Journal of Organometallic Chemistry, 329 (1987) 267–279
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Decarboxylation syntheses of transition metal organometallics

V *. Preparations and structures of 2-carboxylato-3,4,5,6-tetrafluorophenyl(*O,C*)platinum(II) complexes

D. Anastasiou, G.B. Deacon and B.M. Gatehouse

Chemistry Department, Monash University, Clayton, Victoria, 3168 (Australia)

(Received January 20th, 1987)

Abstract

The complexes $Pt[\overline{C_6F_4\text{-}o\text{-}C(O)O}](PPh_3)L$ (L = py, 2,4-$Me_2C_5H_3N$ or 2,6-$Me_2C_5H_3N$) and $Pt[\overline{C_6F_4\text{-}o\text{-}C(O)O}]L_2$ [$L_2 = (Ph_2PCH_2)_2$ or $(Ph_2P)_2(CH_2)_3$] have been prepared by decarboxylation reactions between *cis*-$PtCl_2(PPh_3)_2$ or $PtCl_2L_2$ and thallium(I) tetrafluorophthalate in boiling pyridine, or 2,4- or 2,6-dimethylpyridine. Reaction of *cis*-$PtCl_2(PPh_3)_2$ with *o*-$C_6F_4(CO_2Tl)_2$ in pyridine at room temprature gives $Pt[o\text{-}(O_2C)_2C_6F_4](PPh_3)_2$, which undergoes decarboxylation at 160–165 °C in the absence of a solvent to give $Pt[\overline{C_6F_4\text{-}o\text{-}C(O)O}](PPh_3)_2$. ^{31}P NMR data suggest that in $Pt[\overline{C_6F_4\text{-}o\text{-}C(O)O}](PPh_3)L$ comlexes, triphenylphosphine is *trans* to the coordinated oxygen. The crystal structure for L = 2,6-$Me_2C_5H_3N$ as a chloroform solvate shows *a,b,c,d*-Pt(*O,C,P,N*) square planar stereochemistry with 2,6-dimethylpyridine near perpendicular to the coordination plane and the tetrafluorophenyl ring near coplanar with this plane.

Introduction

Thermal decomposition of mercuric arene- and heteroarene- *ortho*-dicarboxylates and naphthalene-1,8-dicarboxylates often results in hemidecarboxylation [1–6] (the Pesci reaction [6]) to give 2-carboxylatoarylmercurials, e.g. $[HgC_6H_4\text{-}o\text{-}C(O)O]_n$ (see [5] for structural comments) and 8-carboxylatonaphthalen-1-ylmercurials. Similar reactions involving other elements are uncommon [5]. Thermal decomposition of *o*-$C_6F_4(CO_2SnPh_3)_2$ into triphenyltin fluoride may involve formation and decomposition of *o*-$Ph_3SnC_6F_4CO_2SnPh_3$ [7]. The complex μ-(*o*-$O_2CC_6F_4$)[*trans*-$Rh(CO)(PPh_3)_2]_2$ has been obtained from a rhodium analogue of the Pesci reaction

* For part IV see Ref. 29.

0022-328X/87/$03.50

[8]. Recently, it has been shown that Pt[*o*-$(O_2C)_2C_6H_4$]$(PPh_3)_2$ undergoes radical or thermal hemidecarboxylation to give Pt[C_6H_4-*o*-C(O)O]$(PPh_3)_2$ [9]. We now report preparations of 2-carboxylato-3,4,5,6-tetrafluorophenyl(*O,C*)platinum(II) compounds by a Pesci-type decarboxylation, and a study of their properties and structures.

Results and discussion

(a) Decarboxylation syntheses

Reaction of *cis*-$PtCl_2(PPh_3)_2$ with thallium(I) tetrafluorophthalate in boiling pyridine, 2,4-dimethylpyridine or 2,6-dimethylpyridine resulted in decarboxylation and formation of a 2-carboxylato-3,4,5,6-tetrafluorophenyl(*O,C*)platinum(II) complex in which one of the triphenylphosphine ligands is replaced by a pyridine (reaction (1)).

$$\textit{cis}\text{-}PtCl_2(PPh_3)_2 + o\text{-}C_6F_4(CO_2Tl)_2 + L \rightarrow Pt[C_6F_4\text{-}o\text{-}C(O)O](PPh_3)L + Ph_3P + 2TlCl + CO_2 \quad (1)$$

(**1a**, L = py; **1b**, L = 2,4-dimethylpyridine; **1c**, L = 2,6-dimethylpyridine)

The arrangement of the ligands is considered in section (b). It is surprising that substitution occurs with the highly hindered 2,6-dimethylpyridine, since this has been successfully used as a non-coordinating decarboxylation medium in the synthesis of organoamidoplatinum(II) complexes [10]. Ligand replacement was obviated when the chelating ligands 1,2-bis(diphenylphosphino)ethane (dpe) and 1,3-bis(diphenylphosphino)propane (dpp) were used (reaction (2); L_2 = dpe or dpp).

$$PtCl_2L_2 + o\text{-}C_6F_4(CO_2Tl)_2 \rightarrow Pt[C_6F_4\text{-}o\text{-}C(O)O]L_2 + 2TlCl + CO_2 \quad (2)$$

(**2a**, L_2 = dpe; **2b**, L_2 = dpp)

Loss of triphenylphosphine during decarboxylation (reaction (1)) was avoided by a two step synthesis. Metathesis without decarboxylation or ligand displacement was observed on reaction of *cis*-$PtCl_2(PPh_3)_2$ with thallium(I) tetrafluorophthalate in pyridine at room temperature.

$$\textit{cis}\text{-}PtCl_2(PPh_3)_2 + o\text{-}C_6F_4(CO_2Tl)_2 \rightarrow \underset{(3)}{Pt[o\text{-}(O_2C)_2C_6F_4](PPh_3)_2} + 2TlCl \quad (3)$$

Careful pyrolysis of **3** in the absence of a solvent yielded the target bis(triphenylphosphine)platinum(II) complex **4**.

$$\underset{(3)}{Pt[o\text{-}(O_2C)_2C_6F_4](PPh_3)_2} \rightarrow \underset{(4)}{Pt[C_6F_4\text{-}o\text{-}C(O)O](PPh_3)_2} + CO_2 \quad (4)$$

Use of thallium dicarboxylates as reagents in Pesci-type decarboxylations, e.g. reactions (1) and (2), provides a convenient alternative approach to use of preformed platinum dicarboxylates, hitherto obtained from $Pt(PPh_3)_2O_2$ [9]. However, no decarboxylation was observed on heating *cis*-$PtCl_2(PPh_3)_2$ and thallium(I)

phthalate in boiling pyridine (this work), whereas preformed Pt[*o*-$(O_2C)_2C_6H_4$]-$(PPh_3)_2$ underwent hemidecarboxylation at 210°C or upon irradiation [9]. The difference in reactivity between thallium(I) phthalate and tetrafluorophthalate further illustrates facilitation of thermal decarboxylation by electron withdrawing substituents [5], and indicates that the transition state has carbanionic character.

(b) Properties and structures

Some complexes were isolated with one (**1b**, **1c** or **2a**) or two (**3**) chloroform molecules of solvation. Besides analytical evidence, the presence of chloroform was established by ^{1}H NMR spectroscopy (Experimental section) and by the X-ray crystal structure of **1c** · $CHCl_3$ (see below). Both **1b** · $CHCl_3$ and **1c** · $CHCl_3$ retain the solvent on prolonged standing, but chloroform is slowly lost from the other compounds, preventing determination of the crystal structure of single crystals of **3** · $2CHCl_3$.

The presence of chelating (*O,C*)-2-carboxylato-3,4,5,6-tetrafluorophenyl groups in **1a–c**, **2a**, **b** and **4** was established by ^{19}F NMR spectroscopy and infrared spectroscopy. Each compound has a low field ^{19}F resonance (Experimental section) typical [11] of fluorine *ortho* to a heavy metal substituent together with ^nJ(PtF) (n = 3 or 4) coupling (Table 1). The $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ values for the complexes (Table 1) are considerably greater than those for the substantially ionic (see molar conductance, Experimental section) *o*-$C_6F_4(CO_2Tl_2)_2$ and *o*-$HC_6F_4CO_2Na$ [12], as expected [13] for unidentate carboxylate coordination.

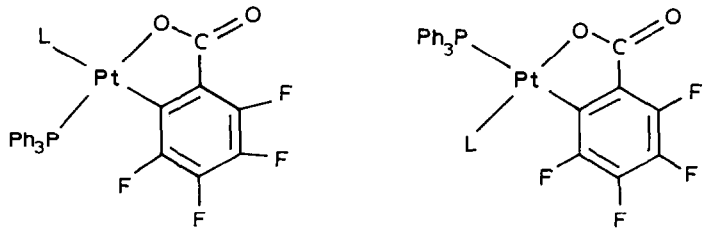
^1J(PtP) coupling constants for **3** and **4** (Table 1) establish clearly that the value for P *trans* to carboxyl is considerably larger than that for P *trans* to a polyfluoro-

Table 1

Spectroscopic data for some 2-carboxylato-3,4,5,6-tetrafluorophenyl(*O,C*)platinum(II) complexes and related compounds

Compound	$\nu_{as}(CO_2)$ [a] (cm^{-1})	$\nu_s(CO_2)$ [b] (cm^{-1})	Δ [c] (cm^{-1})	^3J(PtF(6)) (Hz)	^4J(PtF(5)) [d] (Hz)	^1J(PtP) (Hz)
o-$C_6F_4(CO_2Tl)_2$	1560	1379, 1364	188			
o-$HC_6F_4CO_2Na$ [e]	1585	1416, 1404	175			
3·$2CHCl_3$	1670, 1650	1300	360			3818
1a	1672	1332	340	161	87	4130
1b·$CHCl_3$	1654	1328	326	171	90	4133
1c·$CHCl_3$	1650	1330	320	165	90	4133
2a·$CHCl_3$	1660, 1641	1339	311	144	102	3759 [f] 2290 [g]
2b	1664	1333	331	141	108	3750 [f] 2326 [g]
4	1668	1332	336	169	90	3898 [f] 2346 [g]
Pt[$\overline{C_6H_4\text{-}o\text{-}C(O)O}$]-$(PPh_3)_2$ [h]						4128 [f] 1977 [g]

[a] Intensities s or vs (br). [b] Intensities m or s. [c] $\Delta = \nu_{as}(CO_2) - \nu_s(CO_2)$. [d] ^4J(PtF3) not resolved. [e] From Ref. 12. [f] For P *trans* to carboxyl. [g] For P *trans* to aromatic carbon. [h] From Ref. 9.



(L = py , 2,4-or 2,6-dimethylpyridine)

aryl carbon. Accordingly, the magnitude of ^1J(PtP) for **1a–c** shows that phosphorus is *trans* to carboxyl (**A**) and not to carbon (**B**). To provide unambiguous stereochemical assignment, the X-ray crystal structure of **1c** · $CHCl_3$ was determined.

Final positional parameters are given in Table 2, bond lengths and selected angles are in Table 3, and mean plane data in Table 4. The structure is shown in Fig. 1.

Platinum has square planar geometry with triphenylphosphine and 2,6-dimethylpyridine ligands *trans* to oxygen and carbon respectively of a chelating (*O,C*)-2-carboxylatotetrafluorophenyl ligand. There is little deviation of platinum and the donor atoms from the mean coordination plane through the donor atoms and metal (Table 4). The plane of 2,6-dimethylpyridine is almost perpendicular (85.0°) to the

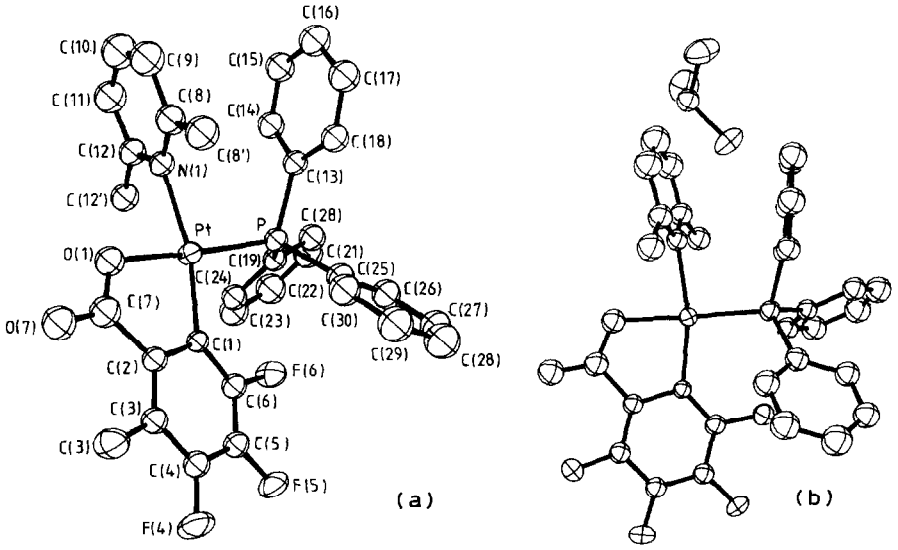


Fig. 1. The crystal structure of $Pt[\overline{C_6F_4\text{-}o\text{-}C(O)O}](PPh_3)(2,6\text{-}Me_2C_5H_3N)\cdot CHCl_3$ (**1c**·$CHCl_3$). (a) A view showing the numbering of the atoms. Chloroform is omitted for clarity. (b) A view showing chloroform of solvation and the relative positions of the 2,6-dimethylpyridine ligand and the C(13)–C(18) ring of triphenylphosphine.

Table 2

Atomic coordinates for $C_{33}H_{25}Cl_3F_4NO_2PPt$ (**1c**·$CHCl_3$) (with e.s.d.'s in parentheses)

Atom	x	y	z	U_{iso} (Å^2)
Pt	0.1941(1)	0.1423(1)	0.1694(1)	0.0282(2) [a]
Cl(1)	−0.2723(3)	0.1806(3)	0.1928(4)	0.072(2) [a]
Cl(2)	−0.3176(4)	0.0701(3)	0.3359(4)	0.085(3) [a]
Cl(3)	−0.4511(3)	0.1074(3)	0.1288(5)	0.083(2) [a]
F(3)	0.3530(6)	0.0707(5)	−0.1388(7)	0.052(4) [a]
F(4)	0.4216(6)	0.2063(5)	−0.1615(8)	0.057(4) [a]
F(5)	0.3835(6)	0.3271(4)	−0.0454(7)	0.047(4) [a]
F(6)	0.2798(6)	0.3112(4)	0.0933(7)	0.043(3) [a]
N(1)	0.1140(7)	0.0817(6)	0.2574(9)	0.033(3)
O(1)	0.1769(6)	0.0468(5)	0.0712(8)	0.043(3)
O(7)	0.2357(7)	−0.0116(6)	−0.0494(9)	0.052(3)
P	0.2242(3)	0.2391(2)	0.2892(3)	0.030(1)
C(1)	0.2642(9)	0.1775(7)	0.0632(11)	0.025(3)
C(2)	0.2796(9)	0.1174(7)	−0.0027(12)	0.030(4)
C(3)	0.3336(9)	0.1276(7)	−0.0758(12)	0.034(4)
C(4)	0.3701(9)	0.1979(8)	−0.0895(12)	0.033(4)
C(5)	0.3513(9)	0.2584(8)	−0.0299(12)	0.033(4)
C(6)	0.2973(9)	0.2469(8)	0.0419(12)	0.033(4)
C(7)	0.2300(11)	0.0450(9)	0.0068(14)	0.045(5)
C(8)	0.1554(11)	0.0285(9)	0.3305(13)	0.044(4)
C(8′)	0.2576(11)	0.0110(9)	0.3522(14)	0.053(5)
C(9)	0.1017(12)	−0.0173(10)	0.3842(14)	0.059(5)
C(10)	0.0095(13)	−0.0032(10)	0.3603(15)	0.065(5)
C(11)	−0.0342(12)	0.0496(9)	0.2823(14)	0.056(5)
C(12)	0.0195(10)	0.0935(8)	0.2319(13)	0.041(4)
C(12′)	−0.0256(10)	0.1540(9)	0.1514(11)	0.045(4)
C(13)	0.2130(9)	0.2067(8)	0.4230(12)	0.033(4)
C(14)	0.1277(10)	0.2010(8)	0.4455(12)	0.039(4)
C(15)	0.1219(10)	0.1670(8)	0.5405(12)	0.045(4)
C(16)	0.1982(10)	0.1388(10)	0.6176(13)	0.052(4)
C(17)	0.2850(10)	0.1467(10)	0.5997(12)	0.048(4)
C(18)	0.2915(10)	0.1817(8)	0.5044(12)	0.039(4)
C(19)	0.1463(10)	0.3199(8)	0.2527(12)	0.034(4)
C(20)	0.1341(9)	0.3716(9)	0.3335(12)	0.043(4)
C(21)	0.0749(11)	0.4318(9)	0.3011(14)	0.055(5)
C(22)	0.0291(12)	0.4418(10)	0.1917(14)	0.060(5)
C(23)	0.0374(11)	0.3924(9)	0.1122(15)	0.055(5)
C(24)	0.0971(10)	0.3300(8)	0.1417(13)	0.038(4)
C(25)	0.3417(10)	0.2770(8)	0.3194(12)	0.040(4)
C(26)	0.3613(10)	0.3520(9)	0.3513(11)	0.043(4)
C(27)	0.4546(10)	0.3774(9)	0.3703(12)	0.048(4)
C(28)	0.5240(13)	0.3320(9)	0.3590(14)	0.061(5)
C(29)	0.5047(12)	0.2580(10)	0.3273(14)	0.058(5)
C(30)	0.4134(11)	0.2305(9)	0.3106(13)	0.049(4)
C(31)	−0.3313(10)	0.0964(9)	0.1986(13)	0.047(4)

[a] $U_{eq} = 1/3\sum_i\sum_j U_{ij} a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j$

coordination plane, and the *ortho* methyl groups are nearly symmetrically above and below the latter plane (Table 4), an arrangement which minimises steric repulsion between methyl and phenyl groups. The carboxylatotetrafluorophenyl ligand approaches coplanarity (dihedral angle 15.8°) with the coordination plane

Table 3

Interatomic distances (Å) and selected angles (°) (with e.s.d.'s in parentheses)

		P–C(19)	1.82(1)
Pt–Cl	2.01(2)	C(19)–C(20)	1.41(2)
Pt–O(1)	2.06(1)	C(20)–C(21)	1.37(2)
Pt–N(1)	2.13(1)	C(21)–C(22)	1.36(2)
Pt–P	2.237(4)	C(22)–C(23)	1.36(3)
C(1)–C(2)	1.40(2)	C(23)–C(24)	1.40(2)
		P–C(25)	1.82(2)
C(2)–C(3)	1.39(2)	C(25)–C(26)	1.39(2)
C(3)–C(4)	1.39(2)	C(26)–C(27)	1.42(2)
C(4)–C(5)	1.38(2)	C(27)–C(28)	1.35(3)
C(5)–C(6)	1.38(2)	C(28)–C(29)	1.37(2)
C(6)–C(1)	1.38(2)	C(29)–C(30)	1.40(2)
C(2)–C(7)	1.50(2)	C(30)–C(25)	1.38(2)
C(7)–O(1)	1.28(2)	C(3)–F(3)	1.36(2)
C(7)–O(7)	1.24(2)		
N(1)–C(8)	1.34(2)	C(4)–F(4)	1.35(2)
C(8)–C(8′)	1.50(2)	C(5)–F(5)	1.34(2)
C(8)–C(9)	1.43(3)	C(6)–F(6)	1.37(2)
C(9)–C(10)	1.35(3)		
C(10)–C(11)	1.38(2)	C(31)–Cl(1)	1.74(2)
C(11)–C(12)	1.39(3)	C(31)–Cl(2)	1.74(2)
C(12)–C(12′)	1.50(2)	C(31)–Cl(3)	1.77(2)
C(12)–N(1)	1.37(2)		
P–C(13)	1.82(2)	O(1)–Pt–C(1)	81.9(5)
C(13)–C(14)	1.38(2)	C(1)–Pt–P	99.5(4)
C(14)–C(15)	1.36(2)	P–Pt–N(1)	94.2(3)
C(15)–C(16)	1.36(2)	N(1)–Pt–O(1)	84.5(4)
C(16)–C(17)	1.38(2)	Pt–O(1)–C(7)	113.7(9)
C(17)–C(18)	1.37(2)	Pt–C(1)–C(2)	110.9(9)
C(18)–C(13)	1.39(2)	Pt–P–C(13)	109.0(5)
		Pt–P–C(19)	116.0(5)
		Pt–P–C(25)	115.0(5)
		Pt–N(1)–C(12)	119.5(9)
		Pt–N(1)–C(8)	119.4(10)

owing to chelation, by contrast with substantial twisting of C_6F_5 groups from the coordination plane in *trans*-$Ni(C_6F_5)_2(PPh_2Me)_2$ [14] and *cis*-$Pt(C_6F_5)_2[S_2CP(c\text{-}C_6H_{11})_3]CO$ [15]. Chloroform of solvation (Fig. 1) is not bonded significantly to the complex, and the closest atoms to chlorine are O(7) (3.61(1) Å) and F(3) (3.45(1) Å).

The Pt–C distance (Table 3) is similar to those of related compounds, e.g. $[Pt\overline{[CH{=}CHC(O)O]}(PPh_3)_2$ (**5**), 2.03(1) Å [9], and *cis*-$Pt(C_6F_5)_2(PhC_2Ph)_2$, 2.05(2) Å [16], whilst Pt–O has the same length as in **5** [9]. There is agreement between the Pt–P length of **1c** · $CHCl_3$ (Table 3) and Pt–P *trans* to oxygen, 2.224(4) Å, of **5** [9], but Pt–P *trans* to C of **5** is longer, 2.341(4) Å. These results reflect the respective *trans* influences of oxygen and carbon [17]. The Pt–N length is slightly longer than that of *trans*-$PtCl_2(\eta\text{-}C_2H_4)$(2,6-dimethylpyridine), 2.08(1) Å [18], but the difference may not be significant when errors are considered.

Two unusual features of the NMR spectra are illuminated by the crystal structure. Firstly, the ^3J(PtF(6)) and ^4J(PtF(5)) coupling constants (Table 1) are smaller and larger respectively than those (240–500 Hz and ca. 60 Hz, respectively)

Table 4

Equations of mean planes and deviations (Å) of individual atoms from planes (with e.s.d.'s in parentheses)

X, Y, Z are orthogonal coordinates and are related to the fractional coordinates x, y, z by the matrix equation:

$$\begin{pmatrix} 14.912 & 0 & -3.305 \\ 0 & 17.671 & 0 \\ 0 & 0 & 12.032 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

Plane 1: N(1), O(1), Pt, P, C(1)

$$(-0.7026)X + (0.4298)Y + (-0.5671)Z - (-1.7370) = 0$$

Pt	0.0462(6)	P	−0.057(4)
N(1)	0.04(1)	C(1)	0.04(1)
O(1)	−0.07(1)	C(2)	−0.29(1)
C(8′)	−2.42(2)	C(7)	−0.36(2)
C(12′)	2.52(2)	O(7)	−0.61(1)

Plane 2: C(1), C(3), C(5)

$$(-0.6696)X + (0.2007)Y + (-0.7151)Z - (-2.4041) = 0$$

Pt	−0.0887(6)	N(1)	−0.06(1)
P	−0.796(4)	O(1)	0.36(1)

Plane 3: C(8), C(10), C(12)

$$(0.0515)X + (-0.6799)Y + (-0.7315)Z - (-3.1910) = 0$$

C(9)	0.03(2)	C(8′)	0.09(2)
C(11)	0.03(2)	C(12′)	−0.04(2)

Plane 4: C(14), C(16), C(18)

$$(0.0145)X + (-0.8817)Y + (-0.4715)Z - (-5.6550) = 0$$

Plane 5: C(20), C(22), C(24)

$$(0.8317)X + (0.5400)Y + (-0.1290)Z - (3.7195) = 0$$

Plane 6: C(26), C(28), C(30)

$$(0.0746)X + (0.2517)Y + (-0.9649)Z - (-2.2027) = 0$$

Dihedral angles

Plane–Plane	(°)
1–2	15.8
1–3	85.0
1–4	97.0
1–5	106.2
1–6	52.9
2–4	81.3
2–5	110.9
2–6	46.3
3–4	19.1

previously obtained for mononuclear polyfluorophenylplatinum(II) complexes [19–21]. X-ray [15] and NMR data [20] for these compounds indicate substantial inclination of the fluorocarbon rings to the coordination plane by contrast with near coplanarity in **1c** · $CHCl_3$ (Fig. 1) and presumably also **1a,b**, **2a,b** and **4**. Thus, the coupling mechanisms should differ for the two groups of complexes. Comparable

^3J(PtF) values to those of Table 1 have recently been observed for some monopentafluorophenyldiplatinum(II) complexes, and ^4J(Pt–*o*-F) (cf. ^4J(Pt–*m*-F) for the present complexes) has been resolved for complexes with the C_6F_5–Pt–Pt group [22].

Secondly, the ^{1}H NMR resonances attributable to triphenylphosphine of **1c** · $CHCl_3$ are more complex than those of **1a,b** and **4**, and resonances for five hydrogens are shifted substantially upfield from values for the other complexes. The structure of **1c** · $CHCl_3$ shows the 2,6-dimethylpyridine ligand to be adjacent to a near parallel (dihedral angle, 19.1° (Table 4)) phenyl ring of triphenylphosphine (by contrast with the other two rings) (Fig. 1). If the ligands are sufficiently bulky to prevent or restrict free rotation in solution, the hydrogen atoms of the unique phenyl ring should be shielded leading to the observed upfield shift.

*(c) The reaction path to **1a–c***

The synthesis of **1a–c** by reaction (1) is considered to proceed by the independently demonstrated (section (a)) reactions (3) and (4) giving the complex **4**. This then undergoes displacement of triphenylphosphine by pyridine, 2,4-, or 2,6-dimethylpyridine (L) (reaction (5)) yielding **1a–c** as the observed isomer **A** rather than **B**, since the *trans* effect of the aryl carbon of **4** is greater than that of oxygen [17].

$$\mathbf{4} + L \rightarrow \mathbf{1a\text{–}c} + Ph_3P \qquad (5)$$

Reaction (5) has been shown to occur for L = py (Experimental section). The alternative path, reaction (3) followed by ligand displacement in **3** to give Pt[*o*-$(O_2C)_2C_6F_4$](PPh_3)L and then hemidecarboxylation would give isomer **B** since the *trans* effect of phosphorus is greater than that of nitrogen [17]. Moreover, facile displacement of triphenylphosphine from **3** is unlikely because of the weak *trans* effect of oxygen [17], and **3** has been isolated from pyridine solution at room temperature.

Experimental

(a) General

Microanalyses were by the Australian Microanalytical Service, Melbourne. Instrumentation was as given previously [19,20]. Infrared bands for compounds as Nujol and hexachlorobutadiene mulls listed below are restricted to intense bands (4000–650 cm^{-1}) of identification importance, apart from the $\nu(CO_2)$ frequencies (Table 1). Each *m/z* value corresponds to the most intense peak (for ^{195}Pt) of a cluster with the correct isotope pattern. Proton, fluorine, and phosphorus chemical shifts are in ppm downfield from internal Me_4Si, upfield from internal $CFCl_3$, and downfield from external H_3PO_4 respectively. Unless indicated otherwise, the solvent was $CDCl_3$. Values of ^nJ(PtF) and ^1J(PtP) are in Table 1.

(b) Solvents and reagents

Pyridine and 2,4-dimethylpyridine were dried over potassium hydroxide at room temperature then under reflux, and were distilled and stored under nitrogen. 2,6-Dimethylpyridine was refluxed over and distilled from potassium hydroxide, aluminium chloride (14 g/150 ml), and then boron trifluoride etherate (4 ml/120 ml solvent) under nitrogen and had < 0.05 mol % impurities of other methylpyridines. Other solvents were purified as given previously [19] or by standard methods.

Petroleum ether refers to the fraction b.p. 60–80 °C. Chelating phosphine ligands were from Strem and tetrafluorophthalic acid was from Bristol Organics. The complexes *cis*-$PtCl_2(PPh_3)_2$, $PtCl_2$(dpe), and $PtCl_2$(dpp) were prepared by reported methods [23,24] and had ^{31}P NMR spectra and ν(PtCl) frequencies in agreement with those reported [24,25].

Thallium(I) tetrafluorophthalate. Stoichiometric amounts of thallium(I) carbonate and tetrafluorophthalic acid were boiled in water until a clear solution was obtained. After filtration, the salt was isolated by evaporation under vacuum (yield, 76%), m.p. 261–263 °C (Found: C, 14.6; F, 11.9; Tl, 63.3. $C_8F_4O_4Tl_2$ calc: C, 14.9; F, 11.8; Tl, 63.4%). IR: 1605s, 1509s, 1060s, 756s, 742s, 728s cm^{-1}. ^{19}F NMR spectrum (D_2O): 142.5 (m, 2F, F(3,6)); 155.2 (m, F(4,5)). Mol. cond. (H_2O): 223 S cm^2 mol^{-1} (9.3×10^{-4} mol dm^{-3}).

Thallium(I) phthalate. The compound was obtained in a similar manner (yield, 100%), dec. temp. > 290 °C. IR: 1520s, 1370s, 1350s, 818s, 750s cm^{-1}.

(c) Preparations of organoplatinum compounds by decarboxylation in pyridines

Equimolar amounts of the appropriate dichlorophosphineplatinum(II) complex (reactions (1) and (2)) and thallium(I) tetrafluorophthalate (0.50–0.80 mmol) in pyridine or 2,4- or 2,6-dimethylpyridine (5 ml) were heated under reflux. Evolved carbon dioxide was carried by a slow stream of purified nitrogen through saturated aqueous barium hydroxide and was determined gravimetrically as barium carbonate. % yields refer to evolution of one molecule of CO_2 (reactions (1), (2), (4)). After reaction (times below), the pyridine was removed under vacuum at room temperature and the residue was washed with petroleum ether. Extraction with chloroform, filtration to remove thallium(I) chloride (yield, 60–80%), and evaporation to crystallization gave the 2-carboxylato-3,4,5,6-tetrafluorophenyl(*O,C*)platinum(II) complex, which was dried for 5–10 h under vacuum at room temperature. Where analysis indicated isolation of chloroform solvates, the presence of chlorine in the product was confirmed by fusion with sodium and qualitative analysis. Unless indicated otherwise, the sole feature in the mass spectrum above *m/z* 262 (Ph_3P^+) was *m/z* 719 [$Pt(PPh_3)_2^+$].

*a,b-2-Carboxylato-3,4,5,6-tetrafluorophenyl(O,C)-d-pyridine-c-triphenylphosphineplatinum(II) (**1a**).* Reaction time 165 min (CO_2, 65%), yield 69%, m.p. 254–255 °C (Found: C, 48.7; H, 2.6; F, 10.6; N, 2.0. $C_{30}H_{20}F_4NO_2PPt$ calc: C, 49.4; H, 2.8; F, 10.4; N, 1.9%). IR: 1480vs, 1450s, 1105s, 1045s, 701vs cm^{-1}. ^1H NMR spectrum: 6.98 (dd, 2H, H(3,5)(py)); 7.28 (m, partly overlapped by solvent absorption, H(3,5)(Ph_3P)); 7.39 (m, 3H, H(4)(Ph_3P)); 7.51 (m, overlapped by 7.60, br s, total integration 7H, H(4)(py) and H(2,6)(Ph_3P)); 8.23 (dd, 2H; H(2,6)(py)). ^{19}F NMR spectrum: 116.1 (m, 1F, F(6)); 145.2 (m, 1F, F(3)); 152.4 (m, 1F, F(5)); 160.9 (t, 1F, F(4)). $^{31}P\{^1H\}$ NMR spectrum: 14.09 (s).

*a,b-2-Carboxylato-3,4,5,6-tetrafluorophenyl(O,C)-d-2,4-dimethylpyridine-c-triphenylphosphineplatinum(II)-chloroform (1 / 1) (**1b** · $CHCl_3$).*

Reaction time 75 min (CO_2, 78%), yield 55%, dec. temp. 252–254 °C (Found: C, 44.1; H, 2.3; N, 1.5. $C_{33}H_{25}Cl_3F_4NO_2PPt$ calc: C, 45.2; H, 2.8; N, 1.6%) *. IR:

* There is better agreement for **1b**·1.25$CHCl_3$: calc: C, 44.1; H, 2.7; N, 1.5%.

1480s, 1450s, 1294s, 1100s, 1031s (br), 761s, 701s cm^{-1}. ^1H NMR spectrum (CD_2Cl_2): 2.17 (s, 3H, 4-Me); 2.72 (s, 3H, 2-Me); 6.61 (d, 1H, H(5py)); 6.83 (s, 1H, H(3py)); 7.29–7.90 (br m with superimposed sharp singlet at 7.33, 16H, H(2-6)(Ph_3P) and $CHCl_3$); 7.97 (d, 1H, H(6py)). ^{19}F NMR spectrum: 115.9 (m, 1F, F(6)); 147.3 (m, 1F, F(3)); 153.6 (m, 1F, F(5)); 162.3 (t, 1F, F(4)). $^{31}P\{^1H\}$ NMR spectrum: 13.59 (s).

*a,b-2-Carboxylato-3,4,5,6-tetrafluorophenyl(O,C)-d-2,6-diimethylpyridine-c-triphenylphosphineplatinum-chloroform (1 / 1) (**1c** · $CHCl_3$).*

Reaction time 180 min (CO_2, 77%), yield, 48%, dec. temp. 265–270 °C (Found: C, 45.5; H, 2.8; F, 9.1; N, 1.6. $C_{33}H_{25}Cl_3F_4NO_2PPt$ calc: 45.3; H, 2.9; F, 8.7; N, 1.6%). IR: 1480s, 1455s, 1440s, 1105s, 1045s (br), 755vs, 705vs cm^{-1}. ^1H NMR spectrum (CD_2Cl_2): 2.85 (s, 6H, Me); 6.55 (br t, 2H, Ph_3P); 6.82 (d overlapping br, 4H, H(3,5)(py) and Ph_3P); 7.04 (br, 1H, Ph_3P); 7.32–7.37 (s superimposed on m, 2H, $CHCl_3$ and Ph_3P); 7.44–7.67 (br m, 7H, H(4)(py) and Ph_3P); 8.08 (br m, 3H, Ph_3P). ^{19}F NMR spectrum: 115.8 (m, 1F, F(6)); 146.0 (m, 1F, F(3)); 152.4 (m, 1F, F(5)); 161.3 (m, 1F, F(4)). $^{31}P\{^1H\}$ NMR spectrum: 13.36 (s).

*2-Carboxylato-3,4,5,6-tetrafluorophenyl(O,C)-1,2-bis(diphenylphosphino)ethaneplatinum(II)-chloroform (1 / 1) **2a** · $CHCl_3$.* Reaction time 150 min (CO_2, 55%), yield 56%, dec. temp. 320–325 °C (Found: C, 45.9; H, 3.1. $C_{34}H_{25}Cl_3F_4O_2P_2Pt$ calc: C, 45.1; H, 2.8%). After standing for several weeks at room temperature, desolvation occurred (Found: C, 50.9; H, 3.2; F, 10.1. $C_{33}H_{24}F_4O_2P_2Pt$ calc: C, 50.5; H, 3.1; F, 9.7%). IR: 1483vs, 1455vs, 1440s, 1108s, 1042s, 780s, 758s, 750s, 728s, 700s cm^{-1}. ^1H NMR spectrum: 2.17 (br m, 2H, CH_2P *trans* to C); 2.37 (br m, 2H, CH_2P *trans* to O); 7.46–7.48 (m, 12H, H(3,4,5)(Ph_2P)); 7.85 (br m, 8H, H(2,6)(Ph_2P)). The corresponding chemical shifts in CD_2Cl_2 are 2.26, 2.38, 7.53, 7.86 with in addition 7.32 (s, $CHCl_3$), but the integrations were unsatisfactory owing to low solubility. ^{19}F NMR spectrum: 113.3 (m, 1F, F(6)); 145.4 (m, 1F, F(3)); 151.9 (m, 1F, F(5)); 159.7 (m, 1F, F(4)). $^{31}P\{^1H\}$ NMR spectrum: 34.45 (m, P *trans* to O); 46.43 (br m, P *trans* to C). Mass spectrum *m/z* 785 [< 2%, M^+], 741 [18, $(M - CO_2)^+$].

*2-Carboxylato-3,4,5,6-tetrafluorophenyl(O,C)-1,3-bis(diphenylphosphino)propaneplatinum(II) (**2b**).* Reaction time 40 min (CO_2, 58%), yield, 63%, m.p. 222–226 °C. Spectroscopic characterization only. IR: 1483vs, 1458s, 1440vs, 1105vs, 1038s, 751s, 739vs, 705vs, 692vs cm^{-1}. ^1H NMR spectrum: 2.11–2.61 (br m, 6H, CH_2); 7.44–7.63 (m, 12H, H(3,4,5)(Ph_2P)); 7.80–7.91 (br m, 8H, H(2,6)(Ph_2P)). ^{19}F NMR spectrum: 111.7 (m, 1F, F(6)); 145.3 (m, 1F, F(3)); 151.3 (m, 1F, F(5)); 159.3 (t, 1F, F(4)). $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2): 34.52 (m, P *trans* to O); 47.31 (br m, P *trans* to C).

(d) The reaction of cis-$PtCl_2(PPh_3)_2$ with thallium(I) tetrafluorophthalate in pyridine at room temperature

The above reactants (each 0.54 mmol) were stirred together in pyridine (5 ml) for 180 min at room temperature under purified nitrogen. No carbon dioxide was evolved. Work up as in (c) gave thallium(I) chloride (83%) and *3,4,5,6-tetrafluorobenzene-1,2-dicarboxylatobis(triphenylphosphine)platinum(II)-chloroform (1 / 2)* (**3** · $(CHCl_3)_2$) (40%), dec. temp. 160–185 °C (Found: C, 45.6; H, 2.8. $C_{46}H_{32}Cl_6F_4O_4P_2Pt$ calc: C, 46.3; H, 2.7%). After standing for several weeks, complete desolvation occurred (Found: C, 55.4; H, 3.0; F, 7.6. $C_{44}H_{30}F_4O_4P_2Pt$

calc: C, 55.3; H, 3.2; F, 7.9%). IR: 1505s, 1370s, 1107s, 1062s, 750s, 740s, 715s, 695s cm^{-1}. ^1H NMR spectrum [$(CD_3)_2CO$]: 7.28–7.56 (complex m, Ph_3P and $CHCl_3$). ^{19}F NMR spectrum [$(CD_3)_2CO$]: 138.5 (m, 2F, F(3,6)); 158.8 (m, 2F, F(4,5)). $^{31}P\{^1H\}$ NMR spectrum [$(CD_3)_2CO$]: 4.56 (s). Single crystals of the solvate could be prepared, but loss of solvent was too rapid for a satisfactory X-ray crystallographic study. There was little evidence for reaction between *cis*-$PtCl_2(PPh_3)_2$ and *o*-$C_6F_4(CO_2Tl)_2$ in ethanol at room temperature. After reflux for 10 min, there was evidence of some gross decomposition, but the reactants were the sole identifiable compounds present.

(e) Thermal decomposition of the dicarboxylatoplatinum(II) complex 3

Compound **3** (0.17 mmol) was heated at 160–165 °C for 20 min in the absence of solvent under a slow stream of purified nitrogen, and CO_2 (50%) was evolved. Extraction with chloroform, filtration, evaporation to dryness and crystallization from dichloromethane gave *2-carboxylato-3,4,5,6-tetrafluorophenyl(O,C)bis(triphenylphosphine)platinum(II) (4)* as a fawn-white solid (49%), m.p. 223–225 °C. Analytically pure white crystals were obtained by slow crystallization from $CDCl_3$/hexane (Found: C, 56.5; H, 3.7; F, 8.4. $C_{43}H_{30}F_4O_2P_2Pt$ calc: C, 56.7; H, 3.3; F, 8.3%). IR: 1478vs, 1440vs, 1101s, 1040s, 756s, 705vs (br) cm^{-1}. ^1H NMR spectrum: 7.11–7.50 (complex br m overlapping solvent absorption with evidence for ^{195}PtH satellites which could not be clearly resolved). ^{19}F NMR spectrum: 112.5 (m, 1F, F(6)); 146.1 (m, 1F, F(3)); 153.1 (m, 1F, F(5)); 160.6 (t, 1F, F(4)). $^{31}P\{^1H\}$ NMR spectrum: 7.89 (m, P *trans* to O); 23.72 (m, P *trans* to C).

(f) Reaction of 4 with pyridine

The complex (0.050 g) was heated under reflux in pyridine (1 ml) for 1 h under nitrogen, and then the solvent was removed under vacuum. The residue was washed with petroleum ether and extracted with chloroform. Addition of petroleum ether gave a fawn precipitate, which was washed with hot petroleum ether, and shown to contain **1a** by ^1H NMR spectroscopy.

(g) Attempted reaction of thallium(I) phthalate with cis-$PtCl_2(PPh_3)_2$

The reactants (each 0.36 mmol) were heated under reflux in pyridine (10 ml) for 5 h under nitrogen. No carbon dioxide was evolved. The residue on evaporation of pyridine showed IR absorption indicative of unchanged reactants.

*(h) Crystal and molecular structure of the complex **1c** · $CHCl_3$*

A representative tabular crystal ($0.14 \times 0.08 \times 0.07$ mm) obtained by slow evaporation from chloroform was selected and mounted on a silica capillary. All crystal data were collected on a Philips PW1100 diffractometer with Mo-$K_{\bar{\alpha}}$ (λ 0.7107 Å).

Crystal data

$C_{33}H_{25}Cl_3F_4NO_2PPt$, M 875.98, monoclinic, a 14.912(2), b 17.671(3), c 12.532(2) Å, β 106.24(4)°, U 3170.54 Å^3. D_m 1.83(3), D_c ($Z = 4$) 1.84 g cm^{-3}, $F(000)$ 1704, systematic absences $h0l$ $h + l$ odd, $0k0$ k odd, space group $P2_1/n$, μ 48.0 cm^{-1} for Mo-$K_{\bar{\alpha}}$ radiation.

Intensity measurements and structure solution

9239 unique reflections were collected by the ω-scan technique with a scan range of $\pm 0.65°$ from the calculated Bragg scattering angle (with an allowance for dispersion) at a rate of $0.04° \ s^{-1}$. The 9239 reflections were reduced to 2911 with $I > 3\sigma(I)$ in a manner described previously [26]. Three approximately axial reflections were monitored every 2 h and showed no systematic variation in intensity. An absorption correction was applied on the basis of indexed crystal faces (100, $\bar{1}00$, 010, $0\bar{1}0$, $10\bar{1}$, $\bar{1}01$, 101 and $\bar{1}0\bar{1}$).

The atomic scattering factors [27] for neutral atoms were corrected for anomalous dispersion. All calculations were carried out on the Monash University DEC Vax 11/780 computers; the major program used was that of Sheldrick [28].

The structure was solved by conventional Patterson and Fourier methods. A total of eight reflections were severely affected by extinction and were omitted in the final stages of refinement. The platinum, fluorine and solvent chlorine atoms were refined anisotropically in the final refinement cycles in which 228 variables were refined. Geometrically idealized hydrogen atom coordinates were calculated for all hydrogen atoms, and a riding model was employed for refinement. The C-H vectors were held constant in magnitude (1.08 Å) and direction, but the carbon atoms were free to move. All hydrogen atoms were given the same isotropic thermal parameter which was allowed to refine. With the data weighted as $1/\sigma^2(F)$ the refinement converged at $R_w = \Sigma w^{1/2}(\,|\,F_o\,| - |\,F_c\,|\,)/\Sigma w^{1/2}\,|\,F_o\,| = 0.049$ and a corresponding unweighted R of 0.056. Lists of anisotropic thermal parameters, hydrogen atom coordinates, observed and calculated structure factors may be obtained from the authors.

Acknowledgement

The work was carried out during the tenure of a grant from the Anti-Cancer Council of Victoria. This support, that of the Australian Research Grants Scheme, and a loan of platinum from Johnson Matthey are gratefully acknowledged. We thank Dr. S.J. Faulks and Dr. G.N. Stretton for preliminary experiments.

References

1 L. Pesci, Atti. Real. Accad. Lincei [V], 10, i (1901) 362, see J. Chem. Soc. Abstr., 80 (1901) 576.
2 G.B. Deacon, Organomet. Chem. Rev., A5 (1970) 355.
3 Yu.A. Ol'dekop and N.A. Maier, Synthesis of Organometallic Compounds by Decarboxylation of Metal Acylates, Science and Technology, Minsk, 1976.
4 R.C. Larock, Organomercury Compounds in Organic Synthesis, Springer Verlag, Berlin and New York, 1985, p. 101.
5 G.B. Deacon, S.J. Faulks and G.N. Pain, Adv. Organomet. Chem., 25 (1986) 237.
6 M.S. Newman and M.C. Vander Zwan, J. Org. Chem., 38 (1973) 319.
7 G.B. Deacon and G.J. Faquharson, J. Organomet. Chem., 135 (1977) 73.
8 S.J. Faulks, Ph.D. Thesis, Monash University (1983).
9 O.J. Scherer, K. Hussong and G. Wolmershäuser, J. Organomet. Chem., 289 (1985) 215.
10 D.P. Buxton and G.B. Deacon, unpublished results.
11 S.C. Cohen and A.G. Massey, Adv. Fluor. Chem., 6 (1970) 83.
12 G.B. Deacon and R.J. Phillips, Aust. J. Chem., 31 (1978) 1709.
13 G.B. Deacon and R.J. Phillips, Coord. Chem. Rev., 33 (1980) 227, see also G.B. Deacon, F. Huber and R.J. Phillips, Inorg. Chim. Acta, 104 (1985) 41.
14 M.R. Churchill and M.V. Veidis, J. Chem. Soc., Dalton Trans., (1972) 670.

15 R. Usón, J. Forniés, M.A. Usón, J.F. Yagüe, P.G. Jones and K. Meyer-Bäse, J. Chem. Soc., Dalton Trans., (1986) 947.
16 R. Usón, J. Forniés, M. Tomás, B. Menjón and A.J. Welch, J. Organomet. Chem., 304 (1986) C24.
17 T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.
18 F. Caruso, R. Spagna and L. Zambonelli, Inorg. Chim. Acta, 32 (1979) L23.
19 G.B. Deacon and I.L. Grayson, Trans. Met. Chem., 7 (1982) 82.
20 G.B. Deacon and K.T. Nelson-Reed, J. Organomet. Chem., 322 (1987) 257.
21 C. Crocker, R.J. Goodfellow, J. Gimeno and R. Usón, J. Chem. Soc., Dalton Trans., (1977) 1448.
22 R. Usón, J. Forniés, P. Espinet and C. Fortuño, J. Chem. Soc., Dalton Trans., (1986) 1849.
23 A.A. Grinberg and Z.A. Razumova, Zhur. Prikl. Khim., 27 (1954) 105.
24 A.R. Sanger, J. Chem. Soc., Dalton Trans., (1977) 1971, see also A.D. Westland, J. Chem. Soc., (1965) 3060.
25 H.G. Alt, R. Baumgärtner and H.A. Brune, Chem. Ber., 119 (1986) 1694.
26 A.J. Canty, N. Chaichit and B.M. Gatehouse, Acta Cryst., B36 (1980) 786.
27 International Tables for X-ray Crystallography, (1974), Vol. IV Birmingham: Kynoch Press. (Present distributor, D. Reidel, Dordrecht).
28 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, Cambridge, England, 1976.
29 G.B. Deacon and I.L. Grayson, Trans. Met. Chem., 8 (1983) 131.