Dinuclear palladium(II) compounds with bridging cyclometalated phosphines. Synthesis, crystal structure and electrochemical study[†]

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The structural characterization of bis-cyclometalated palladium(II) compounds of formula $Pd_2[(\mu-(C_6X_4)PPh_2]_2(\mu-O_2CR)_2 [X = H, R = CH_3 (3), CF_3 (4), C(CH_3)_3 (5) and C_6F_5 (6); X = F, R = CH_3 (7) and CF_3(8)]$, has confirmed its paddle wheel structure with two palladium atoms bridged by two acetates and two metalated phosphines in a head-to-tail arrangement. The Pd ··· Pd distances are in the range 2.6779(16)–2.7229(8) Å. Under cyclic voltammetric conditions, compounds 3–6, in CH_2Cl_2 solution, were found to undergo a reversible oxidation peak in the range of potential values 0.84–1.25 V. A second partially-reversible oxidation is observed at more positive potentials (1.37–1.55 V). For compounds 3–5 in the presence of chlorides, the first oxidation becomes a two-electron process presumably leading to a neutral [Pd(III)–Pd(III)] species with a metal–metal bond.

Introduction

Palladium complexes have been extensively used in catalysis.¹⁻⁵ The chemistry of palladium is dominated by the oxidation state II and monometallic compounds are the most frequent for this metal in this particular oxidation state. There is a relatively large family of palladium compounds that are bimetallic and have two palladium atoms at a variable distance. The most representative contain two bridging ligands, frequently carboxylate ligands and two cyclometalated ligands in a chelating coordination mode (type A in Scheme 1).⁶ The shortest reported distances between palladium atoms in compounds of this type are 2.831 Å.^{7,8} However, the number of dinuclear palladium compounds with bridging metalated ligands is considerably smaller. Palladium compounds with bridging O-C,9-13 N-C14-19 or S-C ligands9,20 have been reported. In most of these compounds the palladium atoms are quite separated and synergic interaction between the two metal centers might only be possible in one case,²⁰ with three bridging ligands. Palladium complexes with ligands spanning a P-C bridging coordination mode are usually restricted to those ligands with the carbon atom being part of the π system: olefin,²¹ acetylene²² or arene.²³ The typical paddle wheel structure (type B in Scheme 1), common for other transition metals, is only observed in a limited number of palladium(II) compounds.24-31

It is remarkable that very little information is available on palladium(III) complexes, though electrochemical investigations on dinuclear palladium(II) complexes confirmed the generation in



solution of species resulting from one or two electron oxidation processes.^{30,31}

We have previously reported the synthesis and characterization of palladium complexes of formula $\{Pd[\mu-(C_6H_4)PPh_2](\mu-Br)\}_4$, **1**, from the reaction of Pd(dba)₂ with (*o*-BrC₆H₄)PPh₂, being the first example of a palladium compound with metalated triphenylphosphine acting as a bidentate P–C donor ligand.³² Further studies confirmed the ability of the ligand $[(C_6H_4)PPh_2]^$ to have bridging (μ -) or chelating (κ^2 -) coordination modes, depending on the auxiliary ligands present in the complex.³³ Bulky phosphines stabilize mononuclear species of formula $\{Pd[\eta^2-(C_6H_4)PPh_2]Br[P]\}$, with a four-atom metallocycle, while small phosphines give dinuclear compounds.

Preliminary reactions allowed us to obtain compounds of formula $Pd_2[\mu-(C_6H_4)PPh_2]_2(\mu-O_2CR)_2$ ($R = CH_3$ (3) and CF_3 (4)) that were not structurally characterized.

We report here the preparation of a new tetranuclear palladium(II) complex of formula $\{Pd[\mu-(C_6F_4)PPh_2](\mu-Br)\}_4$, (2) and the synthesis and characterization of compounds $Pd_2[\mu-(C_6X_4)PPh_2]_2(\mu-O_2CR)_2$ (type C in Scheme 1) [X = H, R = CF₃ (4), C(CH₃)₃ (5) and C₆F₅ (6); X = F, R = CH₃ (7) and CF₃ (8)]. Compounds 3–6 exhibit two reversible oxidation peaks by cyclic voltammetry, being potential starting products in the synthesis of dinuclear palladium compounds in higher oxidation states. In future reports we shall describe the application of these compounds in the synthesis of self assembled molecules containing Pd₂[μ -(C₆H₄)PPh₂]₂ building blocks.²⁸

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[†] Electronic supplementary information (ESI) available: ORTEP diagrams for the compounds (Fig. S1–S3); cyclic voltammograms (Fig. S4–S10); ³¹P NMR spectra (Fig. S11) and bond distances and angles for compounds **4–8** (Table S1). See DOI: 10.1039/b609829k

Experimental

General comments

The starting compounds $Pd(dba)_2^{34}$ and $P(o-BrC_6F_4)Ph_2^{35}$ were prepared according to literature procedures. Reagent grade solvents, dichloromethane, hexane, toluene, diethyl ether, acetonitrile were used without purification. The solution ¹H and ³¹P NMR spectra were recorded from CDCl₃ solutions on Bruker Avance 300 and Avance 400 spectrometers. The chemical shifts were referenced to residual solvent resonance and external 85% H₃PO₄ in the ¹H and ³¹P spectra, respectively. Microanalyses were carried out at the Analytical Laboratory of the University of Joensuu, Finland. Column chromatography was performed on silica, 35– 70 µm. The electrochemical measurements were performed in CH₂Cl₂ at a scan rate of 0.05 V s⁻¹, using tetrabutylammonium hexafluorophosphate (Fluka) (0.1 M) as supporting electrolyte.

Synthesis of $\{Pd[\mu-(C_6F_4)PPh_2](\mu-Br)\}_4$ (2). Method (a): Pd(dba)₂ (300 mg, 0.522 mmol) and toluene (1.5 mL) were put into a Schlenk tube and were degassed. $P(o-BrC_6F_4)Ph_2$ (210 mg, 0.508 mmol) was added in one portion in a flow of argon and the reaction mixture was stirred at room temperature for 1 h. Then, the temperature was gradually increased to 90 °C and stirring was continued for 15 h. After that, a fine greenish precipitate and a dark brown solution were formed. The reaction mixture was allowed to reach room temperature and the precipitate was isolated by filtration, washed with toluene $(2 \times 4 \text{ mL})$, diethyl ether $(2 \times 4 \text{ mL})$ and vacuum dried (205 mg). From this solid, 135 mg (52%) of compound 2 can be extracted by refluxing in dichloromethane, filtering off the insoluble material and crystallization from dichloromethane-methanol mixtures. Due to the low solubility of compound 2 this purification process is very time consuming. Fortunately, the crude compound 2 can be used for the synthesis of carboxylate derivatives 7 and 8 with moderate yields (see later).

Method (b): compound **2** was readily obtained from the reaction of compound **7** with excess of tetraethylammonium bromide in an acetone–methanol mixture. In these conditions a yellow precipitate was slowly formed. The filtered solid was washed with methanol, acetone, diethyl ether and dried under vacuum to give **2** (93%) as a yellow crystalline solid. Anal. Calc. for $C_{72}H_{40}Br_4F_{16}P_4Pd_4$: C, 41.6; H, 1.9. Found: C, 41.5; H, 2.0%. δ_P 27.0 (m).

Synthesis of the silver carboxylate salts

All the remaining compounds were prepared, reacting compounds **1** or **2** with the corresponding silver salt. Silver acetate or trifluoroacetate were commercially available. The remaining silver salts were prepared as follows. A solution of AgNO₃ (850 mg, 5 mmol) in water (3 mL) was added, under vigorous stirring, to a solution of HO₂CR (R = C(CH₃)₃, C₆F₅) (5 mmol) in 5 mL of 1M ammonium hydroxide solution. After filtration, AgO₂CR was obtained as a white precipitate, that was washed with water (2 × 4 mL) and vacuum dried (70–80%). It was used without further purification.

Synthesis of $Pd_2[\mu-(C_6H_4)PPh_2]_2(\mu-O_2CR)_2$. R = CH₃ (3), CF₃ (4), C(CH₃)₃ (5) and C₆F₅ (6)

Compounds **3** and **4** were prepared by the reported method.³³ The other two compounds were prepared by reaction of **1** and stoichiometric amounts of the corresponding silver salt in dichloromethane. After filtration, dilution with hexanes and evaporation of the solvents, **5** and **6** were obtained as yellow crystalline solids (yield 85–95%). **5**. Anal. Calc. for C₄₆H₄₆O₄P₂Pd₂: C, 58.9; H, 4.9. Found: C, 58.5; H, 5.0%. $\delta_{\rm P}$: 17.4 (s). $\delta_{\rm H}$: 7.71 (m, 2H), 7.41 (m, 3H), 7.29 (m, 1H), 7.20 (m, 1H), 7.00 (m, 2H), 6.80 (m, 3H), 6.58 (m, 2H), 0.54 (s, 9H). **6**. Anal. Calc. for C₅₀H₂₈F₁₀O₄P₂Pd₂: C, 51.9; H, 2.4. Found: C, 51.9; H, 2.5%. $\delta_{\rm P}$: 19.4 (s). $\delta_{\rm H}$: 6.6–7.7 (m, phenyl protons). Single crystals of these complexes, suitable for X-ray diffraction, were grown at room temperature by diffusion of heptane into their chloroform solutions.

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crystal structure data compound X-Ray for 4. $C_{40}H_{28}F_6O_4P_2Pd_2$, monoclinic, space group P2(1)/n, a =12.315(3), b = 21.427(6), c = 14.530(4) Å, $\beta = 94.822(7)^{\circ}$, V =3820.6(17) Å³, Z = 4, $\rho_{calcd} = 1.671$ g cm⁻³, crystal dimensions: $0.30 \times 0.24 \times 0.22$ mm³; Bruker P4 diffractometer; Mo Ka radiation, 153(2) K; 32 408 reflections, 11 655 independent; ($\mu =$ 1.095 mm⁻¹); refinement (on F^2) with SHELXTL (version 6.1), 487 parameters, 0 restraints, $R_1 = 0.0479 (I > 2\sigma)$ and wR_2 (all data) = 0.1197, GOF = 1.007, max/min residual electron density: $0.987/-0.767 \text{ e} \text{ Å}^{-3}$.

X-Ray crystal structure data for compound 5. $C_{46}H_{46}O_4P_2Pd_2$, orthorhombic, space group *Pccn*, a = 10.9390(3), b = 15.9320(4), c = 23.5800(6) Å, V = 4109.53(19) Å³, Z = 4, $\rho_{caled} =$ 1.515 g cm⁻³, crystal dimensions: 0.28 × 0.25 × 0.23 mm³; Kappa CCD diffractometer; Mo K α radiation, 293(2) K; 20 460 reflections, 4694 independent; ($\mu = 0.996$ mm⁻¹); refinement (on F^2) with SHELXTL (version 6.1), 248 parameters, 0 restraints, $R_1 = 0.0957$ ($I > 2\sigma$) and wR_2 (all data) = 0.3302, GOF = 1.047, max/min residual electron density: 1.877/-1.819 e Å⁻³.

X-Ray crystal structure data for compound 6. $C_{50}H_{28}F_{10}O_4P_2Pd_2$, triclinic, space group *P*-1, *a* = 14.56300(10), *b* = 14.9110(2), *c* = 23.1350(3) Å, *a* = 95.5460(5), β = 94.822(7), γ = 113.1221(5), *V* = 4541.94(9) Å³, *Z* = 4, ρ_{calcd} = 1.693 g cm⁻³, crystal dimensions: 0.24 × 0.23 × 0.23 mm³; Kappa CCD diffractometer; Mo K α radiation, 293(2) K; 47 438 reflections, 20 179 independent; (μ = 0.949 mm⁻¹); refinement (on *F*²) with SHELXTL (version 6.1), 1225 parameters, 0 restraints, *R*₁ = 0.0614 (*I* > 2 σ) and w*R*₂ (all data) = 0.2005, GOF = 1.017, max/min residual electron density: 0.945/-1.129 e Å⁻³.

Synthesis of $Pd_2[\mu-(C_6F_4)PPh_2]_2(\mu-O_2CR)_2$. R = CH₃ (7), CF₃ (8)

Crude 2 (150 mg) was suspended in a $CH_2Cl_2-HO_2CR$ (30 : 1 v/v) mixture (30 mL) and excess of AgO₂CR was added; the mixture was gently refluxed in the absence of light for 24 h. The resulting dark suspension was cooled at room temperature, diluted with diethyl ether (5 mL) and passed through a silica column (1.5 × 6 cm). The solvents were removed under vacuum to give an orange residue that was extracted with diethyl ether. After addition of

hexanes and partially removing the solvent under vacuum **7**(62 mg, 43%) and **8**(67 mg, 42%) were obtained as yellow crystalline solids. **7**: (Anal. Calc. for C₄₀H₂₆F₈O₄P₂Pd₂: C, 48.2; H, 2.63. Found: C, 48.3; H, 3.02%. $\delta_{\rm P}$: 15.5 (m). $\delta_{\rm H}$: 7.78 (m, 2H), 7.55 (m, 3H), 7.44 (m, 1H), 7.23 (m, 2H), 7.00 (m, 2H), 1.19 (s, 3H). **8**: Anal. Calc. for C₄₀H₂₀F₁₄O₄P₂Pd₂ : C, 43.4; H, 1.8. Found: C, 43.2; H, 1.9%. $\delta_{\rm P}$: 18.0 (m). $\delta_{\rm H}$: 6.6–7.7 (m, phenyl protons).

Single crystals suitable for X-ray diffraction study were grown, at room temperature, by slow evaporation of a hexane solution of 7 and by diffusion of heptane into a chloroform solution of 8.

compound 7. X-Ray crystal structure data for $C_{40}H_{26}F_8O_4P_2Pd_2$, monoclinic, space group C(2)/c, a =22.0070(9), b = 9.7540(4), c = 20.5150(11) Å, $\beta = 106.3300(18)^{\circ}$, V = 4226.0(3) Å³, Z = 4, $\rho_{calcd} = 1.568$ g cm⁻³, crystal dimensions: $0.30 \times 0.27 \times 0.23$ mm³; Kappa CCD diffractometer; Mo Ka radiation, 293(2) K; 13 617 reflections, 4604 independent; ($\mu =$ 0.999 mm⁻¹); refinement (on F^2) with SHELXTL (version 6.1), 255 parameters, 0 restraints, $R_1 = 0.0856$ ($I > 2\sigma$) and w R_2 (all data) = 0.2757, GOF = 1.044, max/min residual electron density: $1.569/-0.857 \text{ e} \text{ Å}^{-3}$.

X-Ray crystal structure for 8. data compound $C_{40}H_{20}F_{14}O_4P_2Pd_2$, orthorhombic, space group *Pbcn*, *a* = 18.5977(17), b = 10.4861(10), c = 19.4574(17) Å, V = 3794.5(6)Å³, Z = 4, $\rho_{\text{calcd}} = 1.694$ g cm⁻³, crystal dimensions: 0.40 × 0.30×0.30 mm³; Bruker Smart diffractometer; Mo Ka radiation, 296(2) K; 32 885 reflections, 4890 independent; ($\mu = 1.145 \text{ mm}^{-1}$); refinement (on F^2) with SHELXTL (version 6.1), 280 parameters, 0 restraints, $R_1 = 0.0612$ $(I > 2\sigma)$ and wR_2 (all data) = 0.1097, GOF = 1.293, max/min residual electron density: $0.832/-0.673 \text{ e} \text{ Å}^{-3}$.

Electrochemical measurements

All experiments were performed at 25 °C under an atmosphere of dry argon in 0.10 M tetrabutylammonium hexafluorophosphate in CH₂Cl₂. LSVs were obtained with a CH 1420 instrument. Glassy carbon (geometrical area 0.071 cm²) was used as the working electrode, a platinum wire was used as the counter-electrode, and an aqueous AgCl (3 M NaCl)/Ag reference electrode (SCE) separated from the bulk solution by a salt bridge containing the solvent and supporting electrolyte only completed the standard three-electrode cell. In these conditions, the potential of the fc⁺/fc

couple was +0.55 V. Prior to each run the working electrode was polished during 60 s with a BAS polishing cloth.

Results and discussion

Following our previous investigations^{32,33} we have reacted the tetranuclear compound $\{Pd[\mu-(C_6H_4)PPh_2](\mu-Br)\}_4$, **1**, with different silver carboxylates to form compounds that, based on spectroscopic data, were tentatively described as dinuclear compounds of formula $Pd_2[\mu-(C_6H_4)PPh_2]_2(\mu-O_2CR)_2$, $R = C(CH_3)_3$ (**5**) and C_6F_5 (**6**). These compounds were isolated in high yield as crystalline materials (Scheme 2).

The new tetranuclear compound **2** was also prepared from the reaction of Pd(dba)₂ (dba = dibenzylideneacetone) with P(*o*-BrC₆F₄)Ph₂, according to the synthetic procedure described for **1**,³² but in considerably lower yield. After careful modification of the reaction conditions, **2** could be isolated with a maximum yield of 40%. However, the purification of this compound became long and tedious, due to its very low solubility that made it difficult to separate from insoluble impurities also formed. The best solution was to treat the reaction mixture with a silver carboxylate; only **2** reacted forming the corresponding compounds of formula Pd₂[µ-(C₆F₄)PPh₂]₂(µ-O₂CR)₂, [R = CH₃ (**7**), CF₃ (**8**)] that were soluble and could be easily crystallized. Pure compound **2** could be readily prepared by reacting either of these two carboxylate compounds with Et₄N⁺Br⁻.

All the isolated compounds show a single resonance in the ³¹P NMR spectra, in the 15–20 ppm chemical shift range, normal for a metalated phosphine acting as a bridging ligand, and consistent with a dinuclear structure. The phosphorus resonances for compounds **7** and **8** are multiples due to long range P–F coupling (see ESI, Fig. S11†).

Solid state structures

The dinuclear structure was confirmed for compounds **3–8** by X-ray methods. The refinement of compound **3** was not fully satisfactory, but confirmed its dinuclear structure. The structures are of tetragonal paddle wheel type, similar to those reported for other Pd_2L_4 compounds^{24–31} and also to the related dirhodium(II) compound of the same stoichiometry.³⁶

For each molecule, the core is composed of two Pd^{2+} ions, two bridging metalated (C_6X_4)PPh₂ ligands in a *cisoid* disposition, and



Scheme 2

two bridging carboxylate ligands as shown in Fig. 1 and 2 for two representative examples. ORTEP diagrams³⁷ for compounds **5**, **6** and **7** are given as ESI (Fig. S1–3).† Thus, each palladium atom is bonded to one carbon atom and one phosphorus atom, each from a different (C_6X_4)PPh₂ ligand, and also to two oxygen atoms from two different carboxylate anions. These bicyclometalated compounds with head-to-tail arrangements of phosphines are inherently chiral. Each crystal is racemic containing the mixture



Fig. 1 ORTEP diagram for compound **4**. Ellipsoids represented at 30% probability. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°) are: Pd(1)–Pd(2), 2.7229(8); Pd(1)–P(1), 2.2273(12); Pd(1)–C(42), 1.982(4); Pd(1)–O(1), 2.158(3); Pd(2)–P(2), 2.2269(12); Pd(2)–C(12), 1.980(4); Pd(2)–O(4), 2.163(3); P(1)–Pd(1)–Pd(2), 87.50(3); P(2)–Pd(2)–Pd(1), 87.35(3).



of S and R molecules, Scheme 3. The P–Pd–Pd–P torsion angles values are between 91.2 and 98.9° for the characterized compounds.



In addition to the chirality (*R* or *S*) that arises from the configurational arrangement of the molecule, there is a second point of chirality in these molecules, induced by the conformational arrangement of the ligands. The P–Pd–Pd–C torsional angles designated with the nomenclature P and M, are shown in Scheme 4. In each molecule, the torsion angles for the carboxylate ligands, O–Pd–Pd–O, show the same sign as for the phosphine. Thus, complete description of the stereochemistry in these molecules requires specification of the two senses of chirality *S* or *R* and P or M. In the palladium compounds described here, only molecules with stereochemistry S_M and R_P have been observed, Scheme 4. The same was observed for other structurally related rhodium(II) compounds with metalated phosphines.^{36,38}



Fig. 2 ORTEP diagram for compound **8**. Ellipsoids represented at 30% probability. Hydrogen atoms omitted for clarity. The additional "A" letter in the atom labels indicates atoms at (2 - x, y, 1/2 - z) Selected bond distances (Å) and angles (°) are: Pd(1)–Pd(1A), 2.7054(6); Pd(1)–P(1), 2.2294(11); Pd(1)–O(1), 2.116(3); Pd(1)–O(2), 2.148(3); Pd(1)–C(12), 1.987(4); P(1)–Pd(1)–Pd(1A), 89.89(3).

Important bond distances and angles are included in the ESI (Table S1).† The Pd–Pd distances are in the range of values 2.675(1) Å for 7 to 2.7229(8) Å for 4. The observed trend in the Pd–O distances deserves some comment. In all the characterized compounds the Pd–O distances *trans* to carbon are slightly shorter or similar to those *trans* to phosphorus. It is remarkable that for the related dirhodium(II) compound with metalated phosphines of general formula $Rh_2(PC)_2(O_2CR)_2^{38-44}$ the Pd–O distances *trans* to

carbon were considerably longer than those *trans* to phosphorus and that was attributed to the higher *trans* influence of carbon compared to phosphorus. While the carboxylate ligands are symmetrically located, the metalated phosphine ligands have a rather non-symmetric coordination. Thus, Pd–Pd–C angles, in the 95.7–93.2° range, are significantly bigger than the Pd–Pd–P angles (in the 87.35–89.89° range of values). The same disposition had been observed for the related dirhodium(II) compound of formula Rh₂(PC)₂(O₂CR)₂.^{36,38-44} Compounds **5**, **7** and **8** have crystallographically imposed twofold symmetry. Further investigations to explain these structural trends are in progress.

Electrochemical study

The cyclic voltammogram of 5 in 0.10M Bu₄NPF₆-CH₂Cl₂ is shown in Fig. 3. Compounds 3, 4 and 6 show similar electrochemical behaviour (see the ESI, Fig. S4-6[†]). In the initial anodic scan, two couples A_1/C_1 and A_2/C_2 appear at potential values between +0.80 and +1.60 V. The first couple (A_1/C_1) can be described in terms of a reversible one-electron transfer as judged by the value of the anodic-to-cathodic peak separation, close to 0.059 V, recorded at low scan rates when the potential is switched at 0.15-0.20 V past the peak A₁. The current function, I_p (= $i_p/Acv^{1/2}$) is close to 450 \pm 10 mA M⁻¹ V^{-1/2} s^{1/2} cm⁻², regardless of the potential scan rate used ($0.05 < v < 0.5 \text{ V s}^{-1}$), thus denoting that the electrochemical process is diffusion-controlled. The formal electrode potentials for the A_1/C_1 couple, calculated as the half sum of the anodic and cathodic peak potentials for the complexes 3-6, are +0.975, +1.250, 0.840 and 1.035 V vs. AgCl/Ag, respectively, decreasing with the electron-donating ability of the carboxylate group.



Fig. 3 CV at glassy carbon electrode for a 1.0 mM solution of 5 in 0.10 M $Bu_4NPF_6-CH_2Cl_2$.

The formal electrode potentials for the A_2/C_2 couple are +1.375, +1.490, +1.310 and 1.350 V vs. AgCl/Ag, respectively. In compounds 4 and 6, the second couple exhibits broader and not so well defined peaks as for 3 and 5. The peak height decreases on increasing the potential scan rate and at the same time, are anodically shifted. These features suggest that there is a chemical reaction preceding the electrochemical oxidation in A_2 . Upon repetitive voltammetric scanning the electrochemical

pattern remains unchanged, denoting that the parent complex is regenerated during the electrochemical turnovers.

On initiating the potential scan in the negative direction, no reduction processes of the parent Pd complexes were detected in the available potential region until a potential of ca. -1.8 V.

The observed electrochemistry can be described in terms of two consecutive one-electron transfer processes in the starting $Pd_2(+4)$ complexes yielding, successively, $[Pd_2(+5)]^+$ and $[Pd_2(+6)]^{2+}$ cationic species. The relatively large separation between the two associated A_1/C_1 and A_2/C_2 couples, can be described as indicative of certain palladium–palladium interaction, as observed in similar systems.^{306,31}

The cyclic voltammogram of 7 (see Fig. S10 of the ESI \dagger) showed two irreversible and poorly defined oxidation peaks at approximately 1.2 and 1.7 V. Similar behaviour was observed for compound **8**.

All these electrochemical data indicated that the presence of electron-donating groups on the phosphine and the carboxylate ligands favours the reversibility of the oxidation process. Thus, the best electrochemical response was obtained for **3** and **5**.

In the presence of chloride anions the voltammetric response changes drastically as shown in Fig. 4 for compound 5. The addition of a stoichiometric amount of Et₄NCl to a solution of 5 produces the appearance of an oxidation peak (A₃) at a potential similar to that of peak A₁ recorded for the parent complex. This peak approaches an irreversible two-electron oxidation process followed, in the subsequent cathodic scan, by a reduction peak at 0.15 V (C_4) whose anodic counterpart is entirely absent. Consequently with these observations, the A_2/C_2 couple vanishes. Compounds 3, 4 and 6 present the same behaviour with the reduction peak shifted, as expected, to more positive values (0.28, 0.48 and 0.35 V respectively) (see Fig. S7-9 of the ESI[†]). Bond et al. have reported a similar electrochemical behaviour for the palladium(II) compounds in the presence of chlorides.^{30b} The observed electrochemistry can be described as a direct oxidation of the starting $Pd_2(+4)$ complex to the $[Pd_2(+6)]^{2+}$ cationic species followed by coordination of the chlorides to generate neutral $[Pd_2(+6)Cl_2]$ species.



Fig. 4 CV at glassy carbon electrode for 1.0 mM solution of 5 in 0.10 M Bu_4NPF_6 -CH₂Cl₂. (a) The first oxidation peak; (b) after the addition of a stoichiometric amount of $Et_4N^+Cl^-$.

Conclusions

New palladium(II) compounds with a mixed set of metalated triarylphosphines and carboxylate ligands have been characterized. They all have a paddle wheel structure and present relatively short palladium–palladium distances. The oxidation properties of these compounds are very much dependent on the electron donating properties of the metalated phosphine and the carboxylate ligands. Thus, compounds **3–6** exhibit two reversible oxidation processes by cyclic voltammetry, while the remaining compounds with electronwithdrawing substituents in the metalated phosphine and/or in the carboxylate groups lose all reversibility and only show poorly defined oxidation processes. The ability of these compounds to form $Pd_2(+6)$ species by chemical oxidation will be explored. The synthetic method can be easily applied to the preparation of other palladium compounds with selected bridging ligands. This will be done as a second part of this study.⁴⁵

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