Reactions involving Transition Metals. Part 15.[1] Reactions of Alkyl- and Acyl-peroxy-anions with $[M(CO)(MeCN)(PPh_3)_2]^+$ (M = Ir or Rh)

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The title compounds react with peroxycarboxylic acids RCO_3H in the presence of NEt_3 to give the compounds $[M(O_2CR)(CO)L_2]$ ($L = PPh_3$), which, with MeI, give $[IrMe(I)(OCOC_6H_4Cl\text{-}m)(CO)L_2]$ and $[RhI(O_2CR)(COMe)L_2]$ ($R = C_6H_4Cl\text{-}m$, Ph, or Me). Reaction between NaO_2COR' ($R' = C_6H_4Cl\text{-}m$) and $[Ir(CO)(MeCN)L_2]^+$ affords an inseparable mixture of $[Ir(O_2CR')(CO)L_2]$, $[Ir(O_2)(O_2CR')(CO)L_2]$, $[Ir(O_3CR')(CO)L_2]$, and $[Ir(O_2)(O_3CR')(CO)L_2]$; under similar conditions the rhodium analogue gives a mixture of $[Rh(O_3CR')(CO)L_2]$ and $[Rh(O_2CR')(CO)L_2]$. Reactions between NaO_2Bu^t and either $[Ir(CO)(MeCN)L_2]^+$ or $[IrF(CO)L_2]$ give only $[Ir(OH)(CO)L_2]$.

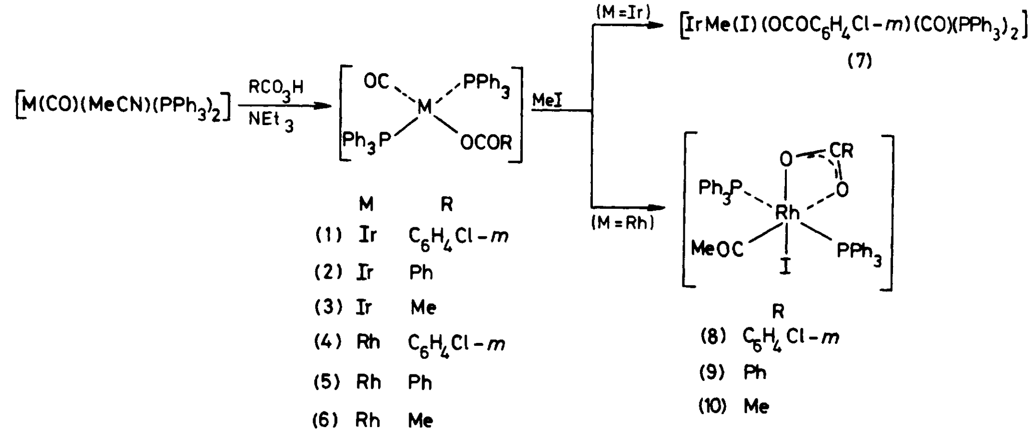
ALKYL peroxy complexes of iridium(III), synthesised in our laboratory,[2] have an interesting chemistry, but, being co-ordinately saturated, their ability to act as oxidizing agents appears to depend upon (*a*) light-initiated homolysis of the O–O bond of the alkyl peroxy-ligand, (*b*) thermolysis of the O–Ir bond, and (*c*) loss of alkyl hydroperoxide upon treatment with acid.[1] It was of interest, therefore, to examine the possibilities of preparing alkyl peroxy- and acyl peroxy-iridium(I) and -rhodium(I) complexes. In addition to the breakdown pathways described above, these compounds, having a vacant co-ordination site, might be expected to possess the ability of bonding to suitable unsaturated ligands and of forming oxidative-addition products with various addends. It was especially interesting to see whether during such reactions there was any evidence for oxygen transfer from the alkyl- or acyl- peroxy-ligand. In this paper we describe our attempts to prepare alkyl peroxy- and acyl peroxy-iridium(I) and -rhodium(I) complexes, and report our observations on their stabilities and reactions.

RESULTS AND DISCUSSION

The acetonitrile ligand in the iridium(I) complex $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ is readily displaced by a variety of nucleophiles, X^-, under mild conditions to give the substitution products $[IrX(CO)(PPh_3)_2]$ in high yields.[3] The rhodium analogue, $[Rh(CO)(MeCN)(PPh_3)_2]ClO_4$, has not been described previously, but can be obtained in 84% yield by reaction of $[RhCl(CO)(PPh_3)_2]$ with silver perchlorate in acetonitrile.

Reactions with Peroxycarboxylic Acids and Triethylamine.—Initial experiments between peroxycarboxylic acids and the complexes $[M(CO)(MeCN)(PPh_3)_2]ClO_4$ (M = Rh or Ir) were carried out by addition of solutions of the metal complexes in dichloromethane to cold, ethanolic solutions of the peroxycarboxylic acids, RCO_3H ($R = C_6H_4Cl\text{-}m$, Ph, or Me), containing an equimolar amount of triethylamine. The yellow, crystalline solids isolated from these reactions were characterized as the carboxylato-iridium(I) and -rhodium(I) complexes (1)—(6) (see Scheme 1), and there was no evidence for any acyl peroxy-species. A possible explanation is that oxidation of the triethylamine by the peroxycarboxylic acid to give the salts $[Et_3N(OH)]^+O_2CR^-$ occurs prior to addition of the metal complex. This is a known reaction of other tertiary and secondary amines with *m*-chloroperoxybenzoic acid in chloroform at 0—25 °C.[4]

The complexes (5) and (6) have been described previously,[5] but the remainder are new, and i.r. and ^1H n.m.r. data for these are given in Table 1. The carboxylato-derivatives react readily with iodomethane to give oxidative-addition products. When the iridium complex (1)



SCHEME 1

TABLE 1

Spectroscopic data for the carboxylato-iridium and -rhodium complexes

	I.r. (cm^{-1}) [a]				^{1}H N.m.r. (δ) [b]
Complex	ν(CO)	$\nu_{asym.}$(OCO) [c]	$\nu_{sym.}$(OCO)	ν(C=O)	
(1)	1 963	1 637	1 331	—	7.47 (m) (12), 7.22 (m) (22), 5.22 (s) (1.25) [CH_2Cl_2]
(2)	1 955	1 632	1 340	—	7.66 (m) (12), 7.35 (m) (23), 5.22 (s) (0.5) [CH_2Cl_2]
(3)	1 944	1 607	1 380	—	1.4 (s) (3) [d]
(4)	1 976	1 624	1 344	—	7.7 (m) (12), 7.40 (m) (22)
(7)	2 027	—	—	—	7.84 (m) (12), 7.40 (m) (22) 1.13 (t) [3, J(P–H) = 6 Hz]
(8)	—	1 527	1 399	1 670	
(9)	—	1 526	1 389	1 687	
(10)	—	1 541	1 400	1 687	

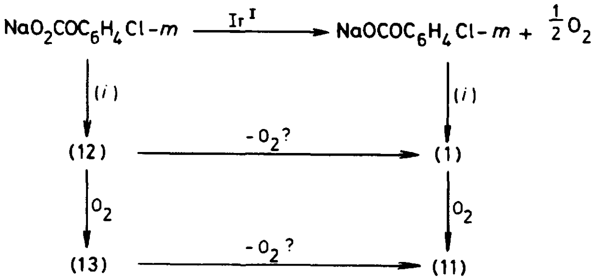
[a] Recorded in Nujol mulls; the metal–carbonyl region was separately recorded on a solution in CH_2Cl_2 with a 10-fold expansion. [b] Solution in $CDCl_3$ with $SiMe_4$ internal reference; s = singlet, m = multiplet, and t = triplet. Relative intensities are given in parentheses. [c] Tentative assignments only as this region also has bands due to the phosphine ligands. [d] Spectrum determined on a solution in benzene; the aromatic region was masked by the solvent.

was stirred with an excess of iodomethane at room temperature (r.t.) the adduct (7) was obtained in high yield (Scheme 1). The triplet at δ 1.13 in the ^{1}H n.m.r. spectrum of (7) (see Table 1) caused by the coupling of the methyl ligand to two equivalent ^{31}P nuclei establishes that the phosphine ligands are ***trans*** in this complex. The rhodium complexes (4), (5), and (6) react with iodomethane under similar conditions to form the acetyl complexes (8), (9), and (10) respectively (Scheme 1). These are all six-co-ordinate complexes in which the carboxylato-groups act as bidentate ligands as evidenced by characteristic bands [6] in the i.r. spectra in the region of 1 526—1 541 [$\nu_{asym.}$(OCO)] and 1 389—1 400 cm^{-1} [$\nu_{sym.}$(OCO)] (see Table 1). Monitoring of these reactions by i.r. spectroscopy failed to detect any evidence for the methyl complexes [$RhMe(I)(OCOR)(CO)(PPh_3)_2$], implying that isomerization of these to the isolated acetyl derivatives is a fast reaction perhaps assisted by chelation of the carboxylate ligand. It is interesting that solutions of these acetyl complexes in dichloromethane on standing for 12 h (r.t.) give [$RhI(CO)(PPh_3)_2$] in almost quantitative yields, presumably with reductive elimination of RCO_2Me.

Reactions with Sodium m-*Chloroperoxybenzoate.*—In an effort to avoid the complications caused by the presence of triethylamine, anhydrous sodium *m*-chloroperoxybenzoate was prepared as a white powder by the dropwise addition of a solution of *m*-chloroperbenzoic acid in diethyl ether to a suspension of sodium hydride in the same solvent at 0 °C. Iodometric titration confirmed that the salt contained 93% of the theoretically available active oxygen, and that in dichloromethane, in which it is slightly soluble, there is little loss of active oxygen content over at least 1 h. In alcoholic solvents the salt loses oxygen rapidly, and in this respect is similar to sodium peroxybenzoate.[7]

Addition of a solution of [$Ir(CO)(MeCN)(PPh_3)_2$]ClO_4 in dichloromethane to a two molar excess of NaO_2CO-C_6H_4Cl-*m* as a suspension in the same solvent at 0 °C under dry nitrogen caused no appreciable colour change. After 15 min, removal of unchanged sodium salt and addition of dry ethanol to the filtrate gave a yellow solid, which was dried and stored under nitrogen. The i.r. spectrum of this solid showed four iridium–carbonyl stretching vibrations at 2 055s, 2 004s, 1 961m, and 1 945m cm^{-1} suggesting that it contained at least four compounds. The band at 1 961 cm^{-1} can be assigned to compound (1) (see Table 1), while that at 2 004 cm^{-1} is probably the dioxygen adduct [$Ir(O_2)(OCOC_6H_4Cl$-*m*)$(CO)(PPh_3)_2$] (11). An authentic sample of compound (11) prepared in 65% yield by stirring a dichloromethane solution of (1) under dioxygen for 2—3 h (r.t.) showed a strong band at 2 010 cm^{-1} [ν(CO)] and a band of medium intensity at 850 cm^{-1} [ν(O–O)]. The i.r. spectrum of a 1 : 1 mixture of compounds (1) and (11) was almost identical to that of the yellow solid except for the bands at 2 055 and 1 945 cm^{-1}, and a band at 870m cm^{-1} [ν(O–O)]. On this basis the other two components of the mixture are tentatively assigned as the *m*-chloroperoxybenzoato-derivatives *trans*-[$Ir(O_2COC_6H_4Cl$-*m*)$(CO)(PPh_3)_2$] (12) [ν(CO) 1 945 cm^{-1}] and [$Ir(O_2)(O_2COC_6H_4Cl$-*m*)$(CO)(PPh_3)_2$] (13) [ν(CO) 2 055 cm^{-1}]. From the relative intensities of the metal–carbonyl absorptions the mixture contains approximately equal amounts of the four compounds, but attempts to separate these have proved unsuccessful.

The mixture is stable in the solid state in air for at least 1 week, and over 2 months it reacts slowly with oxygen in the air resulting in an increase in the proportions of the dioxygen complexes (11) and (13), and a corresponding decrease in the complexes (1) and (12). A solution of the mixture in dichloromethane under nitrogen showed no change over 3 h, but on longer standing the dioxygen complex (11) slowly loses oxygen. This reversibility of oxygen uptake has been confirmed by monitoring a solution of pure complex (11), in dichloromethane under nitrogen. Over 24 h (r.t.) this was found to lose 20—30% of the co-ordinated dioxygen. Similar behaviour has been noted previously [3] for the complex [$Ir(O_2)$-$(O_2CCF_3)(CO)(PPh_3)_2$]. When the mixture of complexes (1), (11), (12), and (13) in CH_2Cl_2–EtOH solution was stirred under dioxygen for 2 h (r.t.) the carbonyl absorptions at 1 945 and 1 961 cm^{-1} disappeared, and the white solid which precipitated contained only compounds (11) and (13). On exposing a solution of this white solid in CH_2Cl_2 to the atmosphere over 6 h (r.t.) the absorption at 1 961 cm^{-1} for complex (1) slowly reappeared, but not the band at 1 945 cm^{-1}. This confirms that the dioxygen complex (13) is more stable to loss of the dioxygen ligand than complex (11). The surprising stability of the acyl peroxyiridium(I) complex (12) and its dioxygen adduct (13) makes them unlikely sources of complexes (1) and (11) in the reaction between $NaO_2COC_6H_4Cl$-*m* and $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$. Additionally, decomposition of complex (12) alone cannot account either for the observed approximate 1 : 1 : 1 : 1 molar ratio of the products, or the total oxygen required for the formation of complexes (11) and (13). The simplest explanation of the results is that $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$, or one of the other iridium(I) complexes, catalyses the decomposition of $NaO_2COC_6H_4Cl$-*m* into $NaO_2CC_6H_4Cl$-*m* and dioxygen, perhaps by a competing electron-transfer process (see Scheme 2).



SCHEME 2 (i) $[Ir(CO)(MeCN)(PPh_3)_2]$

The acyl peroxyiridium(I) complex (12) does not appear to be an oxidizing agent for alkenes. A solution of the mixture of compounds (1), (11), (12), and (13) in dichloromethane fails to react with an excess of styrene over 2 h (r.t.).

Addition of a suspension of $NaO_2COC_6H_4Cl$-*m* in CH_2Cl_2 to a solution of $[Rh(CO)(MeCN)(PPh_3)_2]ClO_4$ in the same solvent gave a yellow solid in *ca.* 65% yield. Its i.r. spectrum showed an intense metal–carbonyl absorption at 1 945 cm^{-1} together with a weak band at 870 cm^{-1} [ν(O–O)] indicative of the expected acyl peroxyrhodium(I) complex $[Rh(O_2COC_6H_4Cl$-*m*$)(CO)(PPh_3)_2]$ (14). The spectrum also contained a weak rhodium–carbonyl absorption at 1 980 cm^{-1} for complex (4) (see Table 1). On exposure to air at room temperature the bands at 1 945 and 870 cm^{-1} slowly disappeared and that at 1 980 cm^{-1} increased until after 2 weeks only complex (4) remained. In solution decomposition occurs much more rapidly and conversion into (4) is complete after only 2 h. In neither case was there any evidence for the formation of dioxygen complexes. Addition of a solution of sodium iodide in acetic acid under nitrogen to a toluene solution containing mainly (14) contaminated with a little of complex (4) caused an immediate colour change from yellow to deep red indicative of iodine liberation. After 5 min (r.t.) an orange solid precipitated. The i.r. spectrum indicates that this is a mixture of $[RhI_3(CO)(PPh_3)_2]$ [ν(CO) 2 089 cm^{-1}] [5] and $[RhI(CO)(PPh_3)_2]$ [ν(CO) 1 968 cm^{-1}].[5] A controlled experiment in which pure compound (4) was treated with sodium iodide under similar conditions only liberated a trace of iodine after 2 h, possibly as a result of traces of oxygen in the nitrogen used. It would appear that complex (14) does have oxidizing power, but this is probably due to liberation of *m*-chloroperbenzoic acid on reaction with the acetic acid, as found for t-butyl peroxyiridium(III) complexes.[1] It is interesting, however, that unlike the acyl peroxyiridium(I) complex the rhodium analogue does show some evidence that it can release an oxygen atom of the acyl peroxy-ligand, and further investigation of its chemistry is warranted.

Reactions of Sodium t-Butyl Peroxide.—When a solution of $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ in dry dichloromethane was added to an excess of NaO_2Bu^t in absolute ethanol under an atmosphere of dry nitrogen at r.t. yellow crystals of the known [3] hydroxy-complex $[Ir(OH)(CO)(PPh_3)_2]$ were obtained in 68% yield. Reed and Roper [3] have reported previously that addition of NaOEt to $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ in absolute ethanol also results in the formation of this hydroxy-complex, and they have attributed this to traces of water present in the solvent. We have confirmed their findings, and in our hands the yield of $[Ir(OH)(CO)(PPh_3)_2]$ was 66%. It must be accepted that the scale of the reactions with both $NaOBu^t$ and NaOEt was such that only *ca.* 0.03% of water impurity would be required to account for the observed yields of the hydroxy-complex. Nevertheless, it seems unrealistic to suppose that even if traces of water were present in this quantity despite rigorous drying precautions the nucleophilic attack of hydroxide ion upon $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ could occur to the total exclusion of attack by the stronger nucleophiles EtO^- and $Bu^tO_2^-$ which are present in large excess. Even when the reaction between NaO_2Bu^t and $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ is carried out in dry dichloromethane, $[Ir(OH)(CO)(PPh_3)_2]$ is formed as the only iridium-containing product in 60% yield. It must be concluded that this product arises by decomposition of intermediate species, possibly $[Ir(OEt)(CO)(PPh_3)_2]$ and $[Ir(O_2Bu^t)(CO)(PPh_3)_2]$ respectively. In both the reaction of NaOEt and NaO_2Bu^t there was no evidence for any volatile reaction products such as dioxygen, alkenes, or oxiranes. Gas–liquid chromatography failed to detect any organic products, but this is not surprising considering the small scale of these reactions. When the reaction between NaO_2Bu^t and $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ in dichloromethane was repeated in the presence of an excess of styrene, $[Ir(OH)(CO)(PPh_3)_2]$ (63% yield) was again the only product isolated; there was no evidence that any oxidation of styrene had occurred.[8] Under similar conditions, but with tetracyanoethene in place of styrene, the product obtained in 70% yield was $[Ir(CO)(MeCN)\{(NC)_2C{=}C(CN)_2\}(PPh_3)_2]ClO_4$, characterized by bands at 2 075s [ν(CO)], 2 222m [ν(CN)], and 2 230 (sh) cm^{-1} [ν(CN)], and a broad absorption at 1 080 cm^{-1} for a free perchlorate anion.[8] In a further attempt to synthesize $[Ir(O_2Bu^t)(CO)(PPh_3)_2]$ a solution of NaO_2Bu^t in dry methanol was added to a solution of $[IrF(CO)(PPh_3)_2]$ [9] in the same solvent. After slight warming this gave a yellow solid, which could not be purified by recrystallization or chromatography, but appeared, from its i.r. spectrum, to be mainly $[Ir(OH)(CO)(PPh_3)_2]$ contaminated with an iridium(III) carbonyl species having prominent bands at 2 080 [ν(CO)], 1 743 [ν(C=O)?], and 1 080 cm^{-1}. The ^1H n.m.r. spectrum showed only a broad aromatic resonance centred at δ 7.25, with no evidence of aliphatic or metal–hydride signals.

These preliminary results indicate that alkyl peroxyiridium(I) complexes are likely to prove difficult to isolate. Further experimentation is necessary to establish the mechanisms by which $[Ir(OH)(CO)(PPh_3)_2]$ is formed in these reactions, and in particular the source of the hydrogen of the hydroxyl group. If this arises from the t-butyl peroxy-ligand in an intermediate such as $[Ir(O_2Bu^t)(CO)(PPh_3)_2]$ then the use of suitable blocking groups may lead to stable complexes.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 621 instrument, and ^1H n.m.r. spectra on a Varian HA 100 instrument. Peroxyacetic acid (78% active oxygen) and *m*-chloroperoxybenzoic acid (98% active oxygen) were commercial samples checked by iodometry. t-Butyl peroxide contained 30% di-t-butyl peroxide. Peroxybenzoic acid,[10] *trans*-$[IrF(CO)(PPh_3)_2]$,[9] and $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ [3] were prepared by standard procedures. Solvents were thoroughly dried and deaerated before use, and except where stated all reactions were carried out under dry nitrogen. Physical and analytical data for the carboxylato-iridium and -rhodium complexes are shown in Table 2.

TABLE 2

Physical and analytical data for the carboxylato-iridium and -rhodium complexes

	Complex	M.p./°C [b]	Analysis [a]/% C	H	Halogen
(1)	$[Ir(OCOC_6H_4Cl\text{-}m)(CO)(PPh_3)_2]\cdot 0.63CH_2Cl_2$	150—155	56.5(56.2)	3.4(3.7)	8.4(8.4) [c]
(2)	$[Ir(OCOPh)(CO)(PPh_3)_2]\cdot 0.25CH_2Cl_2$	145	59.4(59.9)	3.7(4.0)	—
(3)	$[Ir(OCOMe)(CO)(PPh_3)_2]$	150—154	56.6(58.3)	4.4(4.1)	—
(4)	$[Rh(OCOC_6H_4Cl\text{-}m)(CO)(PPh_3)_2]$	145—155	64.6(65.2)	4.3(4.2)	4.9(4.4) [c]
(5)	$[Rh(OCOPh)(CO)(PPh_3)_2]\cdot 0.5CH_2Cl_2$	180—182	65.1(65.2)	4.7(4.4)	—
(6)	$[Rh(OCOMe)(CO)(PPh_3)_2]$	150	64.9(65.5)	4.8(4.7)	—
(7)	$[IrMe(I)(OCOC_6H_4Cl\text{-}m)(CO)(PPh_3)_2]$	162—164	52.0(51.9)	3.5(3.6)	12.1(12.2) [d]
(8)	$[RhI(OCOC_6H_4Cl\text{-}m)(COMe)(PPh_3)_2]$	142—144	56.3(56.7)	3.9(3.9)	—
(9)	$[RhI(OCOPh)(COMe)(PPh_3)_2]$	138—140	58.7(58.8)	4.1(4.2)	13.6(13.8) [d]
(10)	$[RhI(OCOMe)(COMe)(PPh_3)_2]$	110—120	54.6(56.1)	4.3(4.2)	14.5(14.8) [d]

[a] Calculated values are given in parentheses. [b] With decomposition. [c] Chloride. [d] Iodide.

Reactions of $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$.—(*a*) *With m-chloroperoxybenzoic acid.* A solution of the iridium complex (0.6 g, 0.68 mmol) in dichloromethane (8 cm^3) was added dropwise to *m*-chloroperoxybenzoic acid (0.21 g, 1.36 mmol) in ethanol (10 cm^3) containing triethylamine (0.28 g, 2.8 mmol) to give yellow crystals of (1) (0.45 g, 0.48 mmol, 70%), which were recrystallized from dichloromethane by addition of ethanol.

(*b*) *With peroxybenzoic acid.* Under similar conditions reaction between the iridium complex (0.86 g, 0.98 mmol), peroxybenzoic acid (0.39 g, 2.86 mmol), and triethylamine (0.30 g, 3 mmol) gave bright yellow needles of (2) (0.53 g, 0.6 mmol, 61%), recrystallized by addition of ethanol to a dichloromethane solution.

(*c*) *With peroxyacetic acid.* Yellow crystals of (3) (0.42 g, 0.52 mmol, 71%) were obtained by addition of a dichloromethane solution of the iridium complex (0.65 g, 0.73 mmol) to peroxyacetic acid (0.11 g, *ca.* 1.1 mmol) in ethanol (10 cm^3) containing triethylamine (0.15 g, 1.5 mmol).

(*d*) *With sodium* m-*chloroperoxybenzoate.* A solution of dry *m*-chloroperbenzoic acid (0.86 g, 5.0 mmol) in ice-cold, anhydrous diethyl ether (15 cm^3) was added dropwise to a stirred suspension of sodium hydride (0.2 g, 5.0 mmol) in ether (75 cm^3) at 0—5 °C. When evolution of hydrogen was complete the sodium salt (0.93 g, 4.8 mmol, 96%) [ν(O–O) 870 cm^{-1}] was filtered off, washed with ether, and dried under vacuum. Iodometric titration [11] indicated a purity of 95%.

A solution of $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ (1.0 g, 1.13 mmol) in dichloromethane (10 cm^3) at 0 °C was added to a suspension of freshly prepared $NaO_2COC_6H_4Cl$-*m* (0.48 g, 2.5 mmol) in dichloromethane (25 cm^3) also at 0 °C and the mixture was stirred for 15 min before removal of insoluble material by filtration. The volume of the filtrate was reduced (5 cm^3) before addition of cold ethanol (10 cm^3) to give a lemon-yellow solid (0.58 g) shown by i.r. spectroscopy to be a mixture of compounds (1), (11), (12), and (13).

(*e*) *With sodium t-butyl peroxide.* Sodium t-butyl peroxide (0.76 g, 6.8 mmol, 97%) [ν(O–O) 885 cm^{-1}] was prepared by the addition of dry Bu^tO_2H (0.90 g, *ca.* 7.0 mmol) dropwise to a stirred suspension of sodium hydride (0.28 g, 7.0 mmol) in dry diethyl ether (75 cm^3) maintained between 0 and 5 °C. The salt is hygroscopic and must be freshly prepared and dried under vacuum prior to use.

A solution of $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ (1.0 g, 1.13 mmol) in dry CH_2Cl_2 (7 cm^3) added to a solution of NaO_2Bu^t (0.19 g, 1.74 mmol) in anhydrous ethanol at r.t. gave fine, yellow microcrystals of $[Ir(OH)(CO)(PPh_3)_2]$ (0.59 g, 0.77 mmol, 68%) [m.p. 178—182 °C (decomp.); lit.,[3] 177—179 °C].

A repeat of this reaction by adding $[Ir(CO)(MeCN)(PPh_3)_2]ClO_4$ (0.88 g, 1.0 mmol) in CH_2Cl_2 (10 cm^3) to a suspension of NaO_2Bu^t (0.22 g, 2.0 mmol) in CH_2Cl_2 (15 cm^3) at r.t. gave $[Ir(OH)(CO)(PPh_3)_2]$ (0.46 g, 0.60 mmol, 60%) after chromatography (Florisil).

Reactions of $[Rh(CO)(MeCN)(PPh_3)_2]$.—(*a*) *With m-chloroperoxybenzoic acid.* Dropwise addition of the rhodium complex (0.95 g, 1.11 mmol) in CH_2Cl_2 (10 cm^3) to a solution of *m*-chloroperoxybenzoic acid (0.39 g, 2.24 mmol) in ethanol (15 cm^3) containing triethylamine (0.44 g, 4.4 mmol) gave yellow crystals of (4) (0.65 g, 0.8 mmol, 72%).

(*b*) *With peroxybenzoic acid.* Using similar reaction conditions between the rhodium complex (0.77 g, 0.91 mmol), peroxybenzoic acid (0.21 g, 1.5 mmol), and triethylamine (0.15 g, 1.5 mmol) gave yellow crystals of (5) (0.50 g, 0.62 mmol, 68%).

(*c*) *With peroxyacetic acid.* Intense yellow crystals of (6) (0.57 g, 0.80 mmol, 50%) were obtained by reaction of [Rh(CO)(MeCN)$(PPh_3)_2$]ClO_4 (0.85 g, 1.0 mmol) with peroxyacetic acid (0.28 g, *ca.* 2.91 mmol) and triethylamine (0.38 g, 3.8 mmol).

(*d*) *With sodium* m-*chloroperoxybenzoate.* Addition of a solution of [Rh(CO)(MeCN)$(PPh_3)_2$]ClO_4 (0.76 g, 0.88 mmol) in CH_2Cl_2 (8 cm^3) at 0 °C to a suspension of the freshly prepared sodium salt (0.46 g, 2.37 mmol) in CH_2Cl_2 (20 cm^3) gave an orange solution. After 15 min the mixture was filtered, and the volume of the filtrate was reduced to *ca.* 5 cm^3 before addition of cold ethanol to precipitate a yellow solid (0.47 g, *ca.* 0.57 mmol, 65%) shown by i.r. spectroscopy to be mainly (14) slightly contaminated with (4).

Reactions with Iodomethane.—(*a*) [Ir($OCOC_6H_4Cl$-*m*)(CO)-$(PPh_3)_2$]. Addition of the iridium complex (0.45 g, 0.47 mmol) as a solid to iodomethane (3 cm^3) at r.t. gave, after 1 min, a cream precipitate. After a further 2 h precipitation was completed by addition of n-pentane (10 cm^3), and the product was recrystallized from CH_2Cl_2–EtOH (5 : 8 v/v) to give cream crystals of (7) (0.38 g, 0.37 mmol, 78%).

(*b*) [Rh($OCOC_6H_4Cl$-*m*)(CO)$(PPh_3)_2$]. The solid rhodium complex (0.67 g, 0.93 mmol) was added to iodomethane (3 cm^3) to give (8) (0.18 g, 0.19 mmol, 86%) as an orange amorphous solid.

(*c*) [Rh(OCOPh)(CO)$(PPh_3)_2$]. Compound (9) (0.41 g, 0.44 mmol, 95%) was obtained as an orange solid on addition of compound (5) (0.38 g, 0.46 mmol) to iodomethane (*ca.* 2 cm^3).

(*d*) [Rh(OCOMe)(CO)$(PPh_3)_2$]. Reaction between (6) (0.67 g, 0.93 mmol) and iodomethane (3 cm^3) gave (10) (0.72 g, 0.84 mmol, 90%) as an orange solid.

When a solution of (10) (0.5 g, 0.58 mmol) in CH_2Cl_2 (10 cm^3) was allowed to stand at r.t. for 16 h, reduction in volume of the solution to *ca.* 5 cm^3 followed by addition of ethanol (10 cm^3) gave [RhI(CO)$PPh_3)_2$] (0.38 g, 0.49 mmol, 84%).

Reaction of [Ir($OCOC_6H_4Cl$-*m*)(CO)$(PPh_3)_2$] *with Dioxygen.*—A solution of (1) (0.29 g, 0.31 mmol) in a mixture of CH_2Cl_2 (5 cm^3) and ethanol (5 cm^3) was stirred under 1 atm * of dioxygen for 2—3 h at r.t. to give white microcrystals of [Ir(O_2)($OCOC_6H_4Cl$-*m*)(CO)$(PPh_3)_2$]·0.25CH_2Cl_2 (0.19 g, 0.2 mmol, 65%), m.p. 144—148 °C (decomp.) (Found: C, 55.7; H, 3.6; Cl, 5.6. $C_{44}H_{34}ClIrO_5P_2$·0.25CH_2Cl_2 requires C, 55.7; H, 3.6; Cl, 5.6%).

Reaction of trans-[IrF(CO)$(PPh_3)_2$] *with Sodium t-Butyl Peroxide.*—Addition of a solution of NaO_2Bu^t (0.44 g, 4.22 mmol) in dry methanol (10 cm^3) to a stirred solution of the iridium complex (0.5 g, 0.65 mmol) in methanol (20 cm^3) followed by stirring at 30—40 °C gave a yellow, amorphous solid (0.32 g), thought to contain mainly [Ir(OH)(CO)-$(PPh_3)_2$].

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* Throughout this paper: 1 atm = (101 325/760) Pa.

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