Reactions involving Transition Metals. Part 14.[1] The Preparation of Novel Alkyl peroxy(carboxylato)iridium(III) Complexes

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Treatment of the di(alkyl peroxy)iridium(III) complexes $[IrX(O_2R^1)_2(CO)(PPh_3)_2]$ (X = Cl or Br) with organic acids, R^2CO_2H, having a $pK_a > ca.$ 4.0 results in the substitution of only one of the alkyl peroxy-ligands with formation of $[IrCl(O_2R^1)(OCOR^2)(CO)(PPh_3)_2]$ ($R^1 = Bu^t$, $R^2 = CF_3$, CCl_3, $CHCl_2$, CO_2H, *cis*-CH=CHCO$_2$H, C_6F_5, or H; $R^1 = CMe_2Ph$, $R^2 = CF_3$), and $[IrBr(O_2Bu^t)(OCOR^2)(CO)(PPh_3)_2]$ ($R^2 = CF_3$ or H). The related compounds $[IrX(Y)(O_2Bu^t)(CO)(PPh_3)_2]$ (X = Y = Cl or Br; X = Cl, Y = Br or NO_3) have also been obtained by reaction of $[IrX(O_2Bu^t)_2(CO)(PPh_3)_2]$ (X = Br or Cl) with HCl, HBr, or HNO_3 at 0 °C. At higher temperatures $[IrCl_2(O_2Bu^t)(CO)(PPh_3)_2]$ and $[IrCl(O_2Bu^t)(OCOCCl_3)(CO)(PPh_3)_2]$ react with HCl to give $[IrCl_3(CO)(PPh_3)_2]$.

ALKYL hydroperoxides react with the iridium(I) complexes *trans*-$[IrX(CO)L_2]$ (X = Cl or Br, L = PPh_3, PPh_2Me, or $AsPh_3$) and *trans*-$[IrI(CO)(PPh_3)_2]$ to give, respectively, di(alkyl peroxy)iridium(III) complexes $[IrX(O_2R)_2(CO)L_2]$ and mono(alkyl peroxy)iridium(III) complexes $[IrI_2(O_2R)(CO)(PPh_3)_2]$ (R = Bu^t or CMe_2Ph). With the exception of the complexes $[Co(Hdmg)(O_2R)L]$ [Hdmg = dimethylglyoximate(1 −), L = H_2O or pyridine] obtained on free-radical oxidation of the corresponding alkyl- and benzyl-cobaloximes,[2] these iridium(III) complexes are, to our knowledge, the only other stable transition-metal compounds containing alkyl peroxy-ligands reported to date, although the hydroperoxyplatinum(II) complexes $[Pt(CF_3)(O_2H)L_2]$ ($L_2 = Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH{=}CHPPh_2$; L = PPh_2Me) have been described recently.[3] We now report the behaviour of the iridium complexes with mineral and organic acids.

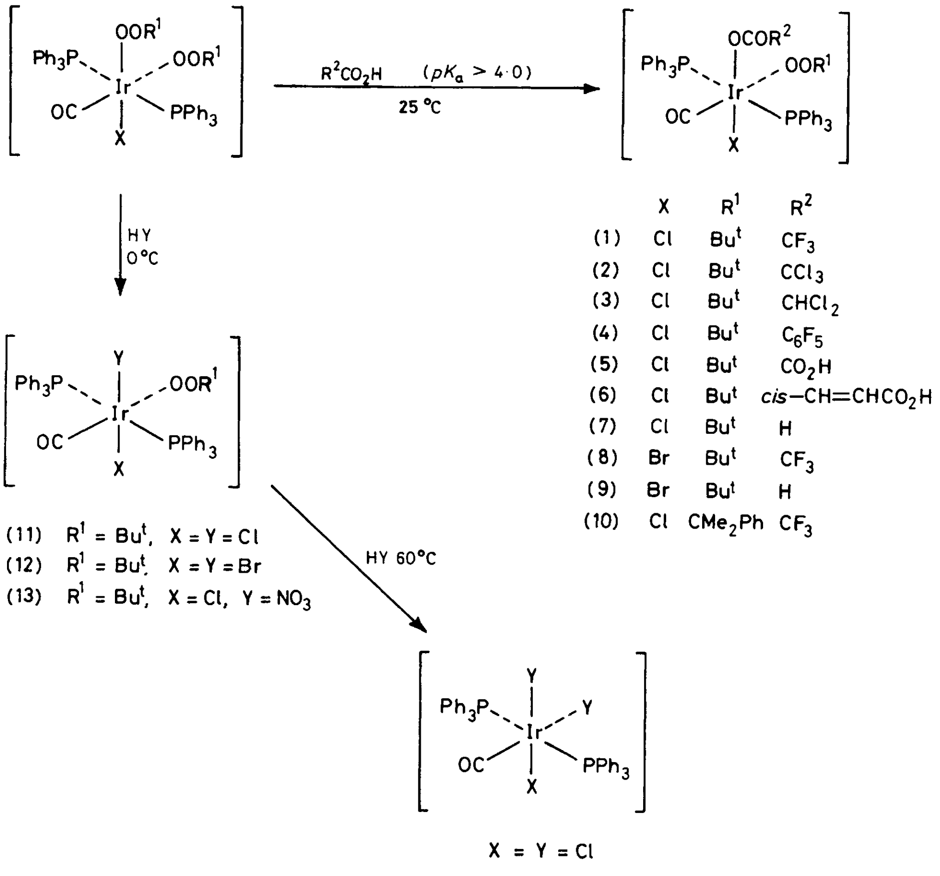
RESULTS AND DISCUSSION

In an effort to estimate the oxidising power of the complex $[IrCl(O_2Bu^t)_2(CO)(PPh_3)_2]$ a solution of NaI in acetic acid was added to a solution of the complex in toluene at room temperature. This produced an immediate colour change from yellow to deep red with the formation of $[IrClI_2(CO)(PPh_3)_2]$ in 93% yield after only 30 min. On the assumption that this reaction occurs by initial protonation of the t-butyl peroxy-ligands with liberation of Bu^tO_2H, a known reaction of alkyl peroxy-derivatives of the main-group elements,[4] the reactions of the di(alkyl peroxy)iridium(III) complexes with carboxylic acids were investigated.

Dropwise addition of an excess of trifluoroacetic acid to a stirred solution of $[IrCl(O_2Bu^t)_2(CO)(PPh_3)_2]$ in tetrahydrofuran (thf) at room temperature gave a high yield of the complex $[IrCl(O_2Bu^t)(OCOCF_3)(CO)(PPh_3)_2]$ (1) with liberation of Bu^tO_2H. Under similar conditions the reaction of $[IrCl(O_2Bu^t)_2(CO)(PPh_3)_2]$ with CCl_3CO_2H, $CHCl_2CO_2H$, $C_6F_5CO_2H$, $(CO_2H)_2$, *cis*-$HO_2CCH{=}CHCO_2H$, and HCO_2H, and those of $[IrBr(O_2Bu^t)_2(CO)(PPh_3)_2]$ with CF_3CO_2H and HCO_2H also proceeded smoothly to give the complexes (2)—(9) (Scheme 1). An analogous reaction between trifluoroacetic acid and $[IrCl(O_2CMe_2Ph)_2(CO)(PPh_3)_2]$ gave compound (10). The reaction is successful only with those relatively strong acids having $pK_a > ca.$ 4.0. Weaker acids, such as acetic acid and 4-toluic acid, fail to react under these conditions.

The i.r. spectra (Table 1) of complexes (1)—(10) show the expected strong ν(CO) band in the region of 2 050—2 066 cm^{-1}, together with a band of medium-weak intensity in the region of 880 cm^{-1} [ν(O–O)]. All the Ir–Cl stretching vibrations absorb in the region of 315—333 cm^{-1}, which is very different from that of 302—304 cm^{-1} found for the di(alkyl peroxy)iridium(III) complexes, and is closer to the ν(Ir–Cl) band at 327 cm^{-1} in the spectrum of $[IrCl(OCOPh)_2(CO)(PPh_3)_2]$. This may indicate that the chlorine is *trans* to the carboxylate ligand. In all the triphenylphosphine complexes the ligand absorption at 1 569 cm^{-1} is stronger than that at 1 582 cm^{-1} which is circumstantial evidence[5] that the two phosphines retain their *trans* arrangement. The ^{1}H n.m.r. and, where applicable, the ^{19}F n.m.r. spectra (Table 1) fully support the assigned structures. It is interesting that the resonance due to the formate proton in complex (10) appears as a 1 : 3 : 1 triplet (J = 1.0 Hz) attributable to long-range coupling with the two ^{31}P nuclei, and provides additional evidence that the two phosphine ligands are *trans*. Therefore, complexes (1)—(10) probably have structure (I), although the alternative structures (II) and (III) cannot be entirely discounted.

The mono(alkyl peroxy)carboxylatoiridium(III) complexes are soluble in benzene, toluene, dichloromethane, chloroform, and thf, considerably less soluble in diethyl ether, acetone, and carbon tetrachloride, and insoluble in n-hexane, methanol, or water. In the solid state they are stable in air at room temperature for several weeks. Even in solution they are stable for several days except in benzene, where decomposition is rapid in the presence of daylight, and within a few hours the clear yellow solutions become intense green. This behaviour mirrors that found with the di(alkyl peroxy)iridium(III) complexes and is possibly a consequence of homolysis of the



SCHEME 1

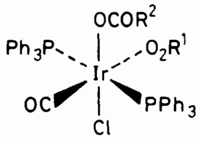
TABLE 1

Spectroscopic data for the iridium(III) complexes

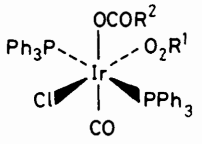
Complex	I.r. (cm^{-1}) [a]				^{1}H N.m.r. δ [c]	^{19}F N.m.r. δ/p.p.m. [d]
	ν(Ir–CO) [b]	ν(Ir–Cl)	ν(O–O)	ν(C=O)		
(1)	2 057	330	882	1 687	7.92 (m) (12), 7.44 (m) (18), 0.91 (s) (9)	−5.5 (s)
(2)	2 066	323	880	1 689	8.00 (m), (12), 7.43 (m) (18), 3.71 (m) (2), 1.81 (m) (2), 0.98 (s) (9)	
(3)	2 058	322	880	1 655	7.87 (m) (12), 7.35 (m) (18), 5.08 (s) (1), 0.91 (s) (9)	
(4)	2 059	326	888	1 653	7.99 (m) (12), 7.37 (m) (18), 0.95 (s) (9)	+58.2 (m) (2), +75.2 (m) (1), +85.2 (m) (2)
(5)	2 059	325	874	1 785, 1 697	7.84 (m) (12), 7.39 (m) (18), 3.71 (m) (4), 1.81 (m) (2), 0.91 (s) (9)	
(6)	2 062	326	888	1 717, 1 562(?)	7.82 (m) (12), 7.37 (m) (18), 3.59 (q) (2), [e] 0.85 (s) (9)	
(7)	2 051	315	882	1 624	7.93 (m) (12), 7.44 (m) (18), 6.24 (s) (1), 5.28 (s) (1), 0.85 (s) (9)	−5.7 (s)
(8)	2 056	—	881	1 684	7.96 (m) (12), 7.44 (m) (18), 0.97 (s) (9)	
(9)	2 050	—	882	1 623	7.91 (m) (12), 7.35 (m) (18), 6.30 (t) (1), [f] 5.28 (s) (1), 0.91 (s) (9)	
(10)	2 056	333	872	1 687	7.80 (m) (12), 7.39 (m) (28), 1.19 (s) (6)	−6.1 (s)
(11)	2 042	335, 308	885	—	7.95 (m) (12), 7.45 (m) (18), 0.75 (s) (9)	
(12)	2 050	—	886	—	8.03 (m) (12), 7.42 (m) (18), 0.96 (s) (9)	
(13)	2 073	324	882	—	8.90 (m) (12), 7.47 (m) (18), 0.82 (s) (9)	
(14)	2 044	320	886	—	8.96 (m) (12), 7.43 (m) (18), 0.82 (s) (5)	

[a] Recorded as Nujol mulls. [b] Separately recorded on solutions in CH_2Cl_2 with a ×10 expansion. [c] Solutions in $CDCl_3$ with $SiMe_4$ internal reference; s = singlet, m = multiplet, t = triplet, and q = quartet. Relative intensities are given in parentheses. [d] Solutions in $CDCl_3$ or $CHCl_3$. Chemical shifts are quoted in p.p.m. relative to external CF_3CO_2H. [e] J_{AB} = 13.0 Hz. [f] J = 1.0 Hz.

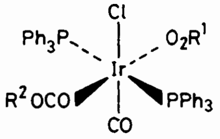
alkyl peroxy-ligand.[1] It is interesting that when a solution of $[\mathrm{IrCl(O_2Bu^t)(OCOCF_3)(CO)(PPh_3)_2}]$ in 1,2-dimethoxyethane was heated under reflux for 5 h loss of both the $\mathrm{Bu^tO_2}$ and $\mathrm{CF_3CO_2}$ groups occurred to give *trans*-$[\mathrm{IrCl(CO)(PPh_3)_2}]$ (28%), and pale yellow crystals of a compound tentatively identified as impure $[\mathrm{IrCl(OCOCF_3)_2(CO)(PPh_3)_2}]$ (34%). The latter had a ^{19}F n.m.r. spectrum ($\mathrm{CDCl_3}$) which showed two singlets of equal intensity at 5.9 and 4.3 p.p.m. downfield from external trifluoroacetic acid. The ^{1}H n.m.r. spectrum ($\mathrm{CDCl_3}$) contained aromatic proton resonances at δ 7.70 and 7.38, together with weak impurity bands at δ 3.35 and 0.89. The i.r. spectrum had a strong ν(CO) band at 2 080 cm^{-1} with a shoulder at 2 050 cm^{-1} indicating either the presence of more than one isomer, or an iridium–carbonyl impurity. The spectrum also had strong bands due to $\mathrm{CF_3CO_2}$ groups [ν(C=O) 1 723 vs, 1 694 (sh), 1 678 (sh) cm^{-1}], and an Ir–Cl stretching frequency at 332 cm^{-1}, but no evidence for a $\mathrm{Bu^tO_2}$ ligand. Attempts to synthesise an authentic sample of $[\mathrm{IrCl(OCOCF_3)_2(CO)(PPh_3)_2}]$ by heating under reflux a solution of $[\mathrm{IrCl(O_2Bu^t)(OCOCF_3)(CO)(PPh_3)_2}]$ in 1,2-dimethoxyethane in the presence of trifluoroacetic acid for 5 h gave yellow crystals which appeared to be a mixture containing mainly the desired $[\mathrm{IrCl(OCOCF_3)_2(CO)(PPh_3)_2}]$, but contaminated with some unidentified impurity.



(I)

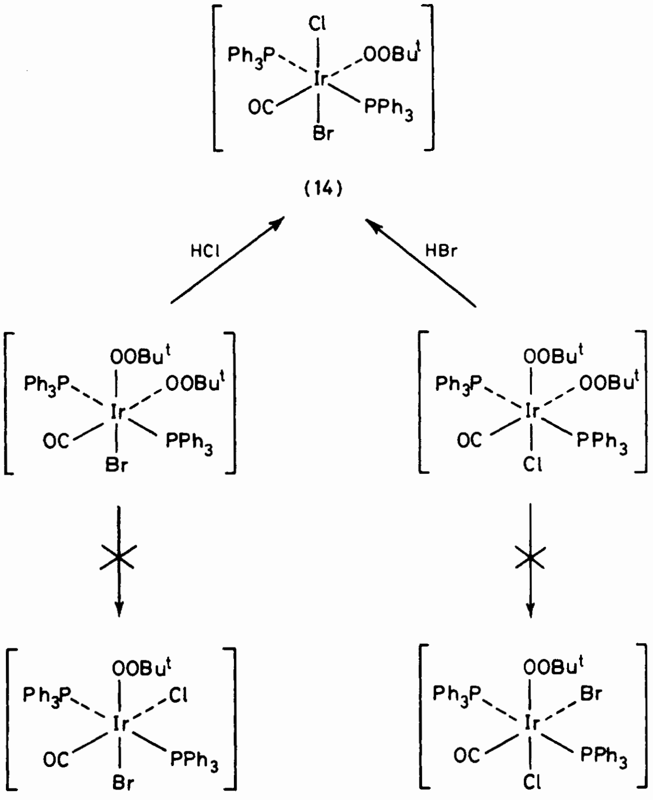


(II)



(III)

Addition of an excess of hydrochloric acid to a stirred solution of $[\mathrm{IrCl(O_2Bu^t)_2(CO)(PPh_3)_2}]$ in thf at 0 °C resulted in precipitation of the complex $[\mathrm{IrCl_2(O_2Bu^t)(CO)(PPh_3)_2}]$ (11). Similarly, reaction between HBr and $[\mathrm{IrBr(O_2Bu^t)_2(CO)(PPh_3)_2}]$, and between $\mathrm{HNO_3}$ and $[\mathrm{IrCl(O_2Bu^t)_2(CO)(PPh_3)_2}]$ at 0 °C, gave complexes (12) and (13) respectively (Scheme 1). When $[\mathrm{IrCl(O_2Bu^t)_2(CO)(PPh_3)_2}]$ was treated with HBr at low temperature it gave the expected product $[\mathrm{IrBr(Cl)(O_2Bu^t)(CO)(PPh_3)_2}]$ (14) in 80% yield. Compound (14) was also obtained in 89% yield upon reaction of $[\mathrm{IrBr(O_2Bu^t)_2(CO)(PPh_3)_2}]$ with HCl. The fact that both these reactions give the same single isomer of compound (14) can be accounted for if substitution of the t-butyl peroxy-ligand *trans* to the halogen ligand is replaced with retention of configuration. Replacement of the t-butyl peroxy-ligand *trans* to the carbonyl ligand with retention would lead to two different isomers of compound (14) from the two reactions (Scheme 2). However, in the absence of *X*-ray crystallographic data on the starting materials and product this conclusion remains speculative.



Scheme 2

The i.r. and ^{1}H n.m.r. spectra of complexes (11)—(13) are given in Table 1. In addition to ν(CO), ν(O–O), and ν(Ir–Cl) bands the spectrum of compound (13) showed bands at 1 546, 1 522, 1 263, and 965 cm^{-1} which are in good agreement with those reported[5] for nitrate ligands co-ordinated to iridium.

At 60 °C the reaction between $[\mathrm{IrCl_2(O_2Bu^t)(CO)(PPh_3)_2}]$ and HCl resulted in loss of the second t-butyl peroxy-ligand giving $[\mathrm{IrCl_3(CO)(PPh_3)_2}]$ in 90% yield. The same product was also obtained in 85% yield on refluxing for 10 min a solution of $[\mathrm{IrCl(O_2Bu^t)(OCOCCl_3)(CO)(PPh_3)_2}]\cdot$0.5thf in thf containing hydrochloric acid.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 621 spectrophotometer, ^{1}H n.m.r. spectra on a Varian Associates HA100 instrument. All reactions were carried out under an atmosphere of dry nitrogen except where stated.

General Procedure for the Reactions between Complexes of *the Type* $[IrX(O_2R)_2(CO)(PPh_3)_2]$ *and Carboxylic Acids.*—The carboxylic acid (8.78 mmol) was added to a stirred solution of the iridium complex (1.25 mmol) in thf (15 cm^3), and after 2 h at room temperature the volume of the solvent was reduced to *ca.* 7 cm^3, before addition of methanol (10 cm^3). On standing, yellow crystals formed slowly over several hours. These were usually analytically pure, but in some cases it was necessary to recrystallise either from toluene or dichloromethane. The yields, m.p.s, and analytical data for the products, compounds (1)—(10), are given in Table 2.

TABLE 2

Physical and analytical data for the iridium(III) complexes

	Complex	Yield (%)	M.p./ °C [a]	Analysis (%) [b] C	H	F	Halogen
(1)	$[IrCl(O_2Bu^t)(OCOCF_3)(CO)(PPh_3)_2]$	89	162—163	52.8(52.6)	4.1(4.0)	5.7(5.8)	—
(2)	$[IrCl(O_2Bu^t)(OCOCCl_3)(CO)(PPh_3)_2]\cdot0.5thf$	77	155—161	50.7(50.7)	4.1(4.1)	—	13.6(13.3) [c]
(3)	$[IrCl(O_2Bu^t)(OCOCHCl_2)(CO)(PPh_3)_2]$	74	151—154	51.7(51.8)	3.9(4.0)	—	10.7(10.7) [c]
(4)	$[IrCl(O_2Bu^t)(OCOC_6F_5)(CO)(PPh_3)_2]$	68	159—163	54.2(53.4)	4.1(3.6)	8.6(8.8)	3.5(3.3) [c]
(5)	$[IrCl(O_2Bu^t)(OCOCO_2H)(CO)(PPh_3)_2]$	72	160	54.8(54.8)	4.6(4.7)	—	—
(6)	$[IrCl(O_2Bu^t)(cis\text{-}OCOCH{=}CHCO_2H)(CO)(PPh_3)_2]$	78	162—165	54.9(54.9)	4.6(4.3)	—	3.6(3.6) [c]
(7)	$[IrCl(O_2Bu^t)(OCOH)(CO)(PPh_3)_2]\cdot0.5CH_2Cl_2$	70	>130 [d]	53.1(53.3)	4.4(4.3)	—	7.8(7.4) [c]
(8)	$[IrBr(O_2Bu^t)(OCOCF_3)(CO)(PPh_3)_2]$	83	150—155	50.6(50.3)	4.0(3.8)	5.4(5.5)	8.0(7.8) [e]
(9)	$[IrBr(O_2Bu^t)(OCOH)(CO)(PPh_3)_2]\cdot0.5CH_2Cl_2$	78	>130 [d]	50.7(51.0)	4.2(4.1)	—	8.2(8.0) [e] 3.1(3.5) [c]
(10)	$[IrCl(O_2CMe_2Ph)(OCOCF_3)(CO)(PPh_3)_2]$	83	145—151	55.5(55.2)	4.3(4.0)	5.5(5.5)	3.6(3.4) [c]
(11)	$[IrCl_2(O_2Bu^t)(CO)(PPh_3)_2]$	81	147—150	55.0(54.4)	4.5(4.3)	—	8.4(7.8) [c]
(12)	$[IrBr_2(O_2Bu^t)(CO)(PPh_3)_2]\cdot PhCH_3$	86	151—154	52.6(53.1)	4.3(4.4)	—	15.2(14.7) [e]
(13)	$[IrCl(NO_3)(O_2Bu^t)(CO)(PPh_3)_2]\cdot0.5CH_2Cl_2$	71	162—163	51.0(51.2)	4.1(4.1)	—	6.9(7.3) [c]
(14)	$[IrBr(Cl)(O_2Bu^t)(CO)(PPh_3)_2]\cdot0.5PhCH_3$	89 [f]					
		80 [g]	144—148	53.9(53.5)	4.3(4.3)	—	—

[a] With decomposition. [b] Calculated values are given in parentheses. [c] Chlorine. [d] Decomposes without melting. [e] Bromine. [f] From reaction between $[IrBr(O_2Bu^t)_2(CO)(PPh_3)_2]$ and HCl. [g] From reaction between $[IrCl(O_2Bu^t)_2(CO)(PPh_3)_2]$ and HBr.

Decomposition of Compound (1) *in* 1,2-*Dimethoxyethane.*—A solution of (1) (0.95 g, 0.97 mmol) in 1,2-dimethoxyethane (20 cm^3) was heated under reflux for 5 h, before reducing the volume of the solution to *ca.* 7 cm^3, and cooling to 0 °C, whereupon yellow crystals of *trans*-$[IrCl(CO)(PPh_3)_2]$ (0.21 g, 0.27 mmol, 28%) precipitated. Addition of methanol (10 cm^3) to the filtrate gave a pale yellow solid (0.33 g, 0.33 mmol, 34%) on standing. This was tentatively identified as $[IrCl(OCOCF_3)_2(CO)(PPh_3)_2]$ (Found: C, 50.1; H, 3.7; F, 9.7. $C_{41}H_{30}ClF_6IrO_5P_2$ requires C, 49.0; H, 3.0; F, 11.3%). I.r.: $\nu_{max.}$ at 3 060m, 2 080vs, 2 050 (sh), 1 723vs, 1 694 (sh), 1 678 (sh), 1 567m, 1 481s, 1 432s, 1 399s, 1 183vs, 1 150vs, 1 089s, 1 027m, 997m, 856m, 848 (sh), 780s, 744s, 734m, 727m, 707s, 690vs, 575m, 548m, 518vs, 510 (sh), 497 (sh), 458m, and 332m cm^{-1}.

Compound (1) (0.80 g, 0.81 mmol) and trifluoroacetic acid (1.0 g, 8.78 mmol) in 1,2-dimethoxyethane (15 cm^3) were heated under reflux for 5 h. Reducing the volume and addition of methanol gave a pale yellow solid (0.45 g) (Found: C, 49.0; H, 3.3; Cl, 7.2; F, 9.3%) which could be recrystallised from a dichloromethane–methanol mixture (1 : 1 v/v), but was shown by thin-layer chromatography (t.l.c.) to contain two components. The ^1H n.m.r. spectrum ($CDCl_3$) showed multiplets due to aromatic protons at δ 7.75 (12 H) and 7.40 (18 H) in addition to a signal for CH_2Cl_2. The ^{19}F n.m.r. spectrum ($CDCl_3$) showed two sharp singlets of equal intensity at −5.9 and −4.3 p.p.m. relative to CF_3CO_2H, and a weaker singlet at −5.6 p.p.m. The i.r. spectrum was almost identical to that of the compound $[IrCl(OCOCF_3)_2(CO)(PPh_3)_2]$, but contaminated with a small amount of unidentified iridium phosphine complex having CF_3CO_2 ligands.

Reactions of $[IrCl(O_2Bu^t)_2(CO)(PPh_3)_2]$.—(*a*) *With* HCl. Dropwise addition of concentrated hydrochloric acid (0.50 g) to a solution of the iridium complex (0.60 g, 0.63 mmol) in thf (5 cm^3) at 0 °C resulted in the precipitation of compound (11) (0.46 g, 0.51 mmol) as a pale yellow solid, which was washed with methanol and recrystallised from toluene–methanol (2 : 1).

(*b*) *With* HNO_3. Under similar conditions, addition of 10 drops of concentrated nitric acid to the iridium complex (0.58 g, 0.56 mmol) gave pale yellow crystals of compound (13) (0.42 g, 0.43 mmol) which were recrystallised from dichloromethane–methanol solution.

(*c*) *With* HBr. Addition of 48.5% hydrobromic acid (0.50 g) to $[IrCl(O_2Bu^t)_2(CO)(PPh_3)_2]$ (0.51 g, 0.53 mmol) in thf (4 cm^3) at 0 °C yielded yellow crystals of compound (14) (0.41 g, 4.25 mmol).

Reaction of $[IrBr(O_2Bu^t)_2(CO)(PPh_3)_2]$ *with* HBr.—Addition of 48.5% hydrobromic acid (0.50 g, 3.00 mmol) to a solution of $[IrBr(O_2Bu^t)_2(CO)(PPh_3)_2]$ (0.45 g, 0.45 mmol) in thf (4 cm^3) at 0 °C gave orange crystals of compound (12) (0.42 g, 0.39 mmol) which were recrystallised from toluene–methanol solution.

Reaction of Compound (11) *with* HCl.—When a solution of concentrated HCl (0.25 g) and compound (11) (0.20 g, 0.22 mmol) in thf (10 cm^3) was warmed to 60 °C white crystals began to appear. After 10 min the solution was cooled to 0 °C and the crystals were then filtered off, washed with methanol and then diethyl ether, and dried over P_2O_5 to give carbonyltrichlorobis(triphenylphosphine)iridium(III) (0.17 g, 0.20 mmol, 90%).

Reaction of $[IrBr(O_2Bu^t)_2(CO)(PPh_3)_2]$ *with* HCl.—Addition of concentrated HCl (0.50 g) to the iridium complex (0.60 g, 0.60 mmol) in thf (5 cm^3) at 0 °C gave compound (14) (0.53 g, 0.53 mmol), which was recrystallised from toluene–methanol solution.

Reaction of Compound (2) *with* HCl.—When a solution of concentrated HCl (0.5 g) added dropwise to compound (2) (0.25 g, 0.23 mmol) in thf (5 ml) was heated under reflux for 10 min white crystals of $[IrCl_3(CO)(PPh_3)_2]$ (0.17 g, 0.20 mmol, 85%) were formed.

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