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Carboxylation of (DPPF)-MCl_2 [DPPF = 1,1′-bis(diphenylphosphino)ferrocene; M = Pt or Pd] in aqueous and non-aqueous solution

Crystal and molecular structures of $[Pt(C_2O_4)(DPPF)]$ and of $[PtCl(NO_3)(DPPF)]$

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Abstract

Treatment of the complexes $[MCl_2(DPPF)]$ (M = Pt or Pd) {readily prepared in high yield from $[MCl_2(DMSO)_2]$ (M = Pt (*cis*-) or Pd (*trans*-) and DPPF in $CHCl_3$} with two molar proportions of $AgNO_3$ in H_2O did not give the expected cation $[M(DPPF)(H_2O)_2]^{2+}$ in solution. Instead the unusual homobimetallic bridged complex $[\{M(\mu\text{-}OH)(DPPF)\}_2](NO_3)_2$ was formed as an insoluble solvolysis solid product. Hence, carboxylation by addition of carboxylate anions to the solution cannot be carried out by this method. In contrast, the complex $[PtCl_2(DPPF)]$ reacted readily with two molar proportions of AgOAc or one of $Ag_2\{1,1'\text{-}(OOC)_2fc\}$ (fc = ferrocene-2H) in acetone to give the corresponding carboxylato complexes. Other carboxylato complexes were obtained from the reaction of the complexes $[MCl_2(DPPF)]$ and the K-salts of e.g. $(COOH)_2$, $CH_2(COOH)_2$, and $\overline{CH_2CH_2CH_2C}(COOH)_2$ in H_2O. With few exceptions, neither the K- nor the Ag-salts of the acids Me_3CCOOH and $C_6H_{11}COOH$ react completely with $[MCl_2(DPPF)]$ in aqueous or non-aqueous solutions. However, the required products were obtained by displacement of DMSO from the corresponding carboxylato complexes by DPPF in $CHCl_3$. All of the new carboxylato complexes and the solvolysis products were characterized physicochemically and spectroscopically. The X-ray structures of $[Pt\{(OOC)_2\}(DPPF)]$ and of $[PtCl(NO_3)(DPPF)]$ were determined, to obtain some additional information on the coordination mode of the unsymmetrical DPPF ligand in this type of complexes.

Keywords: Platinum; Palladium; 1,1′-Bis(diphenylphosphino)ferrocene; Carboxylato complexes; NMR and X-ray studies; Structures

1. Introduction

The 1,1′-bis(diphenylphosphino)ferrocene (DPPF) ligand has received much attention in the past two decades because it is a readily available versatile ligand which coordinates smoothly with metal ions, and there have been several reports of its complexes with transition and non-transition metals [1–6]. Almost all of these reports were concerned with its coordination to metal ions and the physical properties of the so formed complexes, and only two articles described the solvolysis behaviour of $[PtCl_2(DPPF)]$ in non-aqueous solutions. One of them involved a determination of the X-ray crystal structure of the solvolysis product $[\{Pt(\mu\text{-}OH)(DPPF)\}_2](BF_4)_2$ [7] and the other a study concerned with its complexation with nucleosides [8]. The carboxylato complexes of (DPPF)–Pt or –Pd species have been given less attention, probably because they cannot be prepared by simple dechlorination of $[MCl_2(DPPF)]$ with $AgNO_3$ followed by addition of

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the carboxylate anion (vide infra). In view of this, and in continuation of our previous work on a similar ligand, viz. (diphenylphosphino)ferrocene [9], and of the carboxylation of $[MCl_2(DMSO)_2]$ (M = Pt or Pd) complexes in aqueous solutions [10], we decided to prepare some new carboxylato complexes of the general formula $[M(OOCR)_2(DPPF)]$, namely those with M = Pt or Pd, OOCR = $^1/_2(OOC)_2$, $^1/_2(OOC)_2CH_2$, $^1/_2\{(OOC)_2CCH_2CH_2CH_2\}$, $^1/_2\{1,1'\text{-}(OOC)_2fc\}$ (fc = ferrocene-2H), OAc, $(OOC)CMe_3$ and $(OOC)C_6H_{11}$ in aqueous and non-aqueous media. Like other similar complexes [1,2,4], the new carboxylato complexes are of interest in a number of fields; the alteration of electron-rich and electron-poor centers make them good candidates for electrochemical and catalytic studies, for example.

2. Experimental

2.1. General

The ^{1}H- and ^{13}C-NMR spectra were recorded on Varian Unity 500 and Gemini 2000 spectrometers, respectively, with $CDCl_3$ as solvent and Me_4Si as internal reference. ^{31}P-NMR spectra were recorded on a Gemini 200 spectrometer with $CDCl_3$ as solvent and H_3PO_4 (85%) as external reference. The NMR spectra and the elemental analyses were determined at the Institut für Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg, Germany. IR spectra were recorded for KBr discs on a Pye-Unicam FT IR spectrophotometer.

2.2. Starting materials

The salts $PtCl_2$ and $PdCl_2$, the free ligand 1,1′-bis(diphenylphosphino)ferrocene (DPPF) and the acids 1,1-ferrocene dicarboxylic acid $\{1,1'\text{-}(HOOC)_2fc\}$, CH_3COOH, $(COOH)_2 \cdot 2H_2O$, $CH_2(COOH)_2$, $CH_2CH_2CH_2C(COOH)_2$, $C_6H_{11}COOH$ and Me_3C-COOH were commercial products and were used as supplied. The Ag- and K-carboxylates were prepared by adding one equivalent of $AgNO_3$ or KOH for each COOH group in ethanol until complete precipitation of the salt occurred. The solid formed was filtered off, washed with ethanol and ether, and dried under vacuum. The yield in all cases was > 80%.

2.3. Preparation of complexes

The *cis*-$[PtCl_2(DMSO)_2]$ and *trans*-$[PdCl_2(DMSO)_2]$ complexes were prepared as described previously [10]. The $[PtCl_2(DPPF)]$ (**1**) and $[PdCl_2(DPPF)]$ (**2**) complexes were prepared by modification of the method described by others [2], and proved to be faster and to give higher yields and greater purity.

Equimolar quantities of $[MCl_2(DMSO)_2]$ {M = Pt (*cis*-) or Pd (*trans*-)} and the ligand DPPF in $CHCl_3$ were heated gently for ca. 30 min with continuous stirring. The clear solution was reduced in volume and ether was added until precipitation was complete. The solid thus formed was filtered off, washed several times with ether, and dried in a vacuum-oven at 80 °C for several hours. The yield was almost quantitative (> 90%).

2.4. $[Pt\{(OOC)_2\}(DPPF)]$ (3)

To a suspension of $[PtCl_2(DPPF)]$ (0.107 g, 0.13 mmol) in water (20 ml) was added a solution of $K_2(OOC)_2$ (0.12 g, 0.67 mmol) in water (5 ml). The mixture was heated under reflux for ca. 3 h then the solid was filtered off, washed several times with water, and dried in a vacuum-oven to constant weight. The product was pure enough for further purposes, but it can be crystallized from chloroform–*n*-pentane as fine yellow crystals. Yield: 87%; m.p. 194 °C (dec.). Anal. Found: C, 45.84; H, 3.28; $C_{36}H_{28}FeO_4P_2Pt \cdot H_2O \cdot CHCl_3$ (974.89) Calcd.: C, 45.58; H, 3.21%. ν(C=O) 1704 and 1674 cm^{-1}, $\nu(H_2O)$ 3450 cm^{-1}.

The following complexes were prepared analogously from the appropriate dichloro complex and potassium salt:

$[Pd\{(OOC)_2\}(DPPF)]$ (**4**); m.p. 245 °C (dec.). Anal. Found: C, 56.83; H, 3.82. $C_{36}H_{28}FeO_4P_2Pd \cdot H_2O$ (766.83) Calcd.: C, 56.39; H, 3.94%. ν(C=O) 1710 and 1685 cm^{-1}, $\nu(H_2O)$ 3452 cm^{-1}.

$[Pt\{(OOC)_2CH_2\}(DPPF)]$ (**5**); m.p. 200 °C (dec.). Anal. Found: C, 49.84; H, 3.94; $C_{37}H_{30}FeO_4P_2Pt \cdot 2H_2O$ (887.56) Calcd.: C, 50.07; H, 3.86%. ν(C=O) 1658 cm^{-1}, $\nu(H_2O)$ 3460 cm^{-1}.

$[Pd\{(OOC)_2CH_2\}(DPPF)]$ (**6**); m.p. 155 °C (dec.). Found: C, 57.13; H, 3.95; $C_{37}H_{30}FeO_4P_2Pd \cdot H_2O$ (780.85) Calcd.: C, 56.91; H, 4.13%. ν(C=O) 1653 (sh) cm^{-1}, $\nu(H_2O)$ 3431 cm^{-1}.

$[Pt\{(OOC)_2CCH_2CH_2CH_2\}(DPPF)]$ (**7**); m.p. 166 °C (dec.). Anal. Found: C, 53.40; H, 4.16; $C_{40}H_{34}FeO_4P_2Pt \cdot H_2O$ (909.61) Calcd.: C, 52.82; H, 3.99%. ν(C=O) 1660 and 1636 cm^{-1}, $\nu(H_2O)$ 3450 cm^{-1}.

2.5. $[Pt\{1,1'\text{-}(OOC)_2fc\}(DPPF)]$ (8)

The complex $[PtCl_2(DPPF)]$ (0.20 g, 0.24 mmol) was dissolved in anhydrous acetone, $Ag_2\{1,1'\text{-}(OOC)_2fc\}$ (0.12 g, 0.25 mmol) was added, and the mixture was stirred under reflux for ca. 2 h. The solvent was evaporated off and the residual solid was extracted with $CHCl_3$. The extract was reduced in volume and ether was added to the point of turbidity. The yellow solid formed was filtered off, washed with ether, and dried under vacuum. Yield: 68%; m.p. 193 °C (dec.). Anal. Found: C, 52.66; H, 3.83; $C_{46}H_{36}$ $Fe_2O_4P_2Pt \cdot 2H_2O$ (1057.56) Calcd.: C, 52.24; H, 3.81%. ν(C=O) 1614 cm^{-1}, $\nu(H_2O)$ 3435 cm^{-1}. The complex had evidently taken up water during the preparation or work up and drying in a vacuum-oven for long time did not change the elemental analysis.

The complex $[Pt(OAc)_2(DPPF)]$ (**9**) was prepared similarly; m.p. 182 °C (dec.). Anal. Found: C, 52.27; H, 4.12; $C_{38}H_{34}FeO_4P_2Pt$ (867.57) Calcd.: C, 52.61; H, 3.95%. ν(C=O) 1623 cm^{-1}.

2.6. *[Pt(OOCCMe$_3$)$_2$(DPPF)] (**10**)*

This complex can be prepared as described for complex **3** by prolonged refluxing of a mixture of an excess of $K(OOC)CMe_3$ and complex **1** in water until complete conversion of the latter into the product. However, the following method is superior:

To a suspension of $[PtCl_2(DMSO)_2]$ (0.106 g, 0.25 mmol) in water (10 ml) was added a solution of $AgNO_3$ (0.085 g, 0.25 mmol) in H_2O (5 ml). The stirred mixture was heated at ca. 80 °C for 2 h then treated with a small amount of charcoal and filtered hot. The filtrate was added to a solution of $K(OOC)CMe_3$ (0.125 g, 0.78 mmol) in water (2 ml) and the mixture was warmed for few minutes then evaporated to dryness. The residual pale yellow solid-gel was suspended in chloroform and DPPF (0.14 g, 0.25 mmol) was added with stirring. The yellow solution was filtered, the filtrate was reduced in volume, and ether was added to the point of turbidity. The solid formed was filtered off, washed with ether, and dried in vacuum. Yield: 72%; m.p. 224 °C (dec.). Anal. Found: C, 53.36; H, 4.67; $C_{44}H_{46}FeO_4P_2Pt \cdot 2H_2O$ (987.76) Calcd.: C, 53.50; H, 5.10%. ν(C=O) 1625 cm^{-1}, $\nu(H_2O)$ 3417 cm^{-1}.

The $[Pt\{(OOC)C_6H_{11}\}_2(DPPF)]$ (**11**) complex was prepared similarly; m.p. 142 °C (dec). Anal. Found: C, 56.75; H, 5.34; $C_{48}H_{50}FeO_4P_2Pt \cdot H_2O$ (1021.84) Calcd.: C, 56.42; H, 5.13%. ν(C=O) 1621 cm^{-1}, $\nu(H_2O)$ 3408 cm^{-1}.

2.7. *[{M(μ-OH)(DPPF)}$_2$](NO$_3$)$_2$ (M = Pt, **12**; M = Pd, **13**)*

To a suspension of $[MCl_2(DPPF)]$ (0.19 mmol) in water (20 ml) $AgNO_3$ (0.063 g, 0.37 mmol) was added. The stirred mixture was heated at 80 °C for 2 h, then filtered hot. The colourless filtrate was evaporated and the residual yellow–orange solid was dried in vacuum for several hours. It was dissolved in $CHCl_3$ and the solution was filtered to remove AgCl and the filtrate reduced in volume. Ether was added to the point of turbidity and the solution kept in the refrigerator overnight. The solid formed was filtered off, washed with ether, and dried in vacuum.

Complex **12**: Yield: 63%; m.p. 194 °C (dec.). Anal. Found: C, 46.38: H, 3.58; N, 1.49; $C_{68}H_{58}Fe_2N_2O_8$-$P_4Pt_2 \cdot CHCl_3 \cdot H_2O$ (1794.40) Calcd.: C, 46.19; H, 3.43; N, 1.56%. $\nu(H_2O)$ 3465 cm^{-1}.

Complex **13**: Yield: 57%; m.p. 164 °C (dec). Anal. Found: C, 51.55; H, 3.89; N, 1.68; $C_{68}H_{58}Fe_2N_2O_8$-$P_4Pd_2 \cdot CHCl_3 \cdot H_2O$ (1617.02) Calcd.: C, 51.25; H, 3.80; N, 1.73%. $\nu(H_2O)$ 3435 cm^{-1}.

Note: The yields of complexes **12** and **13** can be enhanced by addition of equimolar quantity of the free ligand DPPF to the reaction mixture.

2.8. *[PdCl(NO$_3$)(DPPF)] (**14**)*

This complex was prepared by a similar method to that for **12** and **13** apart of using equimolar quantities of the reactants $[PdCl_2(DPPF)]$ and $AgNO_3$ in water. Upon crystallization of the solid thus formed from hot $CHCl_3$, dark maroon crystals separated out suitable for X-ray analysis. No further analyses were done on this complex.

2.9. *X-ray structure determination of **3** and **14***

Crystals suitable for single-crystal diffraction analyses of ($\mathbf{3} \cdot 3CHCl_3$) and ($\mathbf{14} \cdot CHCl_3$) were grown at 25 °C by slow evaporation of their chloroform solutions. Intensity data were collected on a STOE-IPDS diffractometer with Mo–K_α radiation ($\lambda = 0.71073$ Å, graphite monochromator) at 220(2) K. A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Table 1. Absorption corrections were carried out numerically (T_{min}/T_{max} 0.377/0.567, $\mathbf{3} \cdot 3CHCl_3$; 0.650/0.837, $\mathbf{14} \cdot CHCl_3$). The structures were solved by direct methods with SHELXS-97 and refined using SHELXL-97 [11]. Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were found in the difference Fourier map ($\mathbf{3} \cdot 3CHCl_3$) and added to the model in their calculated positions according to the riding model ($\mathbf{14} \cdot CHCl_3$), respectively. They were refined isotropically.

3. Results and discussion

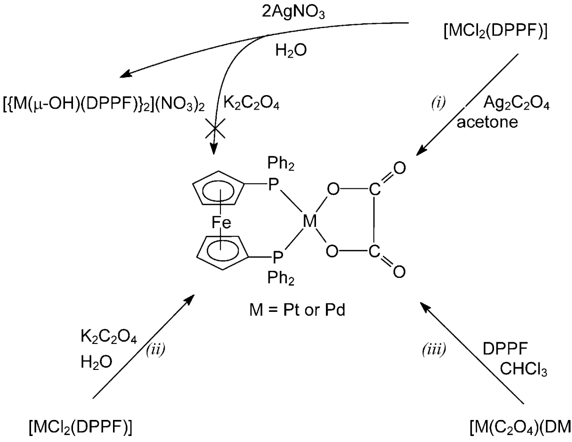
It is well known that dechlorination of platinum(II) or palladium(II) complexes of the type $[MCl_2L_2]$, $L_2 =$ 2DMSO or cyclohexane-1,2-diamine, by silver nitrate in aqueous media leads to formation of the cation $[ML_2(H_2O)_2]^{2+}$ and this is converted into the corresponding carboxylato complex upon treatment with carboxylate ion [10,12]. However, when L_2 was the chelate 1,1′-bis(diphenylphosphino)ferrocene (DPPF), the reaction of $[MCl_2(DPPF)]$ with silver nitrate (in

Table 1
Crystal data and structure refinement for **3**·3CHCl$_3$ and **14**·CHCl$_3$

	[Pt{(OOC)$_2$}-(DPPF)]·3CHCl$_3$	[PdCl(NO$_3$)-(DPPF)·CHCl$_3$
	(**3**·3CHCl$_3$)	(**14**·CHCl$_3$)
Empirical formula	$C_{39}H_{31}Cl_9FeO_4P_2Pt$	$C_{35}H_{29}Cl_4FeNO_3P_2Pd$
Formula weight	1195.57	877.58
T (K)	220(2)	220(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
b (Å)	18.904(3)	16.511(2)
c (Å)	21.967(4)	17.279(4)
β (°)	93.73(2)	91.08(3)
V (Å^3)	4383.7(13)	3598.4(13)
Z	4	4
$\rho_{calc.}$ (g cm^{-3})	1.812	1.620
μ (Mo–K$_\alpha$) (mm^{-1})	4.180	1.325
Scan range 2Θ (°)	4.30–51.92	4.04–51.64
Reciprocal lattice segments h, k, l	$-12 \rightarrow 11$, $-22 \rightarrow 23$, $-26 \rightarrow 26$	$-15 \rightarrow 15$, $-18 \rightarrow 18$, $-21 \rightarrow 20$
Reflections collected	27 292	26 001
Reflections independent	8434 [$R_{int} = 0.0615$]	6480 [$R_{int} = 0.1154$]
Data/restrains/parameters	8434/0/629	6480/0/424
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0298$ $wR_2 = 0.0714$	$R_1 = 0.0587$ $wR_2 = 0.1456$
R indices (all data)	$R_1 = 0.0440$ $wR_2 = 0.0788$	$R_1 = 0.1045$ $wR_2 = 0.1688$
Largest difference peak and hole (e Å^{-3})	1.046, −0.793	0.880, −0.843

1:1 molar ratio) in water was found to take a different course and not to give the cation [M(DPPF)(H$_2$O)$_2$]$^{2+}$ in solution. Thus carboxylation by addition of carboxylate ion could not be achieved by this method. The rather unusual homobimetallic hydroxo-bridged complexes [{M(μ-OH)(DPPF)}$_2$](NO$_3$)$_2$, (M = Pt (**12**); M = Pd (**13**)) were obtained by the treatment of complexes **1** and **2** with silver nitrate in aqueous solution (Scheme 1). Complexes **12** and **13** remained in the reaction mixture as solids mixed with silver chloride and no metal ion could be detected in the colourless filtrate (see Section 2). An X-ray diffraction analysis of complex [{Pt(μ-OH)(DPPF)}$_2$](NO$_3$)$_2$ (**12**) could not be completely solved due to severe disorder, but showed unambiguously the topology of this complex as OH-bridged dinuclear species.

Possible methods for the formation of carboxylato complexes of the DPPF ligand are shown in Scheme 1. The first (i) involves the reaction of the precursors **1** or **2** with silver carboxylate in dry acetone. The second (ii) involves the reaction of the precursors **1** or **2** with the potassium salt of an appropriate carboxylic acid in water. This method was found to be effective when the potassium salts of dicarboxylic acids, namely, oxalic acid, malonic acid or 1,1-cyclobutane dicarboxylic acid were used along with complexes precursors **1** or **2** and the reactions were allowed to proceed for completion. In the case of monocarboxylic acids, e.g. pivalic acid or cyclohexane carboxylic acid, the formation of the product is slower than that of the potassium dicarboxylate and proceeds through the formation of an intermediate complex, i.e. [PtCl(carboxylato)(DPPF)] (vide infra). In the case of the salt K(OOC)C$_6$H$_{11}$, the reaction with complex **1** did not go into completion and so a pure product could not be obtained. These results were monitored by ^{31}P-NMR spectroscopy (vide infra). It is evident that the most useful method is the third one, (iii), involving a ligand displacement reaction. Thus the platinum and palladium complexes **10** and **11** were prepared by a simple displacement of DMSO by DPPF in an organic solvent, e.g. chloroform. The platinum and palladium carboxylato complexes of the ligand DPPF prepared by the three methods (Scheme 1) have been fully characterized. Their physical properties are reported in Section 2, with the ^{1}H-, ^{31}P-, and ^{13}C-NMR spectral data listed in Tables 2 and 3. All the palladium complexes **2**, **4**, **6**, and **13** are maroon in colour while the platinum complexes **1**, **3**, **5**, and **7**–**12** are yellow–orange. Both the palladium and the platinum complexes are stable solids in air and decompose only above 150 °C. With few exceptions, most of the complexes were isolated from their solutions bearing water of solvation, as is apparent from the broad bands in the IR spectra at ca. 3450 cm^{-1} due to ν(H$_2$O) and confirmed by the appearance of the proton signals from H$_2$O as broad signals at δ 1.64 ppm in the ^{1}H-NMR spectra (in CDCl$_3$).



Scheme 1. Possible routes to the (DPPF)–Pt or –Pd carboxylato complexes with the oxalate anion used as example.

Table 2
^{1}H- and ^{31}P{^{1}H}-NMR data (δ in ppm and J in Hz) for the complexes **1**–**13**

Complex	^{1}H-NMR			^{31}P-NMR	
	δ(C_5H_4) [a]	δ(C_6H_5) [b]	δ(Others) [e]	δ	J(Pt–P)
1	4.17, 4.34	7.37–7.87		14.2 (13.06) [c]	3761.5 (3769) [c]
2	4.18, 4.38	7.35–7.91		35.0 (34) [c]	
3	4.27, 4.45	7.33–7.87		9.6	3850
4	4.30, 4.49	7.39–7.75		37.4	
5	4.30, 4.44	7.38–7.81	3.29s (CH_2)	8.3	3844
6	4.33, 4.47	7.43–7.83	3.33s (CH_2)	36.6	
7	4.31, 4.43	7.38–7.80	1.61t (CH_2) 2.48q (CH_2)$_2$	7.7	3844
8	4.10, 4.60	7.31–8.00	4.37 [d] (C_5H_4)$_2$	8.3	4016
9	4.34 [d]	7.30–7.85	1.32s (CH_3)	6.2	3935
10	4.30, 4.32	7.31–7.86	0.61s (CH_3)$_3$	7.4	3941
11	4.33 [d]	7.29–7.83	0.89–1.55m (C_6H_{11})	7.2	3935
12	4.24, 4.44	7.25–8.00		10.3	3824
13	4.30, 4.48	7.31–8.10		38.7	

[a] Broad signals.

[b] Multiplet signals.

[c] Data obtained from Ref. [2] using CH_2Cl_2 as solvent.

[d] Two signals are superimposed.

[e] Abbreviations: s, singlet; t, triplet; q, quintet; m, multiplet.

3.1. NMR studies

The ^{1}H-NMR spectra of all complexes **1**–**13** revealed the presence of multiplets at 7.2–8.0 ppm due to the phenyl protons and two broad signals at 4.2 and 4.5 ppm due to the protons of the cyclopentadienyl group. These are in addition to the signals of the anion protons if there are any (Table 2).

The ^{31}P{^{1}H}-NMR spectra (Table 2) of all the palladium complexes **2**, **4**, **6**, and **13** each showed a single signal expected for symmetrical phosphines while those of the platinum complexes **1**, **3**, **5**, and **7**–**12** showed singlets and doublets (due to the Pt, H couplings). The $^{1}J(^{195}Pt–^{31}P)$ coupling constant of complex **1**, 3761.5 Hz is typical for phosphine *trans* to a chlorine atom, c.f. [$PtCl_2$(DPPE)] 3621 Hz [13] and

Table 3
^{13}C-NMR chemical shifts (δ in ppm) of the complexes **1**–**13** [a]

Complex	Phenyl				Cyclopentadienyl			Carboxylato	
	δC1 [b]	δC2/6 [b]	δC3/5 [b]	δC4 [c]	δC1 [b]	δC2/5 [b]	δC3/4 [b]	δCO [d]	δ(others)
1	131.5	135.5	128.4	131.7	73.4	76.4	74.2		
2	131.4	135.5	128.6	131.7	73.3	76.7	74.3		
3	128.5	134.2	128.7	132.0	71.0	76.0	74.3	166.8	
4	128.9	134.4	129.3	132.1	71.3	76.5	74.5	166.8	
5	128.5	134.3	128.7	132.0	70.5	75.8	74.3	172.6	50.3(CH_2)
6	128.6	134.5	128.8	132.1	70.6	76.3	74.4	173.2	51.7(CH_2)
7	128.7	134.4	128.5	131.9	[e]	75.8	74.2	176.3	55.6(C), 15.5 (CH_2), 30.2(CH_2)$_2$
8	130.0	135.1	128.5	131.7	70.5	76.7	74.1	175.5	80.9(C1), 72.6(C2/3), 71.0(C4/5)
9	129.9	134.4	128.1	131.0	71.8	76.2	73.5	176.3	23.6(CH_3)
10	130.1	134.4	128.0	130.8	[e]	76.3	73.4	182.1	40.2$C(CH_3)_3$, 28.0$C(CH_3)_3$
11	130.0	134.4	128.0	130.9	72.3	76.3	73.4	180.3	46.0(C1), 29.6 (C2/6), 25.8 (C3/5), 26.1(C4)
12	127.2	133.5	128.8	132.2	69.3	76.3	74.7		
13	127.2	133.5	128.7	132.1	69.2	76.3	74.7		

[a] NMR data of **9**: $J(PP')$, 20.8 Hz. Phenyl carbon atoms: δC1, 129.9 ppm; J(PC), 64.8 Hz; $J(P'C)$, −0.04 Hz. δC2/6, 134.4 ppm; J(PC), 10.9 Hz; $J(P'C)$, 0.8 Hz. δC3/5, 128.1 ppm; J(PC), 11.1 Hz; $J(P'C)$, −1.9 Hz. δC4, 131.0 ppm. Cyclopentadienyl carbon atoms: δC1, 71.8 ppm; J(PC), 70.3 Hz; $J(P'C)$, 8.2 Hz. δC2/5, 76.2 ppm; J(PC), 13.8 Hz; $J(P'C)$, −2.8 Hz. δC3/4, 73.5 ppm; J(PC), 10.1 Hz; $J(P'C)$, −1.9 Hz. Acyl carbon atoms: δCO, 176.3 ppm (broad). δCH_3, 23.6 ppm; J(PC), 4.8 Hz; $J(P'C)$, 0.8 Hz.

[b] Multiplet signals.

[c] Singlets.

[d] Broad signal.

[e] Signals obscured by the noise.

$[PtCl_2(PPh_3)_2]$ 3679 Hz [14], and the coupling constants for the platinum complexes with a carboxylato group, i.e. with phosphine *trans* to oxygen, are higher than that for complex **1** by ca. 100–250 Hz (Table 2) reflecting electronegativity effects.

Unexpectedly, the ^{31}P-NMR spectrum of the solid obtained from the reaction between complex **1** and a large excess of $K(OOC)CMe_3$ in H_2O under reflux for ca. 3 h, revealed the presence of, in addition to the platinum starting material (10%) and the product **10** (14%), a complex (76%) with parameters, δ 3.2 ppm; ^{1}J(PtP) 3682.5 Hz and δ 18.0 ppm; ^{1}J(PtP) 4076.1 Hz; ^{2}J(PP) 15.5 Hz. The first coupling constant is typical for phosphine *trans* to chlorine and the second for phosphine *trans* to oxygen, and they are tentatively assigned to the intermediate complex $[PtCl\{(OOC)CMe_3\}(DPPF)]$. The latter was converted (100%) into the dicarboxylato complex **10** upon more prolonged refluxing of the reaction mixture. Similarly, ^{31}P-NMR spectroscopy showed that the reaction of complex **1** with a large excess of $K(OOC)C_6H_{11}$ in water under reflux for ca. 3 h gave a solid containing unchanged **1** (80%) and a new complex (20%) with the parameters δ 3.3 ppm; ^{1}J(PtP) 3673 Hz and d 18.4 ppm; ^{1}J(PtP) 4074 Hz; ^{2}J(PP) 16.2 Hz. These parameters are tentatively assigned to the monocarboxylato complex, i.e. $[PtCl\{(OOC)C_6H_{11}\}(DPPF)]$. When the mixture with an excess of $K(OOC)C_6H_{11}$ was refluxed further for about 3 h, the ^{31}P-NMR spectrum of the solid revealed that the proportion of the monocarboxylato complex increased to 32%. None of the dicarboxylato complex **11** was detected even after more prolonged refluxing. However, the dicarboxylato complex **11**, like the other complexes can be obtained in a pure form by treating the corresponding DMSO complex, i.e. $[Pt\{(OOC)C_6H_{11}\}_2(DMSO)_2]$ [10] with DPPF in chloroform.

We believe that the reaction of complex **1** or **2** with silver nitrate in water to give the dimeric complex **12** or **13** probably takes place in through two steps, the first step involving the removal of one chlorine atom and the second step the removal of the second chlorine atom. This was tentatively confirmed by the formation of a complex with the ^{31}P-NMR parameters δ 3.4 ppm; ^{1}J(PtP) 3843.7 Hz and δ 18.4 ppm; ^{1}J(PtP) 3965.0 Hz; ^{2}J(PP) 15.4 Hz, which are consistent with the presence of two different phosphine nuclei, with the lower J value being for phosphine *trans* to chlorine and the higher J value for phosphine *trans* to oxygen. The complex is most likely to be $[Pt_2(\mu\text{-}Cl)(\mu\text{-}OH)(DPPF)_2](NO_3)_2$. However, we have not attempted to isolate any of the three intermediates, $[PtCl\{(OOC)CMe_3\}(DPPF)]$, $[PtCl\{(OOC)C_6H_{11}\}(DPPF)]$, and $[Pt_2(\mu\text{-}Cl)(\mu\text{-}OH)(DPPF)_2](NO_3)_2$.

The ^{13}C-NMR spectra (Table 3) of all complexes **1**–**13** showed signals due to the phenyl and cyclopentadienyl groups in addition to those from the carboxylato group. The spectra of the complexes are of the AA′X form [15]. The AA′ represent the two phosphine atoms of DPPF and X represents the carbon atom of the phenyl or the cyclopentadienyl. The ^{13}C-NMR chemical shifts for all the complexes are listed in Table 3 but no coupling constants are shown since the ^{13}C-NMR data, calculated with the computer programme PERCH [16], for complex **9**, i.e. $[Pt(OAc)_2(DPPF)]$, represent a model for the rest of complexes (footnote Table 3).

3.2. *Crystal structures of **3** and **14***

Single crystals of the oxalato complex $[Pt\{(OOC)_2\}(DPPF)]\cdot 3CHCl_3$ (**3**$\cdot 3CHCl_3$) were obtained by the crystallization of the complex from chloroform in well shaped orange crystals. The molecular structure is shown in Fig. 1, selected bond lengths and angles are given in Table 4. The platinum atom is coordinated by two oxygen atoms of the oxalato ligand and two phosphorous atoms of the DPPF ligand. The $[PtO_2P_2]$ unit and the oxalato ligand $(COO)_2$ are planar in good approximation (greatest deviations from the mean plane 0.028(3) Å for O3 and 0.046(3) Å for O2, respectively). Both planes are nearly coplanar (interplanar angle: 6.1(1)°). The 'bite' of the DPPF ligand causes a P1–Pt–P2 angle of 97.42(4)° that is in the expected range (P–M–P′, M = transition metal: median 99.0°, lower/upper quartile 97.9/100.8°, 25 observations [17]). Due to that the opposite O1–Pt–O2 angle (81.1(1)°) is lowered and is in the expected range for O–M–O′ angles of transition metal oxalato complexes (median 81.7°, lower/upper quartile 76.3/84.2°, 546 observations [17]). The ferrocene moiety is staggered (P1–C3···C8–P2 35.1(2)°). As expected the C–O bonds coordinated to platinum are much longer than the non-coordinated ones (1.289(6)/1.302(6) vs. 1.216(6)/1.217(6) Å). In the solid state, two of the three chloroform molecules are involved in hydrogen bonds C=O···$HCCl_3$ to the non-coordinated oxygen atoms of the oxalato ligand (Fig. 1):

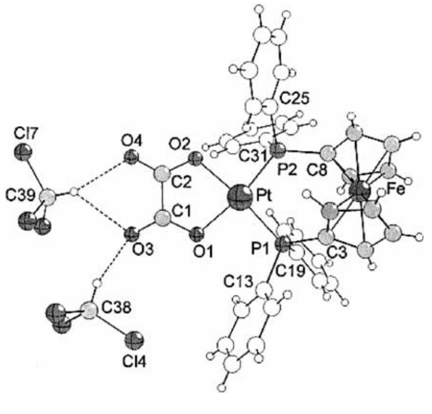


Fig. 1. Solid-state structure of crystals of $[Pt\{(OOC)_2\}(DPPF)]$ $3CHCl_3$ (**3**$\cdot 3CHCl_3$). One solvate molecule is omitted for clarity.

Table 4
Selected bond lengths (in Å) and angles (in °) for $[Pt\{(OOC)_2\}(DPPF)]\cdot 3CHCl_3$ (**3**$\cdot 3CHCl_3$)

Bond lengths			
Pt–O1	2.062(3)	C1–O1	1.302(6)
Pt–O2	2.065(3)	C1–O3	1.216(6)
Pt–P1	2.241(1)	C2–O2	1.289(6)
Pt–P2	2.247(1)	C2–O4	1.217(6)
C1–C2	1.563(6)	Fe–C	2.012(5)–2.093(5)
Bond angles			
P1–Pt–P2	97.42(4)	O2–Pt–P1	173.08(9)
O1–Pt–O2	81.1(1)	O2–Pt–P2	89.17(9)
O1–Pt–P1	92.37(9)	Pd–Pt–C3	114.1(2)
O1–Pt–P2	170.22(9)	Pd–Pt–C8	123.3(2)

Table 5
Selected bond lengths (in Å) and angles (in °) for $[PdCl(NO_3)(DPPF)]\cdot CHCl_3$ (**14**$\cdot CHCl_3$)

Bond lengths			
Pd–Cl1	2.360(2)	N–O1	1.267(9)
Pd–O1	2.100(5)	N–O2	1.236(9)
Pd–P1	2.290(2)	N–O3	1.266(8)
Pd–P2	2.275(2)	Fe–C	1.985(8)–2.064(9)
Bond angles			
P1–Pd–P2	98.63(7)	Cl1–Pd–P1	173.26(8)
Cl1–Pd–O1	86.2(2)	Cl1–Pd–P2	86.65(8)
O1–Pd–P1	89.3(2)	Pd–P1–C1	116.2(3)
O1–Pd–P2	167.7(2)	Pd–P2–C6	122.8(2)

So the $Cl_3C39{-}H$ molecule acts as hydrogen donor for a three-center hydrogen bond (C39–H···O4: H···O4 2.31(6) Å, C39–H···O4 157°; C39–H···O3: H···O3 2.51(6) Å, C39–H···O3 133°) whereas the $Cl_3C38{-}H$ molecule acts as a two-center hydrogen bond (C38–H···O3: H···O4 2.22(7) Å, C38–H···O3 156°). All of these values are within the geometrical cut-offs given for C=O···H–C hydrogen bonds [18]. The complex $[PdCl(NO_3)(DPPF)]$ (**14**) crystallized from chloroform as **14**$\cdot CHCl_3$ in well shaped dark maroon crystals. The X-ray structure analysis revealed that there are no unusual intermolecular interactions between the complex and the solvate molecule (shortest intermolecular contact between non-hydrogen atoms: C31···Cl4 3.336(4) Å). The molecular structure of **14** is shown in Fig. 2, selected bond lengths and angles are given in Table 5. The geometry of the Pd(DPPF) fragment is essentially the same as that in complex **3**$\cdot 3CHCl_3$ (P1–Pt–P2 98.63(7)°, P1–C1···C6–P2 32.6(4)°). There is a substantial deviation of the $[PdClOP_2]$ moiety from planarity: The greatest deviation from the mean plane amounts to 0.159(6) Å for O1. The nitrato ligand is monohapto coordinated to palladium. The complex plane is nearly perpendicular to the plane of the nitrato ligand (83.8(4)°).

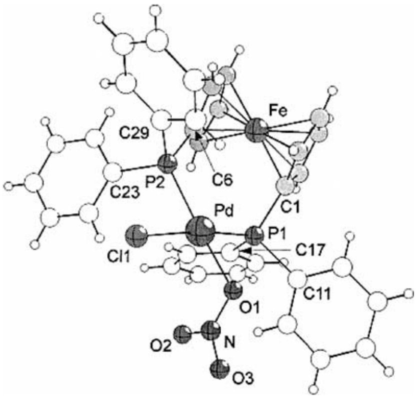


Fig. 2. Molecular structure of $[PdCl(NO_3)(DPPF)]\cdot CHCl_3$ (**14**$\cdot CHCl_3$). The solvate molecule is omitted for clarity.

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Center, CCDC nos. 208350 and 208349 for compounds **3**$\cdot 3CHCl_3$ and **14**$\cdot CHCl_3$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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