1** (0.30 g, 0.33 mmol) in anhydrous acetone (30 cm^3). The suspension immediately cleared. In a few minutes the colour of the solution turned to green and a solid started to precipitate. The suspension was stirred for a further 30 min and then most of the solvent was removed under reduced pressure. A greenish solid precipitated and was recovered by filtration (0.40 g, 73%). Recrystallization from dichloromethane–acetone afforded the light yellow complex **2** (60%). $\text{C}_{25}\text{H}_{27}\text{O}_4\text{PPdS}$ (FW 560.93): Calc. C, 53.53; H, 4.85; S, 5.71. Found: C, 53.48; H, 4.78; S, 5.71%. $^1\text{H-NMR}$ (27°C; CDCl_3): $\delta = 0.92$ (t, 3H, CH_3CH_2), 1.67 (s, 3H, CH_3CO_2), 2.49

(d, 3H, CH_3S , $^4J_{\text{HP}} = 4.6$ Hz), ca. 3.5 (m, 2H, CH_2CH_2), 3.70 (s, 1H, SCH), 7.43–7.59 (m, 15H, C_6H_5). $^{13}\text{C-NMR}$ (27°C; CDCl_3): $\delta = 13.7$ (CH_3CH_2), 22.1, 23.3 (CH_3S and CH_3CO_2), 52.0 (CH), 60.7 (CH_3CH_2), 128.1–134.1 (C_6H_5), 169.5 ($\text{C}(\text{O})\text{OEt}$), 177.8 (CH_3CO_2). $^{31}\text{P-NMR}$ (27°C; CDCl_3): $\delta = 31.77$ (s, PPh_3). $^1\text{H-NMR}$ (27°C; $[\text{D}_7]$ DMF): $\delta = 0.82$ (t, 3H, CH_3CH_2 , $^3J_{\text{HH}} = 7.1$ Hz), 1.68 (s, 3H, CH_3CO_2), 2.58 (d, 3H, CH_3S , $^4J_{\text{HP}} = 4.9$ Hz), 3.56 (AB system m, 2H, CH_2CH_2 , $^2J_{\text{AB}} = 11.0$ Hz), 4.15 (s, 1H, SCH), 7.50–7.56 (m, 15H, C_6H_5). $^{31}\text{P-NMR}$ (27°C; $[\text{D}_7]$ DMF): $\delta = 32.99$ (s, PPh_3). FTIR (KBr disk): $\nu(\text{CO}) = 1705$ (s, ester); 1601, 1373 (s, acetate).

2.3. Reaction of $[\text{Pd}_3(\mu\text{-OAc})_3(\mu,\eta^2\text{-MeSCHCO}_2\text{Et})_3]$ (**1**) with PPh_3

The progress of the reaction in THF and DMF solution was followed by means of FTIR and ^1H - and ^{31}P -NMR spectroscopy, respectively. In the first case, **1** (0.25 g, 0.28 mmol) was dissolved in THF (20 cm^3) and PPh_3 (0.44 g, 1.78 mmol, 2:1 P:Pd) was added to the solution. Aliquot portions of the reaction mixture were periodically analysed by FTIR in the 4000–1000 cm^{-1} range. As we first found (see Section 3) that under these conditions half of the phosphine is consumed to form complex **2**, in the second case we used it directly as the starting material. Thus, **2** (8.4 mg, 15 μmol) was transferred into a NMR tube and dissolved with 300 μl of $[\text{D}_7]$ DMF, and PPh_3 (3.9 mg, 15 μmol) was added to the solution. The reaction was allowed to proceed in the NMR tube at 27°C without stirring and in contact with air. ^1H - and ^{31}P -NMR spectra of the reaction mixture were periodically recorded. Apparently, no solid precipitated from the solution, which remained clear for at least 6 days: in particular, no metallic palladium formed.

2.4. Reaction of $[\text{Pd}_3(\mu\text{-OAc})_3(\mu,\eta^2\text{-MeSCHCO}_2\text{Et})_3]$ (**1**) with PhI in the presence of PPh_3

The reaction of **1** with iodobenzene (equimolar amount vs. palladium) was studied in anhydrous benzene in the presence of PPh_3 and several bases. Typical reaction conditions were as follows: **1** (0.16–0.20 g, 0.18–0.22 mmol) was dissolved in anhydrous benzene and PPh_3 (0.29–0.35 g, 1.08–1.34 mmol, P:Pd = 2) was added to the solution. Iodobenzene (62.2–75.9 cm^3 , 0.54–0.66 mmol, PhI:Pd = 1) and the base were added immediately thereafter to the solution. The base:Pd molar ratio was equal to 1 for $n\text{-Bu}_4\text{NOAc}$ and NPh_3 , whereas it was equal to 2 for 1,8-dimethyl-aminonaphthalene ('proton sponge', PS). After stirring for several days (3–7), the solvent was removed, mostly or completely, from the reaction mixtures under reduced pressure. Upon treatment with anhydrous diethyl ether, the

obtained residues (oils or concentrated solutions) yielded solid products, whose colours ranged from brick red to brown. Typical analytical and spectroscopic data were as follows (reaction with NPh_3). The elemental analysis is not coherent with the formation of pure $[\text{Pd}(\eta^1\text{-OAc})(\text{Ph})\text{PPh}_3]$, which requires C, 61.86 and H, 4.59. The values found (C, 58.12; H, 4.26%) are consistent with a mixture of $[\text{Pd}(\eta^1\text{-OAc})(\text{Ph})\text{PPh}_3]_2$, $[\text{PdI}(\text{Ph})\text{PPh}_3]_2$ and $[\text{PdI}(\text{Ph})(\text{PPh}_3)_2]$ (7:4:4, mol; C, 58.01; H, 4.18). The expected ratio between aromatic protons and acetato protons in this mixture is 14. $^1\text{H-NMR}$ (27°C; CDCl_3): $\delta = 1.67$ (s, 3H, CH_3CO_2), 7.5–7.7 (m, 45H, $\text{PC}_{18}\text{H}_{15} + \text{C}_6\text{H}_5$), weak singlets also at 0.58, 0.95, 1.20, 1.28 ppm. $^{31}\text{P-NMR}$ (27°C; CDCl_3): $\delta = 22.94, 21.33, 20.46, 12.85$.

When the reaction was performed in the presence of $^n\text{Bu}_4\text{NOAc}$, a second solid product spontaneously separated within a few days from the solution recovered after the separation of the first precipitate. After washing with ethyl acetate to remove triphenylphosphine oxide, the solid was dried and characterized. $\text{C}_{26}\text{H}_{23}\text{O}_2\text{PPd}$ ($[\text{Pd}(\eta^1\text{-OAc})(\text{Ph})\text{PPh}_3]$, FW = 504.8): Calc.: C, 61.86; H, 4.59. Found: C, 59.26; H, 4.37%. $^1\text{H-NMR}$ (27°C; CDCl_3): $\delta = 1.67$ (s, 3H, CH_3CO_2), 7.3–7.8 (m, 20H, $\text{PC}_{18}\text{H}_{15} + \text{C}_6\text{H}_5$). $^{31}\text{P-NMR}$ (27°C; CDCl_3): $\delta = 28.8$.

2.5. Reaction of $[\text{Pd}_3(\mu\text{-OAc})_3(\mu, \eta^2\text{-MeSCHCO}_2\text{Et})_3]$ (1) with MeI in the presence of PPh_3

Complex **1** (0.25 g, 0.28 mmol) was dissolved in anhydrous toluene (10 cm^3). PPh_3 (0.65 g, 2.5 mmol, P: Pd = 3) was added to the solution and iodomethane (55 μl , 0.84 mmol, MeI: Pd = 1) immediately thereafter. The colour of the solution immediately turned from red to dark red. After 5 h under magnetic stirring, traces of a solid were filtered off and an orange solid precipitated upon addition of ethyl ether to the filtrate. $\text{C}_{23}\text{H}_{24}\text{IO}_2\text{PPdS}$ ($[\text{PdI}(\text{MeSCHCO}_2\text{Et})\text{PPh}_3]$, FW = 628.81): Calc. C, 43.93; H, 3.85; S, 5.10. $\text{C}_{59}\text{H}_{54}\text{IO}_2\text{P}_3\text{PdS}$ ($[\text{Pd}\{\eta^1\text{-CH}(\text{SMe})\text{CO}_2\text{Et}\}(\text{PPh}_3)_3\text{I}]$, FW = 1153.39): Calc.: C, 61.44; H, 4.72; S, 2.78. Found: C, 51.80; H, 4.25; S, 3.75%. $^1\text{H-NMR}$ (27°C; CDCl_3): $\delta = 0.91$ (2t, 3H CH_3CH_2), 1.96 (s, br, 1.2H, CH_3S), 2.35 (d, $^4J_{\text{HP}} = 4.9$ Hz, 1.8H, CH_3S), ca. 3.5 (m, 2H, CH_3CH_2), 3.77 (s, br, 1H, CHS), 7.3–7.8 (ca. 30H, Ph).

2.6. Electrochemistry

N,N-Dimethylformamide (Janssen, 99%) and tetrabutylammonium perchlorate (TBAP, 99%, Fluka) were purified as previously described [10]. Electrochemical measurements were conducted in an all-glass cell and under an argon atmosphere. The glassy carbon (Tokai GC-20) disk electrode was prepared and activated be-

fore each measurement [10]. The gold (Goodfellow, 99.99%) disk electrode was prepared and activated in a similar way. The reference electrode was a homemade Ag/AgCl, calibrated after each experiment against the ferrocene/ferricinium couple and then against the KCl saturated calomel electrode, SCE (in DMF–0.1 M TBAP, $E_{\text{Fc}/\text{Fc}^+}^0 = 0.464$ V vs. SCE). In the following all of the potential values will be reported against SCE. The counterelectrode was a 1 cm^2 Pt plate. The voltammetric curves were obtained by using an EG&G-Parc 173 potentiostat, an EG&G-Parc 175 universal programmer, and a Nicolet 3091 12-bit resolution digital oscilloscope. The feedback correction was applied in order to minimize the ohmic drop between the working and reference electrodes. In most of the experiments, the cyclic voltammograms were recorded in a selected potential range and for scan rates ranging from 0.1 to 200 V s^{-1} by the digital oscilloscope (digitalized 1 point/mV) and then transferred to a PC. The curves were then analysed by the conventional voltammetric criteria [11], using our own laboratory software. Digital simulations of the cyclic voltammetry curves were performed by using the DigiSim 2.1 software by Bioanalytical Systems Inc.

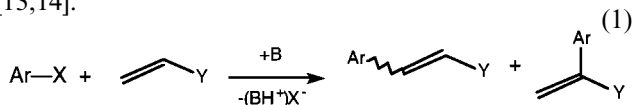
2.7. Crystal-structure determination of $[\text{Pd}(\eta^1\text{-OAc})(\eta^2\text{-MeSCHCO}_2\text{Et})(\text{PPh}_3)]$ (2)

Suitable crystals for X-ray diffraction were obtained upon slow evaporation of acetone solutions of **2**. 4964 independent reflections up to $\theta = 28^\circ$ were collected by means of a Philips PW 1100 four-circle diffractometer using the θ – 2θ technique and the monochromatic Mo-K_α radiation with $\lambda = 71.07$ pm. The positional parameters for C, S, O and Pd atoms were determined directly with SHELXS-86 and were refined on F^2 (SHELX-93) through least-squares cycles using anisotropic thermal parameters. All of the hydrogen atoms were identified in the difference Fourier map, constrained to the parent site and refined with isotropic thermal parameters. An idealized geometry was imposed on the phenyl rings. The conventional final $R(F)$ value is 0.026 (for the observed 4338 reflections with $F > 4\sigma(F)$), whereas the $R_w(F^2)$ value is 0.0765 for all data ($w = 1/[\sigma^2(F^2) + (0.0499P)^2]$, $P = (F_o^2 + 2F_c^2)/3$). Molecular formula: $\text{C}_{25}\text{H}_{27}\text{O}_4\text{PPdS}$ (FW = 560.93); crystal system: monoclinic; space group: $C2/c$; a, b, c (pm): 145.08(2), 109.82(1), 306.63(3), β ($^\circ$) = 96.3(1); V (Å^3) = 4851(3); $Z = 8$. D_{calc} . (g cm^{-3}) = 1.536.

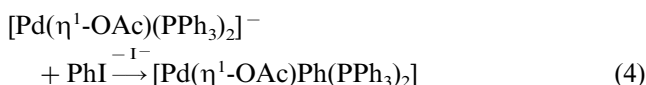
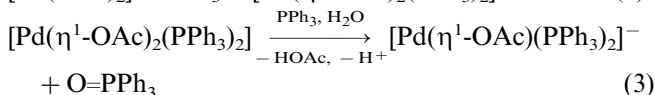
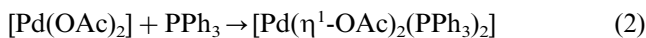
3. Results and discussion

Palladium acetate is the precursor of many catalytic systems employed in organic synthesis [12]. The olefination of aryl halides (Heck reaction, Eq. (1)), in particu-

lar, has been the subject of several recent studies [13,14].



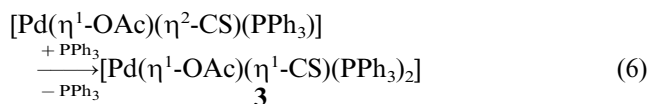
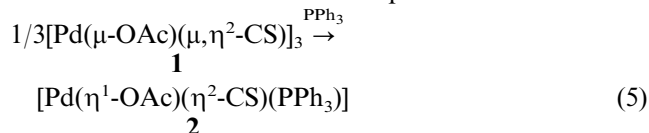
One of the most interesting features is that this reaction is rather insensitive to the nature of the reactants, yielding a wide range of products. It is promoted by palladium(II) acetate in the presence of an excess amount of alkyl or aryl phosphines ($\text{P}:\text{Pd} = 2$). In this context, both the behaviour of palladium(II) acetate and its reactivity with iodobenzene in the presence of tertiary phosphines have been investigated by means of electrochemical and spectroscopic ($^3\text{P-NMR}$) techniques [6–8]. These studies demonstrated the intermediacy of zero-valent palladium species, such as $[\text{Pd}(\eta^1\text{-OAc})(\text{PPh}_3)_x]^-$, undergoing oxidative addition of iodobenzene. The rate-determining step of this process is the slow reductive elimination of AcOPPh_3^+ from $[\text{Pd}(\eta^1\text{-OAc})_2(\text{PPh}_3)_2]$, which forms quickly upon coordination of two phosphine molecules (Eqs. (2)–(4)):



These steps are believed to be involved in the catalyst formation and the activation of the aryl halides in the Heck reaction. The complex $[\text{Pd}_3(\mu\text{-OAc})_3(\mu, \eta^2\text{-MeSCHCO}_2\text{Et})_3]$ (**1**) bears a close structural relationship with palladium(II) acetate. Whereas the latter has trimeric molecules with six bridging acetato ligands, complex **1** has three bridging acetato ligands and three bridging C,S (methylthio)(ethoxycarbonyl)methyl lig-

ands. In addition, the three acetato ligands and the three sulfur ligands lie on opposite sides with respect to the plane of the palladium atoms. The sulfur ligands displayed a greater affinity to palladium(II) than acetate. In fact, despite the much lower acidity of ethyl (methylthio)acetate than acetic acid (the $\text{p}K_a^{\text{DMF}}$ values are 24.9 and 13.5, respectively) [15,16], half of the acetates were displaced as acetic acid and substituted by an equal number of $\text{MeSCHCO}_2\text{Et}^-$ ligands.

In agreement with its structural analogy with palladium(II) acetate, complex **1** readily reacts with phosphines. The presence of the sulfur ligand, however, stabilizes the adducts with triphenylphosphine. In fact, we obtained evidence for the stepwise reaction:



The stabilization brought about by the sulfur ligand is such that we were able to isolate complex **2** in a pure form and obtain crystals suitable for XRD analysis (Fig. 1).

The phosphine attacks the trimeric complex **1** and disrupts its polynuclear structure. Although both the acetato and the sulfur ligands are bidentate (O,O and C,S, respectively) in the starting complex, only the sulfur ligand is still bidentate in complex **2**. This is a consequence of the higher affinity of the soft sulfur donor atoms towards the soft palladium(II) centres, in comparison with the hard oxygen donor atoms. It is remarkable that in this chelate mode the coordinated C and S atoms also adopt the same absolute configuration as observed in the starting bridged trimer. The main structural feature of complex **2** is the presence of a strained three-membered metallacycle. The oxygen and phosphorus donors also lie in the plane of the metallacycle. The structure is quite similar to that of $[\text{PdCl}(\eta^2\text{-CH}_2\text{SMe})(\text{PPh}_3)]$ (**5**) [9]. The bond distances (pm, Table 1) of the four donor atoms from the palladium atom in **2** are as follows: 203.5(3) (Pd–C), 234.4(1) (Pd–S), 226.9(1) (Pd–P), 209.2(2) (Pd–O). They are very close to the values observed for **5**: 204.2(6) (Pd–C), 237.1(1) (Pd–S), 226.7(1) (Pd–P) pm. The difference between the Pd–O distance and the Pd–Cl distance, 240.2(1) pm, is the same as the difference in the covalent radii of oxygen and chlorine, respectively, and reflects only the different sizes of the two donor atoms. Also, the bond angle values compare well with those observed in the dimethylsulfide derivative. The S–Pd–C angle, for instance, is 46.72(6)° wide with respect to 45.4(3)° in **5**. The opposite angles, O–Pd–P in **2** and Cl–Pd–P in **5**,

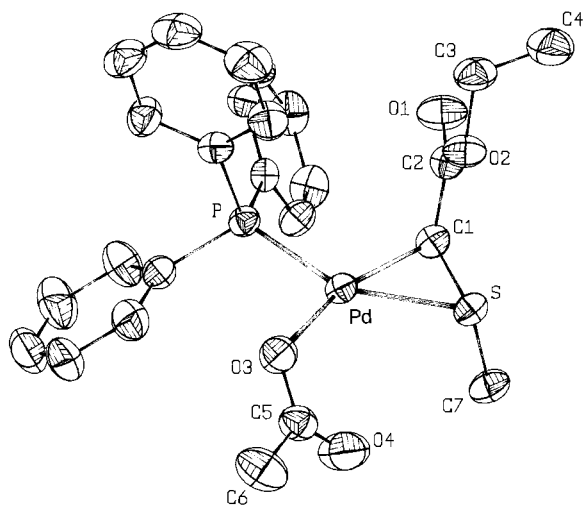
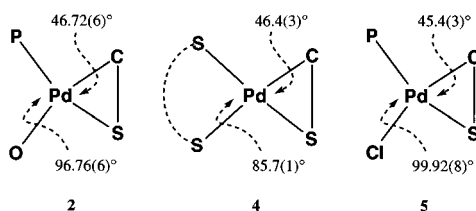


Fig. 1. ORTEP view of $[\text{Pd}(\eta^1\text{-OAc})(\eta^2\text{-MeSCHCO}_2\text{Et})(\text{PPh}_3)]$ (**2**).

Table 1
Selected bond distances (pm) and angles (°) for [Pd(η^1 -OAc)(η^2 -MeSCHCO₂Et)(PPh₃)] (**2**)

| Bond distances | | | |
|----------------|-----------|----------------|-----------|
| Pd–P | 226.9(1) | Pd–S | 234.4(1) |
| Pd–O(3) | 209.2(2) | Pd–C(1) | 203.5(3) |
| S–C(1) | 175.9(2) | S–C(7) | 180.3(2) |
| O(1)–C(2) | 120.2(3) | O(2)–C(2) | 134.5(2) |
| O(2)–C(3) | 145.5(3) | O(3)–C(5) | 127.2(3) |
| O(4)–C(5) | 122.1(3) | C(1)–C(2) | 147.3(3) |
| C(3)–C(4) | 146.3(5) | C(5)–C(6) | 150.7(4) |
| Bond angles | | | |
| O(3)–Pd–C(1) | 159.37(8) | S–Pd–C(1) | 46.72(6) |
| S–Pd–O(3) | 112.76(6) | P–Pd–C(1) | 103.58(6) |
| P–Pd–O(3) | 96.76(6) | P–Pd–S | 150.18(2) |
| Pd–S–C(7) | 104.5(1) | Pd–S–C(1) | 57.35(8) |
| C(1)–S–C(7) | 102.4(1) | C(2)–O(2)–C(3) | 116.2(2) |
| Pd–O(3)–C(5) | 114.2(2) | Pd–C(1)–S | 75.9(1) |
| S–C(1)–C(2) | 117.6(2) | Pd–C(1)–C(2) | 116.5(2) |
| O(2)–C(2)–C(1) | 112.8(2) | O(1)–C(2)–C(1) | 123.7(2) |
| O(1)–C(2)–O(2) | 123.5(2) | O(3)–C(5)–O(4) | 124.9(2) |
| O(4)–C(5)–C(6) | 119.9(3) | O(3)–C(5)–C(6) | 115.1(3) |



Scheme 1.

are, respectively, equal to 96.76(6) and 99.92(8)°. The C–S distances in the three-membered rings are 175.9(2) and 175.6(6) pm in **2** and **5**, respectively: both these values are lower than the respective S–CH₃ bond lengths, 180.3(2) and 180.7(7) pm. This suggests that the C–S bond order in the palladacycle is higher than one. No electronic delocalization, however, involves the ethoxycarbonyl substituent, which maintains well-defined single and double bonds.

The strongly distorted square-planar geometry around the palladium atom is unaffected by substitution of the chloro ligand with the acetato and by replacement of one hydrogen atom at the metal-bound carbon atom with the bulkier ethoxycarbonyl group. The geometry of the palladium(II) coordination sphere is apparently dominated by the formation of the three-membered palladacycle, at least in monomeric complexes. We observed a slightly different situation in the tetranuclear cationic complex [Pd₄(μ -OAc)₃(μ , η^2 -CS)(μ_3 , η^2 -CS)₂(η^2 -CS)](BF₄) (**4**) [2]. This compound can be considered as a complex between **1**, acting as a bidentate S,S Lewis base, and the cationic, cyclic fragment [Pd(η^2 -MeSCHCO₂Et)]⁺. In this case, the constraint imposed by the relatively rigid structure of the bidentate S,S ligand onto the palladacycle also influ-

ences its geometry around the palladium atom: in fact, although the C–Pd–S angle in the ring is equal to 46.4(3)°, the opposite S–Pd–S angle, 85.7(1)°, is relatively sharp (Scheme 1).

The analytical and spectroscopic data are fully consistent with the crystal structure of **2**. The asymmetric and symmetric stretching bands of the coordinated acetate shifted to 1601 and 1373 cm⁻¹ (1557 and 1414 in **1**), respectively, whereas the ester carbonyl stretching band was observed at 1705 cm⁻¹, the same as in **1**. Several bands due to the presence of the phosphine were observed at 1582, 1480, 1435 and 1097 cm⁻¹. More valuable information can be gathered from the ¹H- and ³¹P{¹H}-NMR spectra in solution. The most interesting features of the ¹H spectrum are the multiplicity of the signal due to the protons of the methylthio group and of the signal from the protons of the methylene in the ethoxy group. The former appears as a doublet, due to the coupling (⁴J_{HP} = 4.6 Hz) with the P nucleus of the phosphine in *trans* to the sulfur donor atom. The same coupling was previously observed in complex **5** (⁴J_{HP} = 4.0 Hz) [9]. A complex multiplet arises from the methylene protons (ethoxy), due to the geminal coupling between them and to the vicinal coupling with the methyl protons. In fact, the two methylene protons are not equivalent due to the asymmetry of the methine carbon atom, which stems from its coordination to the palladium atom. The analysis of the multiplet in [D₇] DMF yielded the ²J_{HH} and ³J_{HH} values of 11.0 and 7.1 Hz, respectively. These are practically the same as those observed in the protonic spectra of complex **1**, in which the signal of the corresponding methylene shows the same hyperfine structure [1]. These results are a clear evidence that in solution the sulfur and methine carbon atoms of the ethyl (methylthio)acetate anion are also both coordinated to the palladium atom and that the phosphine is *trans* to the former. The different mode of coordination of both the acetate and the sulfur ligands are highlighted by the chemical shifts of the relevant signals with respect to **1**.

Thus, the protons of the η^1 acetate resonate at 1.81 ppm versus 2.08 in complex **1**. Also, the methyl and the methylene protons of the ethoxy group resonate 0.3–0.5 ppm upfield in comparison with **1** (0.92 and ca. 3.5 vs. 1.24 and 4.10, respectively). By contrast, the chemical shift of the CH₃S hydrogen nuclei is ca. 0.4 ppm downfield with respect to **1** (2.49 vs. 2.14). The proton resonance of the coordinated methine strongly depends on the solvent employed. It was observed at 3.70 ppm in CDCl₃ and at 4.14 ppm in [D₇] DMF (3.63 ppm in CDCl₃ for **1**). The difference between the ¹³C chemical shifts of the methine carbon atom in **1** and **2**, respectively, are even more significant. In fact, whereas the methine carbon atom in **1** resonates at 25.09 ppm (CD₂Cl₄ [1]), its resonance was observed at 52.0 ppm (CDCl₃) in **2**. The ³¹P{¹H} spectrum is exceedingly

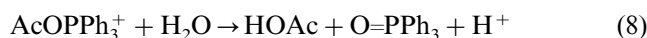
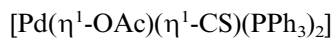
simple, with a single sharp resonance at 31.77 ppm (32.99 ppm in $[D_7]$ DMF). This means that **2** does not undergo any exchange reaction at room temperature. The overall NMR picture demonstrates that complex **2** holds in solution the same structure as in the solid state.

The formation and isolation of complex **2** is considered as particularly interesting. In fact, whereas the reaction of $Pd(OAc)_2$ with PPh_3 to form $[Pd(\eta^1-OAc)_2(PPh_3)_2]$ is immediate [6], in our case the monophosphino species is stabilised by the sulfur ligand and could be isolated. The relatively high stability arises from the chelate effect, which enhances the effective coordination capability of the sulfur donor atom relative to that of the second phosphine. It is worth noting that complex **2** is stable, despite the presence of both one phosphine and one monohapto acetato, in *cis* position, in the coordination sphere of palladium(II). This is the same situation holding for $[Pd(\eta^1-OAc)_2(PPh_3)_2]$, the key precursor of the active catalyst of the Heck reaction. However, whereas the latter complex spontaneously gives reductive elimination, **2** does not.

Starting from complex **2**, a second molecule of triphenylphosphine can be coordinated to the palladium centre. This is clearly demonstrated by 1H -NMR in $[D_7]$ DMF: upon addition of one equivalent of phosphine the coupling of the methylthio protons with the phosphorus nucleus immediately disappeared. Their chemical shift, in comparison with **2**, is slightly upfield (2.53 vs. 2.58 ppm) and that of the coordinated methine 0.20 ppm downfield (4.34 vs. 4.14 ppm). This pattern is similar to that of $[PdCl(\eta^1-CH_2SMe)(PPh_3)_2]$ (**6**) [17]. Accordingly, these results indicate that the second phosphine displaces the sulfur donor atom from the palladium centre and that $[Pd(\eta^1-OAc)\{\eta^1-CH(SMe)CO_2Et\}(PPh_3)_2]$ (**3**, Eq. (6)) is formed. The relevant $^{31}P\{^1H\}$ -NMR spectrum in $[D_7]$ DMF at 27°C shows a single, broad peak observed at 17.19 immediately after the addition of the phosphine, which suggests the occurrence of fast phosphine exchange equilibria. The reversible formation of cationic species upon detachment of the acetato ligands can be ruled out on the basis of the protonic spectrum of **3**, although it is known that complex **6** can lose reversibly the chloro ligand [13].

Attempts to isolate a pure sample of **3** were unsuccessful, due to the rapid equilibrium reactions involving **1–3** and to the progressive reduction of Pd(II) to Pd(0). The reaction of **1** and of **2** with triphenylphosphine to yield **3** was followed, respectively, by FTIR in THF solution and 1H - and $^{31}P\{^1H\}$ -NMR spectroscopy in DMF solution. The FTIR investigation on the disappearance of **1** revealed a rapid change of the coordination mode of the acetato ligands. The typical band of the monohapto acetate at 1609 cm^{-1} appeared within 5

min after the addition of the phosphine to the starting metal complex. After 4 h two bands, at 1202 and 1119 cm^{-1} and attributed to the presence of $O=PPh_3$, were detected. At the same time, the intensity of the bands of the coordinated acetate decreased. After several hours (overnight), the appearance of the band at 1732 cm^{-1} revealed the presence of the protonated sulfur ligand, $MeSCH_2CO_2Et$. These results indicate that (i) the formation of complex **2** and its further reaction with PPh_3 (Eqs. (5) and (6)) are fast and that (ii) the reductive elimination of $AcOPPh_3^+$ from **3**, followed by the hydrolysis of the cation, takes place (Eqs. (7) and (8)) slowly. The latter observation is in agreement with the results obtained with the $[Pd(OAc)_2]/PPh_3$ system, where the same slow reductive elimination was observed (first order in palladium concentration, $t_{1/2} = ca. 45\text{ min}$, Pd:P = 1:20, DMF) [7].



Our NMR results are in full agreement with the above picture. In fact, whereas after ca. 2 h only traces of $O=PPh_3$ were detectable by means of ^{31}P -NMR, after ca. 3.5 h the oxide amounted to about 10% of the total phosphorus species in the reaction mixtures. After ca. 24 h, the triphenylphosphine oxide represented ca. 30% of the total phosphorus, corresponding to the reduction of ca. 60% of palladium(II) initially present. No further formation of $O=PPh_3$ was observed up to 122 h. The occurrence of the reductive elimination was also confirmed by the formation of significant amounts of $[Pd(O_2)(PPh_3)_2]$, which is known to be formed by the oxidative addition of dioxygen to some zero-valent palladium species. This complex, which accounts for ca. 25% of the total phosphorus in solution after 122 h, was detected by the ^{31}P resonance at 33.49 ppm (33.42 ppm in a 0.3 M solution of nBu_4NBF_4 in DMF) [18]. The formation of $[Pd(O_2)(PPh_3)_2]$ suggests that its parent zero-valent palladium species already contained at least two phosphine molecules per palladium atom. It is noteworthy that, no evidence for the formation of metallic palladium was gained and all the reaction mixtures always remained as clean solutions. The proton spectra of the reaction mixture ($t > 4\text{ h}$) are rather complex. Several resonances were observed in the higher field region ($\delta < 4.5$), but none of them could be attributed to either the free sulfur ligand or the palladium(II) complexes **1**, **2** and **3**. Since protons are supposed to form upon hydrolysis of the acetoxytriphenylphosphonium cation (Eqs. (7) and (8)), it seems likely that the sulfur ligand was protonated and that the observed resonances stemmed from coordinated, neutral $MeSCH_2CO_2Et$.

The reductive elimination stopped at about 50% yield. One possible explanation is that as soon as the first reaction product, $[\text{Pd}(\text{MeSCHCO}_2\text{Et})(\text{PPh}_3)]^-$ (**7**), is formed, it reacts with PPh_3 to give $[\text{Pd}(\text{MeSCHCO}_2\text{Et})(\text{PPh}_3)_2]^-$ (**8**) (Scheme 2), which eventually transforms into $[\text{Pd}(\text{O}_2)(\text{PPh}_3)_2]$. In fact, **7** is expected to be unstable because of coordinative unsaturation and the strain of the three-membered palladacycle. The strain could be released by ring opening, but an even less coordinated species would be obtained. Therefore, **7** took up a further phosphine molecule. As only two equivalents of phosphine per palladium were present in the system, **7** competed effectively with **2** for the additional phosphine molecule. This implies that when about half of the total palladium has been reduced, **3** is essentially no longer present in solution and the reductive elimination stopped. The electrochemical data reported below fully support this hypothesis. The addition of excess triphenylphosphine to a solution of **1** in anhydrous benzene (P:Pd = 5:1) led to the formation

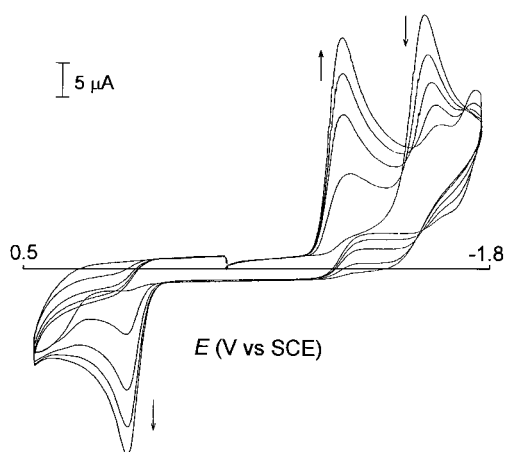
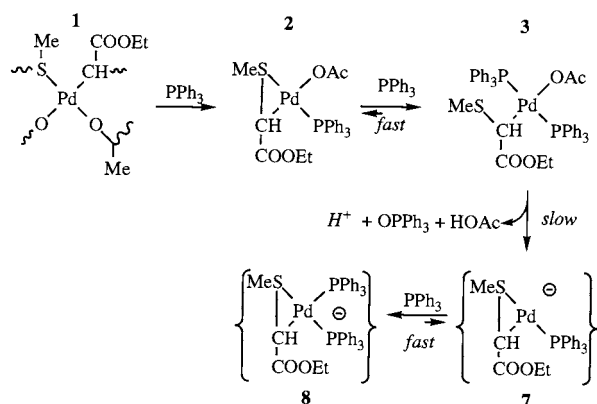


Fig. 2. Cyclic voltammetry curves for the reduction of 2.7 mM **2** in DMF–0.1 M Bu_4NClO_4 at a glassy carbon electrode. The five curves were recorded after addition of 0, 0.25, 0.50, 0.75, and 1 equivalent of PPh_3 . The arrows indicate the corresponding variations of the reduction and oxidation peaks, 0.2 V s^{-1} , 25°C .

of $[\text{Pd}(\text{PPh}_3)_4]$, which was isolated from the reaction mixture.

Cyclic voltammetry allowed us to confirm the above findings and provided additional information on both the solution equilibria and the reactivity of zero-valent palladium species. The voltammetric analysis was carried out in DMF–0.1 M Bu_4NClO_4 , using a glassy carbon electrode. Although we found that the voltammetric pattern at a gold electrode was essentially the same, the glassy carbon electrode proved to be superior from the point of view of both the quality of the curves and the reproducibility of the results. At a scan rate of 0.2 V s^{-1} , the electroreduction of **1** is chemically irreversible and the peak is located at -1.31 V . Starting from 0.5 V s^{-1} , however, the anodic peak corresponding to the re-oxidation of the species electrogenerated upon reduction of **1** is detectable during the return scan. Digital simulation of the voltammetric curve led us to estimate the lifetime of the reduction product to be ca. 0.1 s. By using the voltammetric data obtained at high scan rates, the standard potential for the reduction of **1** could be calculated to be -1.24 V . The complex was found to be stable in solution, up to several hours. Upon addition of PPh_3 (1:1 Pd:P), complex **2** was rapidly formed. In fact, the same voltammetric pattern was observed by using an authentic sample of **2**. The voltammetric behaviour of **2** was quite different from that of **1**. When scanning the potential first in the negative going direction, a main irreversible reduction peak at -1.46 V (at 0.2 V s^{-1}) was observed (Fig. 2).

The peak was preceded by a small wave at ca. -1.1 V , the current of the wave decreasing slightly with respect to the main peak when the scan rate was increased. In fact, the two processes are linked. While the main peak decreases upon stepwise addition of PPh_3 , the wave increases accordingly. Finally, when 1 equivalent of PPh_3 was added to the solution of **2**, i.e. under the conditions in which **3** is formed, a nearly complete transformation of the two peaks was observed: The original wave was now a fully developed peak having the same height as the main peak of **2**, but a more positive peak potential, -1.06 V . The voltammetric pattern is in agreement with Eq. (6) being very displaced to the right-hand side. In addition, it suggests that there is an equilibrium in which **2** can exchange PPh_3 with another **2** molecule to form **3**, although to a very small extent.

Reduction of **2** produces irreversibly a palladium(0) species that can be oxidised on the backward scan, giving rise to a broad and irreversible peak that, at 0.2 V s^{-1} , is located at 0.42 V (Fig. 2). The peak is preceded by a much smaller peak at 0.0 V . Both peaks can be observed only after reduction of **2**, the reduction wave of **2** being connected to the most positive oxidation peak. Upon stepwise addition of PPh_3 , the oxida-

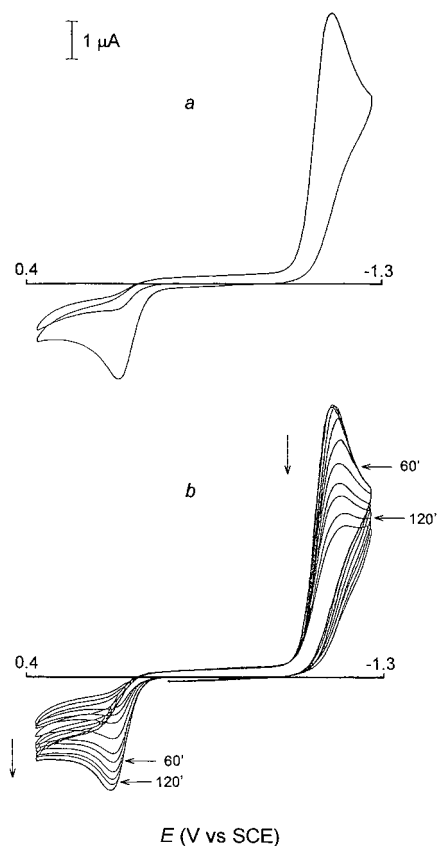


Fig. 3. Cyclic voltammetry curves obtained in a solution containing 4.0 mM **3** in DMF–0.1 M Bu₄NClO₄ at 60°C. Plot (a) was recorded a few minutes after taking the solution to 60°C. The curves in plot (b) show, qualitatively, the evolution of the voltammetric pattern during ca. 3 h. The arrows indicate the corresponding variations of the reduction and oxidation peaks. For both plots the initial scan was from –0.3 V to more positive potentials. Gold electrode, 0.2 V s^{–1}.

tion peaks undergo a similar pattern as that already described for the negative going scan. While the broad peak decreases, the smaller, less positive oxidation peak develops into a sharp and irreversible peak located at –0.04 V (at 0.2 V s^{–1}). If more than 1 equivalent of PPh₃ is added to the solution of **2** (or more than 2 equivalents to a solution of **1**), both this oxidation peak and the main reduction peak (at –1.06 V) do not change significantly, again pointing to the equilibrium for the formation of **3** (Eq. (6)) being almost completely displaced on the right-hand side.

As described above, complex **3** is more easily reduced than **2**, by ca. 0.4 V. Analogously, the reduction product of **3** is more easily oxidised than that of **2** by ca. 0.4 V. This points to a greater reactivity of **3** relative to **2**. In fact, whereas complex **2** appears to be stable in solution, even after several hours, we found that addition of PPh₃ leading to **3** leads to chemical instability of the palladium(II) complex. Although the effect is small at 25°C, if the solution is taken at 60°C, an oxidation peak spontaneously forms at ca. 0 V in a few minutes (Fig. 3(a)). This was ascertained by running the cyclic

voltammetry experiment starting from –0.3 V, where neither oxidation nor reduction may take place, and scanning the potential first toward positive values. Fig. 3(a) also shows that by reversing the potential scan past the oxidation peak and running a full cyclic voltammetry to include reduction of **3**, an oxidation peak, having the same potential as that of the peak that forms spontaneously by chemical decay of **3**, develops. Fig. 3(b) illustrates the evolution of the voltammetric pattern during ca. 3 h.

While the cathodic peak decreases until the peak current levels off, the current of the anodic peak increases, reaches a maximum, and (not shown in the figure) starts to decrease. The fact that the spontaneous reduction of **3** is not quantitative but stops after ca. 3 h and that decomposition of the palladium(0) species is observed afterwards is completely coherent with the FTIR and NMR findings. Again the picture coming from these experiments is that the formation of the palladium(0) species is followed by some equilibrium in which a further PPh₃ molecule is requested to stabilise the low oxidation state of palladium. In the absence of an excess of PPh₃, the additional PPh₃ molecule seems to be provided by **3** itself, which transforms into **2**, leading to a dramatic decrease of the rate of the reductive elimination.

Cyclic voltammetry experiments were carried out to study the reactivity of the zero-valent palladium species toward PhI, at 25°C. This is a typical oxidative addition previously used with another palladium(0) system and thus considered as a good test to evaluate the relative reactivity of these two electron-donating systems. The experiments were carried out by voltammetric electro-generation of the reactive zero-valent species, through reduction of **3**, first in the absence and then in the presence of 20 equivalents of PhI. Fig. 4 shows very convincingly that whereas at 0.2 V s^{–1} no oxidation peak was observed in the presence of PhI, at 10 V s^{–1} the oxidation peak is reduced to ca. half of its original value. At 200 V s^{–1} the oxidation peak is practically the same as if the halide was not present in solution. Analysis of the cyclic voltammograms obtained in the 0.1–200 V s^{–1} range, in comparison with the corresponding digitally simulated curves, led us to estimate the rate constant for the oxidative addition to be in the range 1–2 × 10² M^{–1} s^{–1}. This value is comparable with 140 M^{–1} s^{–1} reported for the corresponding oxidative addition of PhI to [Pd(η¹-OAc)(PPh₃)₂][–] [8]. The latter value, however, was determined for [Pd(η¹-OAc)(PPh₃)₂][–] generated from [Pd(OAc)₂] + 3PPh₃. Under these conditions, hydrogen ions form and this has been envisaged as a factor enhancing the rate of oxidative addition of PhI to palladium(0) [8]. On the other hand, the value reported here pertains to electro-generated palladium(0), i.e. to conditions under which no hydrogen ions form. This would support the idea

that the palladium(0) species obtained by electrochemical reduction of **3** is more reactive than $[\text{Pd}(\eta^1\text{-OAc})(\text{PPh}_3)_2]^-$. The electrochemical reduction of **3** should afford directly **8** (Scheme 3(a)), which in turn could undergo at least two equilibrium reactions (Scheme 4).

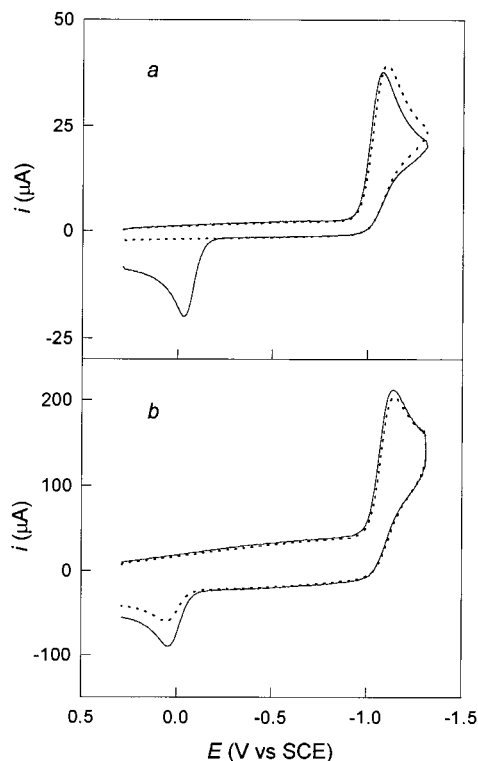
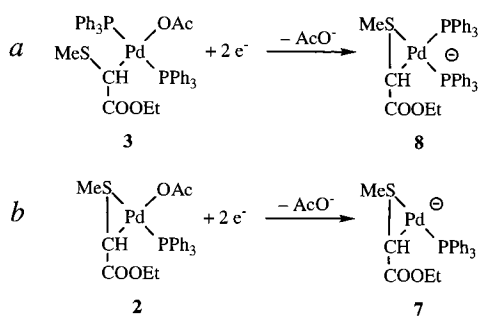
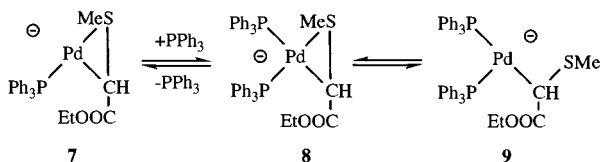


Fig. 4. Cyclic voltammetry curves for the reduction of 2.7 mM **3** in DMF–0.1 M Bu_4NClO_4 at 0.2 (plot a) and 10 V s^{-1} (plot b). For both plots, the curves were obtained first in the absence (—) and then in the presence (·····) of 20 equivalents of PhI. Glassy carbon electrode, 25°C.



Scheme 3.



Scheme 4.

Complex **7** is the most likely product of electroreduction of **2** (Scheme 3(b)). As mentioned above, its oxidation peak is observed at a more positive potential with respect to **8**. This suggests that it should be less reactive in the oxidative addition of PhI than **8** (or **9**). Under these conditions, the intermediacy of a species without the sulfur ligand can be ruled out. In fact, the protonation of the ligand cannot occur and its release in solution seems unlikely. On the other hand, **8** is coordinatively saturated and this would suggest that the active palladium(0) species is **9**. The presence of a σ -bonded carbon ligand would suggest even higher reactivity than observed: kinetic constants as high as $10^4 \text{ M}^{-1} \text{ s}^{-1}$ have been reported for related σ -aryldiphosphino-palladate(0) complexes, $[\text{Pd}(\text{Ar})(\text{PPh}_3)_2]^-$ [19]. However, in our case the expected effect of the carbon ligand is likely mitigated by the low concentration of **9** in equilibrium with the main species **8**.

The oxidative addition of PhI was also observed under conditions of chemical reduction. In the presence of PPh_3 (1:2 Pd:P) and one out of several bases ($^t\text{Bu}_4\text{NOAc}$, NPh_3 , PS; 1:1, 1:1, 2:1 base:Pd), the reaction of PhI and **1** in anhydrous benzene gave mixtures of acetato- and iodo-phenyl derivatives of palladium(II). In the presence of $^t\text{Bu}_4\text{NOAc}$, the $^1\text{H-NMR}$ data show that the main product was $[\text{Pd}(\eta^1\text{-OAc})(\text{Ph})\text{PPh}_3]_2$, although the elemental analysis indicated that it was contaminated by some iodo derivative. The presence of acetato ligands in the products of oxidative addition of iodobenzene to palladium(0) has been already observed [8].

We also believe that in this case the anionic species **8** is the key Pd(0) intermediate. However, the presence of hydrogen ions and acetic acid (side products of the reductive elimination from **3**) could lead to neutral Pd(0) complexes containing the protonated thioether ligand.

Finally, we attempted to carry out the reaction of **1** with iodomethane, in the presence of PPh_3 (3:1 P:Pd), as an example of reaction with a different aliphatic halide. However, in this case no base was added to the reaction mixtures. The analytical and spectroscopic data show the presence of $[\text{PdI}(\eta^2\text{-MeSCHCO}_2\text{Et})(\text{PPh}_3)]$ and $[\text{Pd}\{\eta^1\text{-CH}(\text{SMe})\text{CO}_2\text{Et}\}(\text{PPh}_3)_3]\text{I}$. The formation of both is easily explained on the basis of an electrophilic attack of MeI to the sulfur atom, followed by AcO^-/I^- [20], I^-/PPh_3 , PPh_3/SMe exchange processes.

4. Conclusions

$[\text{Pd}_3(\mu\text{-OAc})_3(\mu, \eta^2\text{-MeSCHCO}_2\text{Et})_3]$ (**1**) shows a substantially similar behaviour towards triphenylphosphine in comparison with $[\text{Pd}(\text{OAc})_2]$. However, due to the stabilization of palladium(II) arising from the chelate

MeSCHCO₂Et⁻ ligand (chelate effect, effective competition of the sulfur donor atom with phosphine for metal coordination) its reactivity towards reductive elimination of AcOPPh₃⁺ can be controlled. This allows the synthesis of the monoacetato-monophosphino intermediate [Pd(η¹-OAc)(η²-MeSCHCO₂Et)(PPh₃)] (**2**) from **1** and the determination of its crystal structure. By contrast, [Pd(η¹-OAc)₂(PPh₃)₂] is formed instantaneously from [Pd(OAc)₂]. Remarkably, complex **2** does not undergo reductive elimination, although an acetato ligand and a triphenylphosphine molecule are present, in mutual *cis* position, in the coordination sphere of palladium(II). This demonstrates that this is not a sufficient condition for the reductive elimination to take place. Elimination occurs only upon addition of an equivalent of PPh₃ to complex **2**, leading to the formation of the intermediate palladium(II) diphosphino complex [Pd(η¹-OAc){η¹-CH(SMe)CO₂Et}(PPh₃)₂] (**3**). The latter is unstable in DMF solution and gives a spontaneous reductive elimination. However, this process is slower than reported for the related complex [Pd(η¹-OAc)₂(PPh₃)₂]. In the presence of PhI, a zero-valent palladium species, most likely arising from **8**, undergoes fast oxidative addition. Conversely, no oxidative addition was observed with MeI in the presence of triphenylphosphine. In this case, the exchange between the acetato and the iodo ligand is faster than reductive elimination and takes place instead.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 113856. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We thank Mr A. Ravazzolo for skilled technical assistance. S.A. and F.M. thank the Consiglio Nazionale delle Ricerche for financial support.

References

- [1] M. Basato, A. Grassi, G. Valle, *Organometallics* 14 (1995) 4439.
- [2] M. Basato, C. Bertani, B. Sesto, M. Zecca, A. Grassi, G. Valle, *J. Organomet. Chem.* 552 (1998) 277.
- [3] M. Basato, C. Bertani, M. Zecca, A. Grassi, G. Valle, *J. Organomet. Chem.* 575 (1999) 163.
- [4] W.A. Herrmann, in: B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, vol. II, VCH, Weinheim, 1996, p. 712.
- [5] F. Ozawa, A. Kubo, T. Hayashi, *Chem. Lett.* (1992) 2177.
- [6] C. Amatore, A. Jutand, M.A. M'Barki, *Organometallics* 11 (1992) 3009.
- [7] C. Amatore, E. Carré, A. Jutand, M.A. M'Barki, *Organometallics* 14 (1995) 1818.
- [8] C. Amatore, E. Carré, A. Jutand, M.A. M'Barki, G. Meyer, *Organometallics* 14 (1995) 5605.
- [9] K. Miki, Y. Kai, N. Yasuoka, N. Kasai, *J. Organomet. Chem.* 135 (1977) 53.
- [10] S. Antonello, M. Musumeci, D.D.M. Wayner, F. Maran, *J. Am. Chem. Soc.* 119 (1997) 9541.
- [11] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Wiley, New York, 1980.
- [12] J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, Chichester, 1995.
- [13] W.A. Herrmann, C. Brossmer, C.P. Reisinger, T.H. Riermeier, K. Öfele, M. Beller, *Chem. Eur. J.* 3 (1997) 1357.
- [14] M. Beller, C.P. Reisinger, *Eur. J. Inorg. Chem.* (1998) 29.
- [15] F.G. Bordwell, X.-M. Zhang, M.S. Alnajjar, *J. Am. Chem. Soc.* 114 (1992) 7623.
- [16] F. Maran, D. Celadon, M.G. Severin, E. Vianello, *J. Am. Chem. Soc.* 113 (1991) 9320.
- [17] G. Yoshida, H. Kurosawa, R. Okawara, *J. Organomet. Chem.* 113 (1976) 85.
- [18] C. Amatore, A. Jutand, M.J. Medeiros, *New J. Chem.* 20 (1996) 1143.
- [19] C. Amatore, E. Carré, A. Jutand, H. Tanaka, Q. Ren, S. Torii, *Chem. Eur. J.* 2 (1996) 957.
- [20] H.D. McPherson, J.L. Wardell, *Inorg. Chim. Acta* 81 (1984) 39.