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Decarboxylation syntheses of transition metal organometallics

VI *. Preparations of polyfluorophenyliridium(I) compounds **

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Abstract

The complexes *trans*-$Ir(CO)R(PPh_3)_2$ ($R = C_6F_5$, *p*-HC_6F_4, or *m*-HC_6F_4) have been prepared by reaction of *trans*-$Ir(CO)Cl(PPh_3)_2$ with the appropriate thallium(I) polyfluorobenzoate in pyridine. The rate of decarboxylation falls in the sequence $R = C_6F_5 >$ *p*-$HC_6F_4 >$ *m*-HC_6F_4. Intermediate *trans*-$Ir(CO)(O_2CR)(PPh_3)_2$ complexes were detected by ^{19}F NMR spectroscopy, and *trans*-$Ir(CO)(O_2CC_6F_5)(PPh_3)_2$ was isolated following reaction of *trans*-$Ir(CO)Cl(PPh_3)_2$ with thallium(I) pentafluorobenzoate in boiling benzene. Heating of *trans*-$Ir(CO)(O_2CC_6F_4H$-*o*$)(PPh_3)_2$, formed *in situ* by a similar metathesis in pyridine, gave the complex $\overline{Ir(CO)(C_6F_4C(O)O})H(PPh_3)_2$, which was formed by cyclometallation and oxidative addition and which, from NMR and spectroscopic data, is considered to have *trans*-Ph_3P ligands, hydride *trans* to carboxyl, and CO *trans* to an aryl carbon.

Introduction

Decarboxylation of metal carboxylates (reaction 1a,b) is a well-established synthetic method for Main Group element organometallics [1–3].

$$-M(O_2CR) \rightarrow -MR + CO_2 \quad (1a)$$

$$-MCl + M'(O_2CR) \rightarrow -MR + M'Cl + CO_2 \quad (1b)$$

Thermally induced reactions provide a variety of derivatives with electron-withdrawing substituents in the organic groups, and radical-initiated reactions give alkyl-, cycloalkyl- and aryl-mercurials [1–3].

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* For Part V, see ref. 6.

** Dedicated to Professor Alwyn G. Davies in recognition of his distinguished contribution to organometallic chemistry and in appreciation of his involvement in our initial studies of decarboxylation in organometallic synthesis.

A limited number of mercurials with electron-donating organic groups have also been obtained in very facile carbon dioxide elimination reactions [1,4]. Uses in transition metal chemistry are more limited but are increasing [1]. A range of organometallics usually with electron-withdrawing organic groups have been prepared for the coinage metals [1], group 10 metals [1,5,6] and rhodium [1,7] by thermal decarboxylation, and a few platinum and cobalt organometallics have been obained by radical-induced decarboxylation [1,5]. Decarboxylation has been observed in other reactions of transition metal complexes but without isolation of the corresponding organometallics (*cf.* eq. 1). Thus, although $W(CO)_5(O_2CCH_2CN)^-$ is a catalyst for the homogeneous decarboxylation of cyanoacetic acid [8], it does not undergo decarboxylation into $W(CO)_5CH_2CN^-$. Furthermore, reaction of *trans*-$Ir(CO)Cl(PPh_3)_2$ with $Na(O_2CCClF_2)$ gives difluoromethyliridium(III) complexes and not chlorodifluoromethyliridium(I) or -(III) derivatives [9]. Carbon dioxide evolution has also been reported in reactions between iridium(I) or -(III) hydrides with trichloro- or tribromo-acetic acid. A reaction path involving trihalogenomethyliridium complexes is likely, although these intermediates have not been isolated or detected [10]. We now report an investigation of the syntheses of iridium(I) polyfluorophenyls by thermal decomposition of iridium(I) polyfluorobenzoates.

Results and discussion

Carboxylato(carbonyl)bis(triphenylphosphine)iridium(I) complexes

The iridium(I) carboxylate reagents (**1**) for the attempted decarboxylations were prepared by the metathesis reaction (2) in benzene ($R = C_6F_5$ (**1a**)) or pyridine ($R = C_6F_5$, p-HC_6F_4 (**1b**), m-HC_6F_4 (**1c**), or o-HC_6F_4 (**1d**)).

$$trans\text{-}Ir(CO)Cl(PPh_3)_2 + Tl(O_2CR) \rightarrow \underset{(\mathbf{1})}{trans\text{-}Ir(CO)(O_2CR)(PPh_3)_2} + TlCl\downarrow \qquad (2)$$

This route avoids the problem of oxidation to stable iridium(III) carboxylates that occurs on reaction of iridium(I) hydrides with carboxylic acids [11,12]. Only **1a** was isolated from the preparation in benzene. The other complexes were identified by their ^{19}F NMR spectra (Table 1), which were similar to those of the corresponding isolated rhodium(I) complexes [13], and were used *in situ* for decarboxylation reactions (next section). The separation (311 cm^{-1}) between the $\nu(CO_2)$ frequencies (see Experimental section) of **1a** is much larger than the value (210 cm^{-1} [18]) for sodium pentafluorobenzoate, indicative [19] of unidentate carboxylate groups, which undergo decarboxylation faster than chelate carboxylates for rhodium(I) [7]. A single ^{31}P NMR resonance and a single $\nu(IrP)$ frequency are observed, as expected for *trans*-phosphines. No parent ion was observed in the mass spectrum of **1a**, the highest m/z value corresponding to the parent ion of the decarboxylation product $Ir(CO)C_6F_5(PPh_3)_2^+$. Yellow crystals of **1a** and solutions in benzene turn green on exposure to air. This is attributed to formation of an oxygen adduct, $Ir(CO)O_2(O_2CC_6F_5)(PPh_3)_2$, which gives rise to a minor impurity $\nu(CO)$ frequency and ^{31}P NMR signal in the spectra of analytically pure **1a** (see Experimen-

Table 1

^{19}F and ^{31}P NMR chemical shifts for *trans*-Ir(CO)(O_2CR)(PPh_3)$_2$ (**1a**)[a], *trans*-Ir(CO)R(PPh_3)$_2$ (**2**)[a] and Ir(CO)($C_6F_4C(O)O$)H(PPh_3)L (**3**)[b] complexes in benzene and pyridine[c,d]

Compound	$-\delta(^{19}F)$					$\delta(^{31}P)$
	F_2	F3	F4	F5	F6	
1a	138.8	165.0	156.7	165.0	138.8	27.2
	(141.6)	(162.7)	(159.6)	(162.7)	(141.6)	(26.2)
1b	(142.2)	(139.5)		(139.5)	(142.2)	
1c	(133.7)	(166.1)	(136.1)		(114.5)	
1d	(136.9)	(156.5)	(154.2)	(140.9)		(27.5)
2a	114.0	164.6	164.6	164.6	114.0	23.0
	(112.8)	(163.5)	(163.5)	(163.5)	(112.8)	(22.9)
2b	115.7	142.6		142.6	115.7	23.4
	(114.8)	(141.5)		(141.5)	(114.8)	
2c	108.3	169.5	144.2		88.8	22.9
	(107.6)	(168.7)	(142.9)		(87.2)	
3a		142.8	164.2	154.8	120.2 [f]	1.39
		(143.4)	(163.4)	(153.2)	(118.1) [f]	(3.92)
3c		(144.3)	(161.1)	(151.0)	(122.4)	(7.4)

[a] **1a**, **2a**, R = C_6F_5; **1b**, **2b**, R = *p*-HC_6F_4; **1c**, **2c**, R = *m*-HC_6F_4; **1d**, R = *o*-HC_6F_4. [b] **3a**, L = Ph_3P; **3c**, L = py. [c] Values for pyridine in parentheses. [d] Where fluorine-fluorine coupling was resolved, ^nJ(FF) values were of the expected magnitude [14,15], and are listed only in the structurally significant case of F6 of **3a**. [e] In good agreement with a ^{19}F NMR spectrum in an unspecified solvent [16] and a $^{31}P\{^1H\}$ NMR spectrum in toluene [17]. [f] m, ^3J(FF) = 27, ^4J(FF) = 18, ^4J(FH(Ir)) = 9 Hz.

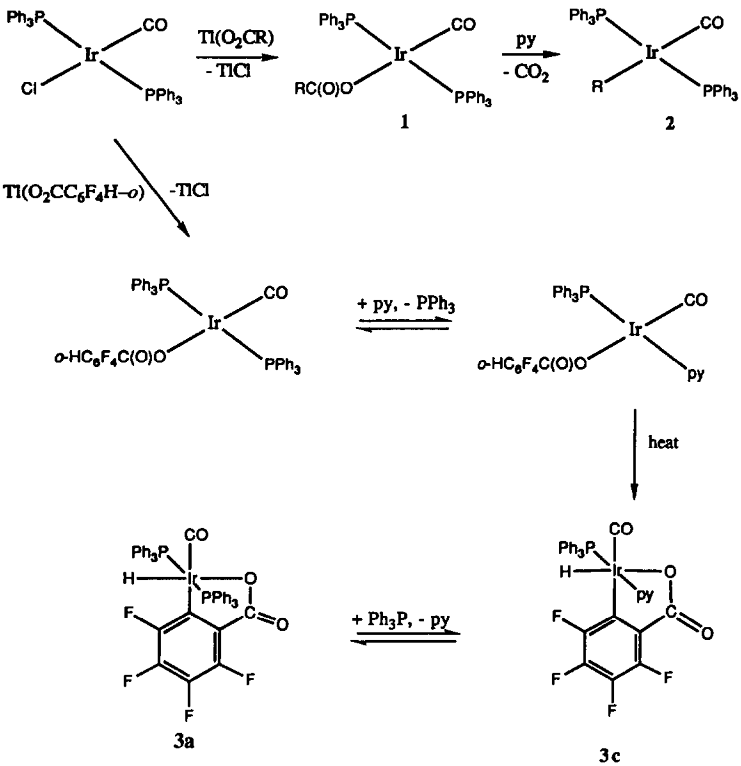
tal section). Similar oxygen derivatives are well known [20] as is oxygen adduct contamination of *trans*-Ir(CO)Cl(PPh_3)$_2$ [21].

Decarboxylation reactions

The reagents *trans*-Ir(CO)(O_2CR)(PPh_3)$_2$ (R = C_6F_5, *p*-HC_6F_4, or *m*-HC_6F_4) (**1a–c**) undergo decarboxylation in pyridine, giving the corresponding polyfluorophenyliridium(I) complexes, **2a–c**.

$$trans\text{-Ir(CO)(O}_2\text{CR)(PPh}_3)_2 \rightarrow \underset{\textbf{(2a–c)}}{trans\text{-Ir(CO)R(PPh}_3)_2} + CO_2 \qquad (3)$$

The overall path to **2a–c** from *trans*-Ir(CO)Cl(PPh_3)$_2$ is shown in Scheme 1. The minimum temperature for satisfactory decarboxylation increases in the sequence R = C_6F_5 (**2a**) < *p*-HC_6F_4 (**2b**) < *m*-HC_6F_4 (**2c**). No decarboxylation is observed for R = *o*-HC_6F_4 (see next section). Progress of the reactions has been monitored by ^{19}F NMR spectroscopy and the details are given in Table 2. In addition to carboxylato- and polyfluorophenyl-iridium(I) complexes, the corresponding polyfluorobenzenes, RH, are detected. Some loss of volatile RH from the reaction mixtures in the nitrogen stream used to collect CO_2, is likely. Thus the percentage distributions of reagents and products (Table 2) cannot be equated with yields. Nevertheless, these data and the lack of reaction for R = *o*-HC_6F_4 clearly indicate that the rate of decarboxylation decreases in the sequence R = C_6F_5 > *p*-HC_6F_4 > *m*-HC_6F_4 ≫ *o*-HC_6F_4, i.e. as the inductive electron-withdrawing character of the organic group decreases. Accordingly, a mechanism where the transition state has considerable carbanionic character is operative. A comparable reactivity order



Scheme 1. Generation, decarboxylation, and *ortho*-metallation of iridium(I) carboxylates.

applies for hydrogen exchange via polyfluorophenyl carbanion intermediates between polyfluorobenzenes and methoxide ions [22]. The present reactions are the first syntheses of iridium(I) organometallics by decarboxylation. In addition, they differ from previous carbon dioxide elimination reactions between iridium complexes and carboxylate ions (RCO_2^-) [9,10] in that the intact organic group (R) is transferred to iridium.

The formation of polyfluorobenzenes can be attributed to hydrolysis of highly carbanionic polyfluorophenyl groups by traces of water in pyridine or nitrogen. However, since these were carefully purified, it is possible there is another route. Cyclometallation of a triphenylphosphine ligand of **2a**–**c** may occur with concurrent oxidation to an iridium(III) hydride, as observed for $IrCl(PPh_3)_3$ [23]. This would give $[\overline{Ir(CO)H(R)(PPh_3)(PPh_2C}_6H_4)]$, which could then undergo reductive elimination of polyfluorobenzene giving an iridium(I) cyclometallated species.

$$[\overline{Ir(CO)H(R)(PPh_3)(PPh_2C}_6H_4)] \rightarrow RH + [\overline{Ir(CO)(PPh_3)(PPh_2C}_6H_4)] \quad (4)$$

The mass spectra of **2a**–**c** all show high intensity ions at *m*/*z* 716 attributable to the cyclometallated ion $[\overline{Ir(PPh_3)(PPh_2C}_6H_4)]^+$. Cyclometallation of the carboxylate ligand is observed on heating **1d** in pyridine (next section).

Complex **2a** has previously been prepared by reaction of *trans*-$Ir(CO)Cl(PPh_3)_2$ with LiC_6F_5 [17,24], C_6F_5MgBr [25], or AgC_6F_5 [16], or by addition of C_6F_5Cl to $Ir(CO)(PPh_3)_3^-$ [26], and the crystal structure has been determined [27]. Decarbox-

Table 2

Syntheses of *trans*-$Ir(CO)R(PPh_3)_2$ complexes **2** by decarboxylation [a]

R	Reagents			Conditions		Composition (%) of reaction mixture [d]		
	$Tl(O_2CR)$ (mmol)	Ir [b] (mmol)	py (cm^3)	Temperature (°C)	Time [c] (min)	1	2	RH
C_6F_5	0.24	0.22	5	25	25	51	46	3
				25	50	30	64	6
				25	79	13	77	10
				25	154	4	84	12
				25	214 [e]	–	92	8
p-HC_6F_4	0.42	0.41	10	25	240	100	Trace	–
				100	15 [f]	–	74	26
p-HC_6F_4	0.41	0.41	9.5	60	15	47	46	7
				60	30	23	65	12
				60	85 [g]	–	89	11
m-HC_6F_4	0.42	0.40	10	25	1080	100	–	–
				116	15 [h]	–	57	43
m-HC_6F_4	0.43	0.42	10	100	25	5	74	21
				100	50 [i]	–	84	16

[a] The reagents initially give *trans*-$Ir(CO)(O_2CR)(PPh_3)_2$ (**1**). Yields of **2** on isolation are in the Experimental section. For R = *p*-HC_6F_4 or *m*-HC_6F_4, **2b** or **2c** was isolated from the first of the two listed reactions. [b] Ir = *trans*-$Ir(CO)Cl(PPh_3)_2$. [c] Time at the temperature in the preceding column. [d] Distribution of fluorine containing products as determined by ^{19}F NMR spectroscopy. [e–i] Yields of CO_2: [e] 82; [f] 87; [g] 84; [h] 87; [i] 59%.

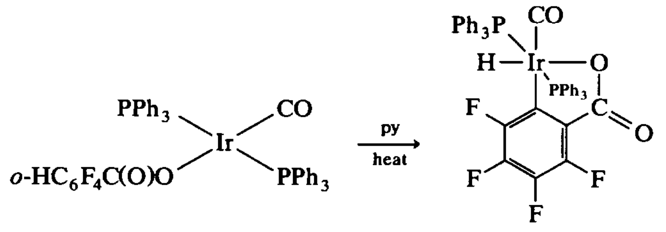
ylation provides **2a** from a stable fluorocarbon source in a yield greater than or equal to those from reported syntheses, and the procedure is probably simpler. The reaction of *trans*-$Ir(CO)Cl(PPh_3)_2$ with $(C_6F_5)_2TlBr$ under CO has been claimed to give *cis*-$Ir(CO)(C_6F_5)(PPh_3)_2$ on the basis of the assignment of two ν(Ir–P) stretching frequencies (452, 420 cm^{-1}) [28]. However, the former, which is also observed for the *trans*-isomer (see Experimental section), should be assigned to the "X-sensitive" mode *t* of coordinated triphenylphosphine [29], hence the reaction probably gives the *trans* complex, **2a**.

The identity and *trans* stereochemistry of the new complexes **2b** and **2c** are evident from observation of parent ions in their mass spectra, single ν(Ir–P) stretching frequencies (Experimental section), and single ^{31}P resonances (Table 1). There is a close similarity between their ^{19}F chemical shifts (Table 1) and those of the corresponding rhodium complexes [13]. Values for the *ortho*-fluorines are in reasonable agreement with calculated chemical shifts derived from substituent chemical shifts for hydrogen [15] and an *ortho*-$Ir(CO)(PPh_3)_2$ group (obtained from δ(*o*-F) of **2a**).

When **2a–c** were recrystallized in air, the resulting complexes showed an additional weak ν(CO) frequency and ^{31}P resonance, which can be attributed to formation of a small amount of the oxygen adduct, $Ir(CO)(O_2)R(PPh_3)_2$. It has been reported that *ortho*-substituted aryliridium(I) complexes do not form oxygen adducts owing to the steric shielding of the metal by the substituent [17]. Their formation by *ortho*-fluorine substituted phenyls reflects the modest steric demands of fluorine substituents (*e.g.* [14]).

Thermal decomposition of trans-*$Ir(CO)(O_2CC_6F_4H$-o$)(PPh_3)_2$ (1d)*

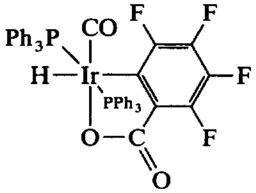
Heating **1d** in boiling pyridine leads to cyclometallation and oxidative addition, in contrast with the failure of *trans*-$Rh(CO)(O_2CC_6F_4H$-*o*$)(PPh_3)_2$ to react under similar conditions [13]. Chromatography of the products after removal of pyridine gave a low yield of a complex identified spectroscopically as **3a**.



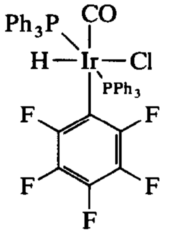
(1d) **(3a)** (5)

A parent ion is observed in the mass spectrum of **3a** in contrast with the iridium(I) carboxylate **1a** (see above). Unidentate carboxylate coordination is evident [19] from the large separation (336 cm^{-1}) between the $\nu(CO_2)$ frequencies (Experimental section). Observation of a high ν(IrH) frequency (2236 cm^{-1}) and ν(CO) significantly above 2000 cm^{-1} eliminates a *trans*-H–Ir–CO arrangement [30–32]. The upfield ^{31}P chemical shift (Table 1) is as expected [33,34] for an iridium(III) species, and the single resonance is consistent with a *trans* arrangement of the Ph_3P ligands, as is a triplet splitting of the hydride resonance (Experimental section). An *ortho*-metallated tetrafluorobenzoate group is indicated [14,15] by the chemical shift values (Table 1) of the four equal intensity fluorine resonances.

The alternative structure **3b** can be ruled out from spectroscopic data. ^1H and ^{19}F NMR spectra reveal a substantial coupling between F6 and the hydride ligand. This is indicative of **3a**, in which the hydride is close to F6, thereby permitting through space coupling, but is unlikely for **3b**. Similar HF coupling is observed for one of the five separate fluorine resonances of **4** [16]. Free rotation of the C_6F_5 group is considered blocked by the bulky Ph_3P ligands, hence one *ortho*-fluorine is close to the hydride.



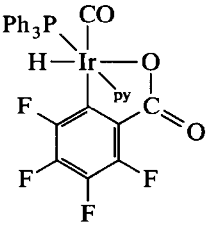
(3b)



(4)

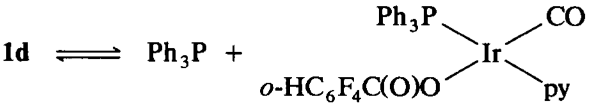
The ν(IrH) and ν(CO) frequencies of **3a** are very close to those of **4**. In both structures, the CO ligand is *trans* to a polyfluorophenyl group, and the hydride is *trans* to a weak *trans* influence [35] ligand, chloride or carboxyl. Furthermore, **3b** with the hydride ligand opposite the strong *trans* influence polyfluorophenyl group would be expected to give a substantially lower ν(IrH) frequency than that observed, see, *e.g.*, 2031 cm^{-1} for Ir(CO)CF$_3$(H)(Cl)(PPh$_3$)$_2$ with hydride *trans* to CF$_3$ [36]. Both the ^{1}H chemical shift of **3a** and the ^2J(HP) coupling constant are consistent with values for iridium(III) complexes with hydride *trans* to carboxyl, and *cis* to a pair of mutually *trans* phosphine ligands [30]. Attempts to obtain crystals of **3a** suitable for X-ray crystallography were unsuccessful, mainly due to loss of solvent of crystallization.

Monitoring decomposition of **1d** in pyridine by ^{19}F, ^{31}P and ^{1}H NMR spectroscopy reveals that appearance of **3a** is preceded by formation of another (2-carboxylato-3,4,5,6-tetrafluorophenyl)hydridoiridium(III) species, which could not be separated or isolated. Although structure **3b** is consistent with the single ^{31}P resonance, it is unlikely as a hydride *trans* to a fluorocarbon group would be well downfield of the observed resonance (Experimental section), *e.g.* δ −9 to −11 for H trans to CF$_3$ [34,36]. Structure **3c** with a single Ph$_3$P ligand is proposed.



(3c)

No feature due to free Ph$_3$P (δ −6.1) is observed in the spectra of the reaction mixtures, but the ^{31}P resonance of **1d** is moved upfield (*e.g.* to δ 22.1 after 70 min at 115°C) and broadened, indicative of fast exchange (eq. 6).



$$\mathbf{1d} \rightleftharpoons \mathrm{Ph_3P} + \mathrm{Ir(Ph_3P)(CO)(py)}(o\text{-}\mathrm{HC_6F_4C(O)O}) \qquad (6)$$

The hydride chemical shift and ^2J(HP) of **3c** are consistent with H *trans* to carboxyl [30], whereas H *trans* to polyfluorophenyl or carbonyl would be further downfield (δ approx. −9 to −12) [30,34], H *trans* to py would be further upfield (< −23 ppm) [37], and H *trans* to Ph$_3$P would give a much larger ^2J(PH) coupling (> 100 Hz) [38,39]. Triplet splitting of the hydride resonance (*cf.* dt for **3a**) can be attributed to coincidence of ^2J(PH) with ^4J(HF) of F6, which is close to the hydride ligand of **3c**.

In the decomposition of **1d**, an equilibrium between **1d**, **3c** and **3a** is eventually obtained with no change in composition from 1.5 to 4.5 h (see Experimental section). Initial replacement of Ph$_3$P of **1d** by the less strongly bound, more labile, pyridine (reaction 6) may be a vital step in the initiation of oxidative addition/cyclometallation, and **3a** probably results from substitution in **3c**. The proposed path is shown in Scheme 1. For **1a**–**1c**, more facile decarboxylation (3) is combined with the impossibility of *ortho*-metallation of the carboxylate ligand. NMR data suggest that decarboxylation syntheses of rhodium(I) [13] and iridium(I) (Table 2) polyfluorophenyls proceed at similar rates, whereas observation of reaction 5 by contrast with the lack of reactivity of *trans*-Rh(CO)(O$_2$CC$_6$F$_4$H-*o*)(PPh$_3$)$_2$ illustrates the greater ease of oxidative addition for iridium(I) than rhodium(I) complexes.

Experimental

General

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. The infrared spectra (4000–400 cm^{-1}) of compounds as Nujol and hexachlorobutadiene mulls were recorded with a Perkin–Elmer 180 spectrophotometer. Weak bands are not listed unless structurally significant. ^{19}F NMR and ^{1}H NMR spectra were obtained with a Bruker WH90 spectrometer. Fluorine chemical shifts (Table 1) are in ppm upfield from internal $CFCl_3$ for spectra of benzene solutions or external $CFCl_3$ (d_6-acetone/$CFCl_3$ capillary) for spectra of pyridine solutions. Satisfactory fluorine integrations were obtained, hence these are not listed. Proton chemical shifts are in ppm downfield from internal tetramethylsilane, and C_6D_6 was the solvent. $^{31}P\{^1H\}$ NMR spectra were obtained with Bruker WP60 and Bruker HX90R spectrometers. Phosphorus chemical shifts (Table 1) are in ppm downfield from external 85% H_3PO_4, and are for solutions in benzene (approx. 10% C_6D_6) and in pyridine (approx. 10% C_5D_5N). Mass spectra were obtained with a VG Micromass 7070F spectrometer. Features below m/z 484 are not listed and those with intensity $< 5\%$ of the main peak are listed only where they have structural significance. The correct isotope pattern was observed for ions containing iridium; the peaks for ^{193}Ir are listed.

Solvent and reagents

Benzene and petroleum spirit (b.p. 60–80°C) were dried over sodium. Pyridine was dried and purified as described previously [6]. The solvents used in column chromatography (Merck silica gel) were deoxygenated by bubbling purified nitrogen though them for 30 min. Reported syntheses were used for *trans*-$Ir(CO)Cl(PPh_3)_2$ [21] and the thallium(I) polyfluorobenzoates [13]. All manipulations of iridium complexes were carried out under an atmosphere of purified nitrogen (BASF R3/11 oxygen-removal reagent and molecular sieves).

trans-*Carbonylpolyfluorobenzoatobis(triphenylphosphine)iridium(I) complexes.* *trans*-$Ir(CO)Cl(PPh_3)_2$ and the stoichiometric amount of $Tl(O_2CR)$ were stirred together in pyridine or in benzene. Samples of the pyridine solutions were transferred by syringe to NMR tubes under nitrogen. In the synthesis of **1a**, the reagents were refluxed in benzene for 10 min, thallium(I) chloride was filtered off and the volume of the solution was reduced by evaporation under vacuum. The yellow product precipitated out on addition of petroleum spirit (b.p. 60–80°C).

trans-*Carbonylpentafluorobenzoatobis(triphenylphosphine)iridium(I) (1a)* Yield 85%, m.p. 169–170°C (dec. 165°C). Anal. Found: C, 54.7; H, 2.9; F, 9.2. $C_{44}H_{30}F_5IrO_3P_2$ calc.: C, 55.3; H, 3.2; F, 9.4%. IR: 1969vs [$\nu(CO)$], 1658s [$\nu_{as}(CO_2)$], 1518m, 1483s, 1437s, 1347vs [$\nu_s(CO_2)$], 1276s, 1098s ["X-sensitive" mode q, Ph_3P], 991m [$\nu(CF)$], 752s, 743m, 708m, 695s, 522s, 511s, 496m, 420w [$\nu_{as}(IrP)$] cm^{-1}. Mass spectrum: m/z 912 [45%, $(M - CO_2)^+$], 716 [97, $(C_{36}H_{29}IrP_2)^+$], 638 [100, $(C_{30}H_{23}IrP_2)^+$]. A weak IR band at 2015 cm^{-1} and a small ^{31}P resonance at 6.86 ppm in benzene are attributable to an oxygen-adduct $Ir(CO)(O_2)(O_2CC_6F_5)(PPh_3)_2$ impurity.

trans-*Carbonylpolyfluorophenylbis(triphenylphosphine)iridium(I) complexes*

trans-Ir(CO)Cl$(PPh_3)_2$ was treated with $Tl(O_2CR)$ in pyridine. The amounts of reagents and reaction conditions are given in Table 2. A slow stream of purified nitrogen was passed over the reaction mixture and then through a saturated barium hydroxide solution. The carbon dioxide evolved (yields, Table 2) was determined gravimetrically as barium carbonate. Samples of pyridine solutions for determination of *in situ* compositions (Table 2) were transferred at the appropriate times by syringe under nitrogen to NMR tubes. On completion of the reaction, the pyridine was evaporated under vacuum. The yellow-brown residue was extracted with acetone and TlCl was filtered off. Evaporation to crystallization gave yellow crystals of **2a–c**. When these complexes were recrystallized in air, an IR band at 2010–2000 cm^{-1} and a ^{31}P resonance at 2.45–3.40 ppm attributable to the oxygen-adducts $Ir(CO)(O_2)R(PPh_3)_2$ were observed.

trans-*Carbonylpentafluorophenylbis(triphenylphosphine)iridium(I) (2a).* Yield 77%, m.p. 198–199°C (lit. [16], 208–210°C). Anal. Found: C, 56.3; H, 3.5; F, 10.0. $C_{43}H_{30}F_5IrOP_2$ calc.: C, 56.6; H, 3.3; F, 10.4%. IR: 1968vs [ν(CO)] (lit. [25] 1968), 1497vs. 1478m, 1445vs, 1434vs, 1096s ["X-sensitive" mode q, Ph_3P], 1065m, 1049m [ν(CF)], 947vs [ν(CF)], 780s ["X-sensitive" $\nu(C_6F_5\text{-Ir})$], 756m, 744s, 695vs, 519vs, 496m, 457w ["X-sensitive" mode t, Ph_3P], 420m [ν_{as}(IrP)] cm^{-1}. Mass spectrum: *m/z* 912 [64%, M^+], 716 [100, $(C_{36}H_{29}IrP_2)^+$], 638 [83, $(C_{30}H_{23}IrP_2)^+$], 485 [26, $(C_{19}H_{17}IrOP)^+$].

trans-*Carbonyl(2,3,5,6-tetrafluorophenyl)bis(triphenylphosphine)iridium(I) (2b).* Yield 44%, m.p. 195–196°C (dec. 194°C). Anal. Found: C, 57.5; H, 3.6; F, 8.2. $C_{43}H_{31}F_4IrOP_2$ calc.: C, 57.8; H, 3.5; F, 8.5%. IR: 1961vs [ν(CO)], 1477m, 1443vs, 1433vs, 1189m, 1164m, 1158m, 1099vs, 998m, 887s [ν(CF)], 857m, 816m, 747s, 695vs, 521vs, 420m [ν_{as}(IrP)] cm^{-1}. Mass spectrum: *m/z* 894 [67%, M^+], 716 [100, $(C_{36}H_{29}IrP_2)^+$], 638 [83, $(C_{30}H_{23}IrP_2)^+$], 484 [23, $(C_{19}H_{16}IrOP)^+$].

trans-*Carbonyl(2,3,4,6-tetrafluorophenyl)bis(triphenylphosphine)iridium(I) (2c).* Yield 18%, m.p. 208°C (dec. 205°C). Anal. Found: C, 57.1; H, 3.9; F, 8.4. $C_{43}H_{31}F_4IrOP_2$ calc.: C, 57.8; H, 3.5; F, 8.5%. IR: 1950vs [ν(CO)], 1480m, 1435s, 1097m, 746m, 707m, 693s, 520vs, 511s, 419m [ν_{as}(IrP)] cm^{-1}. Mass spectrum: *m/z* 894 [3%, M^+], 716 [83, $(C_{36}H_{29}IrP_2)^+$], 638 [100, $(C_{30}H_{23}IrP_2)^+$, 484 [42, $(C_{19}H_{16}IrOP)^+$].

Decomposition of trans-*carbonyl(2,3,4,5-tetrafluorobenzoato)bis(triphenylphosphine)iridium(I) (1d) in refluxing pyridine*

Equimolar amounts (approx. 0.50 mmol) of *trans*-Ir(CO)Cl$(PPh_3)_2$ and $Tl(O_2CC_6F_4H\text{-o})$ were stirred together in pyridine (10 cm^3) for 15 min at room temperature. The resulting solution of **1d** was heated under reflux under purified nitrogen. No carbon dioxide was evolved. Samples of the pyridine solution were transferred at the appropriate times (below) by syringe under nitrogen to NMR tubes. The pyridine was evaporated under vacuum and a solution of tetramethylsilane in d_6-benzene was syringed into the tube under nitrogen. The reaction mixtures from which **3a** was isolated were heated under reflux for 4 h. The pyridine was evaporated *in vacuo* at room temperature and the yellow residue was extracted with a small volume of benzene. The extract was chromatographed under nitrogen on a column of silica gel, which was successively eluted with benzene, methylene chloride and absolute ethanol. The yellow band eluted by benzene contained impure **1d** (^{19}F NMR identification). No product was obtained from the colourless methylene chloride eluate. Evaporation of the absolute ethanol eluate gave light-brown **3a**, which was recrystallized from hot benzene to give off-white transparent crystals.

a-*Carbonyl*-bf-*(2-carboxylato-3,4,5,6-tetrafluorophenyl*-O,C*)*-d-*hydrido*-c,e-*bis(triphenylphosphine)iridium(III) (3a).* Yield 9–14%, m.p. 223–225°C (dec.). IR: 2236w, [ν(IrH)], 2041vs, [ν(CO)], 1654vs, [$\nu_{as}(CO_2)$], 1476s, 1454s, 1435s, 1318m [$\nu_s(CO_2)$], 1290m, 1238m, 1097vs, 1032s, 805m, 761m, 751m, 708s, 696s, 676m, 524vs, 516s, 502m, 498m, 421w [ν_{as}(IrP)] cm^{-1}. ^{1}H NMR spectrum: 7.60 (m, br); 6.95 (m, PPh_3); −17.32 (dt, ^2J(HP) = 12.5 Hz, ^4J(HF6) = 9.6 Hz, H(Ir)). Mass spectrum: m/z 938 [27%, M$^+$]; 910 [27, $(M-CO)^+$]; 717 [100, $(C_{36}H_{30}IrP_2)^+$]; 676 [27, $(C_{26}H_{16}F_4IrO_3P)^+$]; 638 [73, $(C_{30}H_{23}IrP_2)^+$].

Carbonyl(2-carboxylato-3,4,5,6-tetrafluorophenyl)hydridopyridinetriphenylphosphineiridium (III) (3c). The resonances (^{19}F, ^{31}P; Table 1) were deduced from NMR spectra of reaction mixtures. ^{1}H NMR spectrum: −16.3 (t, ^2J(HP) = ^4J(HF6) 11.4 Hz, H(Ir)); the aromatic protons could not be distinguished from those of the solvent and other compounds.

Composition of reaction mixtures on heating 1d. Reaction of **1d** (0.56 mmol) in pyridine (10 cm^3) gave **1d**:**3c**:**3a** as follows: 100:0:0 after 15 min at 25°C; 74:26:0 after 5 min at 116°C; 55:29:16 after 30 min at 116°C; 56:23:23 after 90 and 270 min at 116°C. Minor unassigned resonances from impurities were observed in some spectra.

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