Reactions involving Transition Metals. Part 18.[1] Reactions of Transition-metal Complexes with Peroxycarboxylic Acids, Diacyl Peroxides, and t-Butyl Peroxybenzoate

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The iridium(I) complexes $[IrX(L^1)(L^2)_2]$ (L^1 = CO or N_2) react with peroxycarboxylic acids, RCO_3H, to give the carboxylato-complexes $[IrX(O_2CR)_2(L^2)_2]$ (X = Cl, R = $3\text{-}ClC_6H_4$, L^2 = PPh_3, PPh_2Me, or $AsPh_3$; X = Cl, R = Ph, L^2 = PPh_3 or $AsPh_3$; X = Cl, R = Me, L^2 = PPh_3; X = Br, R = $3\text{-}ClC_6H_4$, L^2 = PPh_3) with evolution of carbon dioxide; the compounds (X = Cl, L^2 = PPh_3, R = Me, Ph, or $3\text{-}ClC_6H_4$) have also been obtained from $[IrCl(N_2)(PPh_3)_2]$ and diacyl peroxides. The iodo-complex $[IrI(CO)(PPh_3)_2]$ behaves anomalously giving $[Ir(O_2CR)_3(PPh_3)_2]$ with RCO_3H (R = Ph or $3\text{-}ClC_6H_4$), and a mixture of $[Ir(O_2CPh)_3(CO)(PPh_3)_2]$ and $[IrI_3(CO)(PPh_3)_2]$ with dibenzoyl peroxide. Diacyl peroxides, $(RCO_2)_2$, react with $[IrCl(CO)(PPh_3)_2]$ to give the complexes $[IrCl(O_2CR)_2(CO)(PPh_3)_2]$ (R = Ph or $3\text{-}ClC_6H_4$) in high yields, and the compound where R = Ph rather than the expected $[IrCl(O_2CPh)(O_2CMe)(CO)(PPh_3)_2]$ is formed under similar conditions with acetyl peroxybenzoate. The palladium(0) complexes $[PdL_4]$ (L = PPh_3 or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$) react to form $[Pd(O_2CPh)_2L_2]$ with dibenzoyl peroxide at room temperature, but $[M\{P(OEt)_3\}_4]$ (M = Pt or Pd) and $[Pd_2(PhCH{=}CHCOCH{=}CHPh)_3]$ do not react under these conditions. Similarly, there is no reaction between $[IrCl(CO)(PPh_3)_2]$ and the peroxy-ester $Bu^tO_2C(O)Ph$ at room temperature, but $[Pt(PPh_3)_4]$ and $[Pd(Ph_2PCH_2CH_2PPh_2)_2]$ give $[Pt(O_2CPh)_2(PPh_3)_2]$ and $[Pd(O_2CPh)_2(Ph_2PCH_2CH_2PPh_2)]$ respectively as the only metal-containing products.

PRELIMINARY studies have shown that alkyl hydroperoxides react with iridium(I) complexes of the type *trans*-$[IrX(CO)L_2]$ (X = Cl, Br, or I; L = phosphine or arsine) to give stable mono- and di-(alkyl peroxy)-iridium(III) complexes.[2] A related investigation[3] has demonstrated that iridium peroxycarboxylate complexes, although difficult to obtain in a pure state, should be at least as stable as the corresponding alkyl peroxy-derivatives. In an attempt to synthesise such complexes the reactions of peroxycarboxylic acids with iridium(I) complexes have been investigated. The related reactions of diacyl peroxides and the peroxy-ester, $Bu^tO_2C(O)Ph$, with these and other transition-metal complexes have also been studied in an effort to gain a deeper understanding of the interaction of peroxy-compounds with metals in low oxidation states.

TABLE 1

Physical and analytical data for the carboxylato-iridium(III) and -palladium(II) complexes

Complex	M.p. (θ_c/°C)[a]	Analysis (%)[b] C	H	Cl
(1) $[IrCl(OCOC_6H_4Cl\text{-}3)_2(PPh_3)_2]\cdot 0.25CH_2Cl_2$	158—162	55.7 (55.7)	3.4 (3.6)	11.6 (11.4)
(2) $[IrCl(OCOC_6H_4Cl\text{-}3)_2(PPh_2Me)_2]$	145—148	50.4 (51.1)	3.8 (3.7)	11.1 (11.3)[c]
(3) $[IrCl(OCOC_6H_4Cl\text{-}3)_2(AsPh_3)_2]$	156—158	51.5 (52.2)	3.4 (3.3)	9.7 (9.2)
(4) $[IrBr(OCOC_6H_4Cl\text{-}3)_2(PPh_3)_2]$	143—145	53.3 (54.2)	3.6 (3.5)	6.5 (7.2)[d]
(5) $[IrCl(OCOCH_3)_2(PPh_3)_2]$	168—172	54.9 (55.2)	4.3 (4.2)	4.4 (4.1)
(6) $[IrCl(OCOPh)_2(PPh_3)_2]$	158—160	59.6 (60.4)	4.3 (4.1)	4.0 (3.6)
(7) $[IrCl(OCOPh)_2(AsPh_3)_2]\cdot 0.75CH_2Cl_2$	160—162	52.3 (53.2)	3.8 (3.7)	7.9 (7.7)
(8) $[Ir(OCOC_6H_4Cl\text{-}3)_3(PPh_3)_2]$	183—187	57.1 (57.9)	3.8 (3.6)	9.1 (9.0)
(9) $[Ir(OCOPh)_3(PPh_3)_2]\cdot 0.25CH_2Cl_2$	208—210	62.2 (62.3)	4.3 (4.2)	
(10) $[IrCl(OCOPh)_2(CO)(PPh_3)_2]$	154	59.6 (59.9)	4.1 (3.9)	3.7 (3.5)
(11) $[IrCl(OCOC_6H_4Cl\text{-}3)_2(CO)(PPh_3)_2]\cdot 0.65CH_2Cl_2$	148—152	53.6 (54.1)	3.5 (3.5)	9.7 (9.8)
(13) $[Pd(O_2CPh)_2(PPh_3)_2]$		68.8 (69.1)	4.5 (4.6)[e]	
(14) $[Pd(O_2CPh)_2(Ph_2PCH_2CH_2PPh_2)]$		64.6 (64.3)	4.8 (4.6)[f]	

[a] With decomposition. [b] Calculated values are given in parentheses. [c] Mol. wt. (isopiestic method, Perkin-Elmer model 115, benzene): 925. Calc.: 939. [d] Br analysis. [e] Phosphorus 6.9 (6.9)%. [f] Phosphorus 8.3 (8.3)%.

RESULTS AND DISCUSSION

Reactions of Peroxycarboxylic Acids.—Addition of a catalytic amount of $[IrCl(CO)(PPh_3)_2]$ to a solution of 3-chloroperoxybenzoic acid in benzene at room temperature did not cause significant decomposition, and after 24 h more than 90% of the acid was recovered unchanged. When an approximate six-fold excess of 3-chloroperoxybenzoic acid was added to the same iridium complex in benzene there was rapid evolution of CO_2 with the formation of compound (1) (Table 1) in 61% yield. The same product was also obtained in 24% yield upon reaction of the peroxy-acid with $[IrCl(N_2)(PPh_3)_2]$. This has been shown to be a general reaction of the chloro- and bromo-iridium(I) complexes. So, for example, reaction between $3\text{-}ClC_6H_4CO_3H$ and $[IrCl(CO)L_2]$ (L = $PMePh_2$ or

$AsPh_3$) or [$IrBr(CO)(PPh_3)_2$] afforded the products (2), (3), and (4) respectively, while the peroxycarboxylic acids RCO_3H (R = Me or Ph) with [$IrCl(CO)(PPh_3)_2$] gave (5) and (6), and the reaction between $PhCO_3H$ and [$IrCl(CO)(AsPh_3)_2$] resulted in the formation of compound (7) (Table 1). In all these reactions the product was isolated by chromatography, and a blue-green by-product remained on the column. This could not be eluted even with polar solvents.

TABLE 2

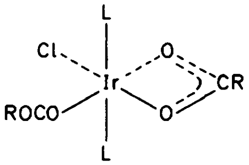
Spectroscopic data

	I.r. (cm^{-1}) [a]							
	Unidentate			Bidentate				^1H N.m.r. (δ) [b]
Complex	$\nu_{asym}(OCO)$	$\nu_{sym}(OCO)$	$\Delta\nu$	$\nu_{asym}(OCO)$	$\nu_{sym}(OCO)$	$\Delta\nu$	$\nu(Ir-Cl)$	
(1)	1 636	1 326	310	1 494	1 424	70	320	7.67 (m, 12), 7.12 (m, 26), 5.28 (s, 0.5, CH_2Cl_2)
(2)	1 610	1 354	256	1 480	1 420	60	323	7.50 (m, 8), 7.20 (m, 20), 2.03 (t, J [c] = 3.7 Hz, 6)
(3)	1 614	1 353	261	1 486	1 425	61	326	
(4)	1 634	1 323	311	1 492	1 420	72		
(5)	1 637	1 360	277	1 484	1 437	47	328	8.00 (m, 12), 7.80 (m, 18), 2.08 (s, 3), 1.79 (s, 3)
(6)	1 653	1 336	317	1 516	1 448	68	316	7.47 (m, 12), 7.22 (m, 28)
(7)	1 603	1 355	248	1 482	1 433	49	325	7.72 (m, 12), 7.30 (m, 28)
(8)	1 648	1 350	298	1 495	1 423	72		7.65 (m, 12), 7.17 (m, 30)
(9)	1 654	1 344	310	1 517	1 413	104		7.65 (m, 12), 7.28 (m, 33), 6.30 (s, 0.5)
(10)	1 647	1 326	321				327	7.90 (m, 12), 7.29 (m, 28)
(11)	1 644	1 320	324				323	7.67 (m, 12), 7.30 (m, 26), 5.30 (s, 1.3)
(13)	*cis* 1 640	1 368	272					
	1 626	1 334	292					
	trans 1 720	1 440	280					
(14)	1 609	1 365	244					7.1—7.6 (m, 20), 3.28 (br s, 4)

[a] Recorded as mulls in Nujol. [b] In CCl_4 solution with $SiMe_4$ as internal reference; s = singlet, m = multiplet, t = triplet. Relative intensities are given in parentheses. [c] Measured apparent coupling constant for the $X_6AA'X'_6$ pattern.

It was difficult to obtain accurate molecular-weight data for the complexes (1)—(7) as they were not very soluble in common solvents. However, the molecular weight obtained for compound (2) (Table 1) supports a monomeric structure, rather than a dimer linked by carboxylate bridges. The mode of co-ordination of the carboxylate ligands is established from the i.r. spectra (Table 2). Robinson and Uttley,[4,5] from their analysis of a large number of carboxylate complexes of ruthenium, osmium, rhodium, and iridium, have concluded that the values of $\nu_{asym}(OCO)$ and [$\nu_{asym}(OCO) - \nu_{sym}(OCO)$ *i.e.* $\Delta\nu$] afford the most sensitive indication of the mode of co-ordination. The bands attributed to $\nu_{sym}(OCO)$ are frequently obscured by bands arising from other ligands such as PPh_3 or $AsPh_3$. Bidentate carboxylate ligands have values of $\nu_{asym}(OCO)$ (1 490—1 540 cm^{-1}) and $\nu_{sym}(OCO)$ (1 400—1 470 cm^{-1}) which are close to those in the free carboxylate ion. Unidentate carboxylate ligands have $\nu_{asym}(OCO)$ at substantially higher frequencies (1 580—1 650 cm^{-1}) and $\nu_{sym}(OCO)$ at the lower frequencies of 1 310—1 390 cm^{-1} resulting in larger values of $\Delta\nu$ of the order of 210—270 cm^{-1}.

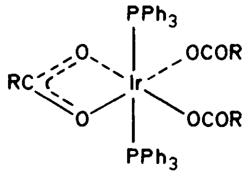
Using these criteria it can be seen from the spectroscopic data given in Table 2 that the complexes (1)—(7) possess one unidentate carboxylate ligand and one bidentate ligand giving a co-ordination number of six. The values of $\nu(Ir-Cl)$ for these complexes fall in the region of 316—330 cm^{-1}, which is more in the region of a chlorine *trans* to a carboxylate ligand rather than chlorine *trans* to a PPh_3 ligand which generally absorbs below 314 cm^{-1}.[6] In the i.r. spectrum of compound (5) the relative intensities of the bands at 1 585vw and 1 570w cm^{-1} suggest a *trans* arrangement for the triphenylphosphine ligands.[7] This region is masked in the i.r. spectra of the other complexes by absorptions of the aromatic carboxylate ligands. The observation of an apparent 1 : 2 : 1 triplet in the ^1H n.m.r. spectrum of compound (2) caused by strong virtual coupling of the two phosphine ligands also supports a *trans* arrangement.[8] This evidence is not entirely unambiguous as cases of strong virtual coupling of *cis* ^{31}P nuclei are known,[9] but when considered together with the i.r. spectroscopic evidence it indicates the stereochemistry (I). The bidentate carboxylate ligand in these complexes is strongly bound, and passage of carbon monoxide through dichloromethane solutions of both complexes (1) and (7) during 6 h failed to produce the compounds [$IrCl(O_2CC_6H_4Cl\text{-}3)_2(CO)(PPh_3)_2$] or [$IrCl(O_2CC_6H_4Cl\text{-}3)_2(CO)(AsPh_3)_2$] respectively.



(I)

As in the reactions with alkyl hydroperoxides [2] the behaviour of the iodo-complex *trans*-[$IrI(CO)(PPh_3)_2$] was anomalous. Solutions of the iodo-complex in toluene reacted with $3\text{-}ClC_6H_4CO_3H$ and $PhCO_3H$ at room temperature to give the tricarboxylate complexes (8) and

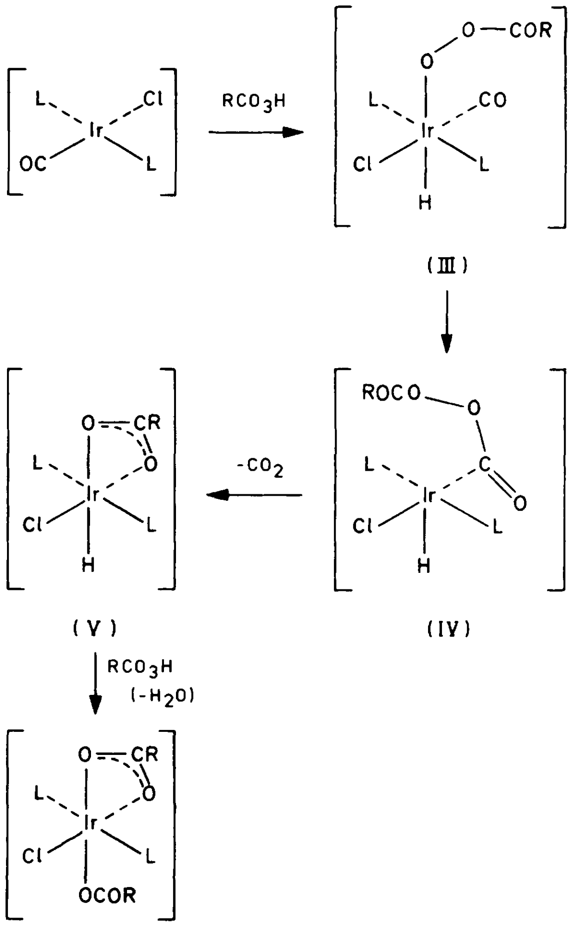
(9) respectively (Table 1) with liberation of iodine. Compound (8) has also been obtained in 51% yield by reaction between $[\mathrm{Ir(O_2CC_6H_4Cl\text{-}3)(CO)(PPh_3)_2}]$ and $\mathrm{3\text{-}ClC_6H_4CO_3H}$ in dichloromethane under similar conditions. To our knowledge compound (8) has not been described previously, but compound (9) has been reported[4] as the product of reaction of $[\mathrm{IrH(CO)(PPh_3)_3}]$ and benzoic acid. A difference of 20 °C in the melting point reported for this compound and that found in our work is attributed to the presence of 0.25 mol of dichloromethane in our sample. The i.r. spectra (Table 2) of these compounds indicate the presence of uni- and bidentate carboxylate ligands as suggested previously.[4,10] The most likely stereochemistry is therefore structure (II), but the *trans* arrangement of the phosphine ligands could not be confirmed.



(II)

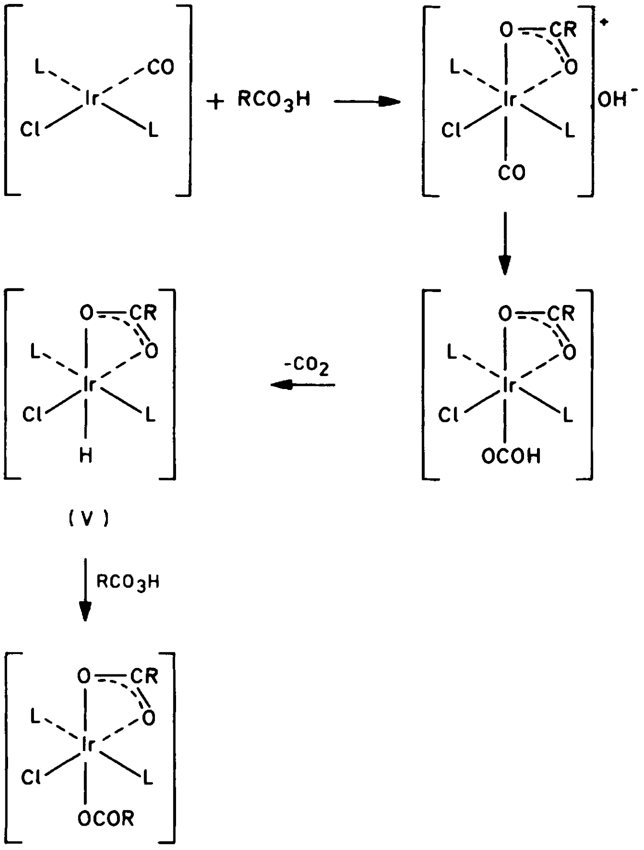
A careful examination of the reaction of *trans*-$[\mathrm{IrCl(CO)(PPh_3)_2}]$ and an excess of $\mathrm{3\text{-}ClC_6H_4CO_3H}$ in benzene has shown that on mixing the two reactants there is an immediate colour change from yellow to red-brown with evolution over a few seconds of *ca.* 1 mol of CO_2 per mol of iridium complex taken; there was no evidence of oxygen evolution. Water is also formed during the reaction, although it was not possible to estimate the amount produced accurately. One of the major reaction products is 3-chlorobenzoic acid, but this must be formed from unchanged peracid during the work-up procedure. It is doubtful that radical intermediates are involved in this reaction. There was no evidence for 1 : 1 copolymer formation expected for a radical process[11,12] when the reaction was carried out in the presence of a 1 : 1 mole ratio of styrene and methyl methacrylate. A similar conclusion was reached by Harvie and McQuillin[13] for the reaction of $\mathrm{3\text{-}ClC_6H_4CO_3H}$ with $[\mathrm{MCl(CH_2Ph)(PPh_3)_2}]$ (M = Pt or Pd), which gave $\mathrm{3\text{-}ClC_6H_4CO_2CH_2Ph}$, $\mathrm{PhCH_2OH}$, and $\mathrm{PPh_3O}$.

A more plausible mechanism is that shown in Scheme 1. The initial step involves oxidative addition of the peracid to the iridium(I) complex to give the intermediate (III). The concentration of this intermediate is likely to be extremely low as $[\mathrm{IrCl(CO)(PPh_3)_2}]$ is known to form stable adducts only with strong acids such as trifluoroacetic acid.[14] With benzoic acid adduct formation is reversible and is estimated to occur to the extent of only 0.02%;[15] peroxycarboxylic acids are approximately a thousand times weaker acids than the corresponding carboxylic acids.[16] Any mechanistic scheme must account for the rapid loss of CO_2, which in the case of the reactions of alkyl hydroperoxides[2,13] has been attributed to oxygen transfer from the peroxy-ligand to the carbonyl group. A possible mechanism for this oxygen transfer is 'insertion' of the carbonyl ligand into the Ir–O bond of the peroxycarboxylate ligand to give intermediate (IV), and hence (V) by loss of CO_2. There are now several reports of reactions which appear to involve CO 'insertion' into *O*-bonded ligands,[17,18] and it may prove to be quite general. If so, it is interesting that no such reaction was observed for the complex $[\mathrm{Ir(O_3CC_6H_4Cl\text{-}3)(CO)(PPh_3)_2}]$,[3] and it may be restricted to the more sterically constrained octahedral iridium(III) complexes as noted for CO 'insertion' into the $\mathrm{(CF_3)_2NO\text{-}Ir}$ bond.[17] An alternative mechanism involving nucleophilic attack of the iridium(I) complex on the peroxycarboxylic acid is shown in Scheme 2. There are many precedents for attack of hydroxide ion on a metal carbonyl ligand;[19,20] loss of CO_2 would give the same hydride intermediate (V), which could react with peroxycarboxylic acid with loss of water to give the isolated product. It is difficult to differentiate between these mechanisms. It might have been anticipated that any mechanism involving formation of OH^- would have resulted in polymerisation of methyl methacrylate during the reaction carried out in the presence of a 1 : 1 mixture of styrene and methyl methacrylate. However, in



SCHEME 1

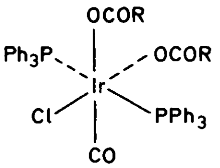
benzene the ionic intermediate would be a tight ion pair and the hydroxide ion may never be free of the coordination sphere of the metal atom. The anomalous behaviour of $[IrI(CO)(PPh_3)_2]$ can be explained by the sensitivity of the Ir–I bond to oxidation, as noted previously.[2]



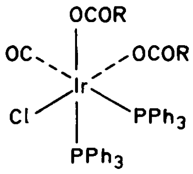
Scheme 2

Reactions of Diacyl Peroxides.—When an excess of dibenzoyl peroxide was added to a solution of $[IrCl(CO)(PPh_3)_2]$ in benzene at room temperature there was no gas evolution and complex (10) was isolated in 80% yield. Under similar conditions $(3\text{-}ClC_6H_4CO)_2O_2$ gave a 78% yield of compound (11). The i.r. spectra of these products show strong metal carbonyl stretching vibrations at 2 075 cm^{-1} [compound (10)] and 2 060 cm^{-1} [compound (11)], and bands in the region of 1 642—1 636 cm^{-1} [$\nu_{asym.}(OCO)$] and 1 361—1 326 cm^{-1} [$\nu_{sym.}(OCO)$] for unidentate carboxylate ligands.[4,5] The observed values of 327 [for (10)] and 323 cm^{-1} [for (11)] assigned to ν(Ir–Cl) are too high for Cl *trans* to CO or Cl *trans* to PPh_3,[6] and are more in the region expected for Cl *trans* to a carboxylate ligand. The most likely structure is (VI), but the alternative structure (VII) cannot be entirely discounted in the absence of evidence for the arrangement of the phosphine ligands.

Interestingly, when an excess of the unsymmetrical diacyl peroxide $PhC(O)OOC(O)CH_3$ was caused to react with $[IrCl(CO)(PPh_3)_2]$ under similar conditions it gave compound (10) in 66% yield, rather than $[IrCl(O_2CPh)(O_2CMe)(CO)(PPh_3)_2]$. The iodo-complex $[IrI(CO)(PPh_3)_2]$ is oxidised by dibenzoyl peroxide to give a mixture of $[IrI_3(CO)(PPh_3)_2]$ and $[Ir(O_2CPh)_3(PPh_3)_2]$, while the dinitrogen complex $[IrCl(N_2)(PPh_3)_2]$ reacts at room temperature to give compound (6) with evolution of nitrogen. Under similar conditions diacetyl peroxide and di(3-chlorobenzoyl) peroxide afford (5) and (1) respectively.



(VI)



(VII)

R = aryl

We have confirmed a previous report[21] that $[Pt(PPh_3)_4]$ reacts with dibenzoyl peroxide at room temperature to give *cis*-$[Pt(O_2CPh)_2(PPh_3)_2]$ (12), and we have shown that under similar conditions the complexes $[Pd(PPh_3)_4]$ and $[Pd(Ph_2PCH_2CH_2PPh_2)_2]$ also react with dibenzoyl peroxide to give (13) (*cis* and *trans* isomers) and (14) respectively. The compounds $[Pt\{P(OEt)_3\}_4]$ and $[Pd_2(PhCH{=}CHCOCH{=}CHPh)_3]$ failed to react under these conditions. With an excess of acetyl benzoyl peroxide the platinum complex $[Pt(PPh_3)_4]$ reacts at room temperature to give (12) in 73% yield, and there was no evidence for any other platinum complex.

Reactions of t-Butyl Peroxybenzoate and Di-t-butyl Peroxide.—There was no reaction between $[IrCl(CO)(PPh_3)_2]$ and $Bu^tO_2C(O)Ph$ at room temperature, but both $[Pt(PPh_3)_4]$ and $[Pd(Ph_2PCH_2CH_2PPh_2)_2]$ reacted with the peroxy-ester in benzene under these conditions to give (12) in 62% yield and (14) in 61% yield respectively. A detailed study of the product mixture from the reaction of the platinum complex showed the presence of PPh_3, PPh_3O, Bu^tOH, and a trace of acetone. When this reaction, carried out in $CDCl_3$ solution, was monitored by ^1H n.m.r. spectroscopy, 4 min after mixing the reagents there was a small signal for Bu^tOH which remained throughout the reaction. In addition there was a small signal at δ 2.95 which increased in intensity over the first 4—6 min before decreasing rapidly and finally disappearing. This may be due to the transient formation of an intermediate $[Pt(OBu^t)(O_2CPh)(PPh_3)_2]$, but the evidence is not conclusive. A repeat of this reaction in an e.s.r. tube containing the spin-trapping agent Bu^tNO gave no e.s.r. signal. Similarly, there was no evidence for the formation of trityl radicals when the reaction was carried out in the presence of triphenylmethane.

Dialkyl peroxides normally only react with low-valent transition-metal complexes under forcing conditions. For example, the reaction of $[Ni(C_2H_4)(PPh_3)_2]$ with $Bu^tO_2Bu^t$ to give $[Ni(OBu^t)_2]$ is reported to require a temperature of 110 °C over 5 h.[22] Formation of $[Cr(OBu^t)_4]$ from dibenzenechromium and $Bu^tO_2Bu^t$ requires 20 h at 90 °C.[23] We now report that $[Pt(PPh_3)_4]$ reacts with $Bu^tO_2Bu^t$ even at room temperature to give an unstable product believed to be $[Pt(OBu^t)_2(PPh_3)_2]$. The compound could not be isolated pure and is characterised from i.r. bands at 1 270 and 1 310 cm^{-1} typical of a Bu^t group, and two singlets at 7.27 and 2.73 p.p.m. in the ^1H n.m.r. spectrum in the expected ratio of 15 : 9. Gas–liquid chromatography of the product mixture also showed the presence of PPh_3 and PPh_3O.

One striking observation from these reactions of peroxy-compounds is that $[IrCl(CO)(PPh_3)_2]$ reacts at room temperature with alkyl hydroperoxides, peroxycarboxylic acids, and diacyl peroxides, but does not react under these conditions with the peroxy-ester $Bu^tO_2C(O)Ph$, and even under forcing conditions it fails to react with the dialkyl peroxide $Bu^tO_2Bu^t$.[2] This order of reactivity $Bu^tO_2Bu^t \leqslant Bu^tO_2C(O)Ph < RO_2H, RCO_3H, (RCO)_2O_2$ is in reasonable agreement with the order of ease of reduction $RO_2R < R^1C(O)O_2R^2 < RO_2H < (RCO)_2O_2 < RCO_3H$ established by measurement of half-wave potentials.[24] There is less satisfactory agreement with the reported order of O–O bond-dissociation energies $RO_2H > RO_2R > R^1C(O)O_2R^2 > (RCO)_2O_2 > RCO_3H$.[25] The electron density at the iridium(I) atom appears to have a significant effect on the reactivity. So, for example, the ionic iridium(I) complex $[Ir(MeCN)(CO)(PPh_3)_2]ClO_4$ and the rhodium analogue do not react with dibenzoyl peroxide at room temperature. To some extent the effect of the positive charge may be offset by increasing electron donation from the ligands, since $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$ catalyses the decomposition of Bu^tO_2H, although we have not studied the reaction of this complex with dibenzoyl peroxide. This trend of increasing reactivity with increasing electron density on the metal atom is also apparent from the reactions of the platinum(0) and palladium(0) complexes.

EXPERIMENTAL

3-Chloroperoxybenzoic acid, dibenzoyl peroxide, and di-t-butyl peroxide were commercial samples purified by standard procedures. Peroxyacetic acid,[26] peroxybenzoic acid,[27] di(3-chlorobenzoyl) peroxide,[16] acetyl benzoyl peroxide,[28] and t-butyl peroxybenzoate [29] were prepared by literature methods. Infrared spectra were recorded on a Perkin-Elmer model 621 spectrophotometer, ^1H n.m.r. spectra on a Varian HA 100 instrument. All reactions were carried out in an atmosphere of dry nitrogen and solvents were dried and deaerated before use.

Reaction of trans-$[IrCl(CO)(PPh_3)_2]$.—(a) *With peroxy-acids*. In a typical procedure 3-chloroperoxybenzoic acid (1.5 g, 8.72 mmol) was added with rapid stirring to a solution of $[IrCl(CO)(PPh_3)_2]$ (1.0 g, 1.28 mmol) in benzene (40 cm^3) at room temperature causing an immediate colour change from yellow to red-brown. After 0.5 h removal of the solvent and chromatography of the residue (Florisil, CH_2Cl_2 eluant) gave pink crystals of *chlorobis(3-chlorobenzoato)bis(triphenylphosphine)iridium*(III)*–dichloromethane* (4/1), (1) (0.85 g, 0.78 mmol, 61%). A grey-blue residue remained on the column.

When benzene (30 cm^3) was condensed under vacuum on to a mixture of 3-chloroperoxybenzoic acid (0.73 g, 4.23 mmol) and $[IrCl(CO)(PPh_3)_2]$ (0.5 g, 0.65 mmol) held in a tapped ampoule connected to a vacuum line there was an immediate colour change and evolution of carbon dioxide (0.52 mmol, 80%) as the benzene solvent melted on warming from −196 °C to room temperature. The mixture was stirred for a further 30 min before removal, and collection, of the solvent under vacuum. The residue was taken up in dichloromethane leaving 3-chlorobenzoic acid (0.66 g, 3.8 mmol), and the extract was chromatographed to give (1) (0.4 g, 0.38 mmol, 58%). An i.r. spectrum of the recovered solvent showed the presence of water, but attempted analysis using the Karl Fischer procedure did not give a reliable result.

Using a similar procedure the following were prepared: *chlorobis(3-chlorobenzoato)bis(methyldiphenylphosphine)iridium*(III) (2) as light yellow crystals (59%); *chlorobis(3-chlorobenzoato)bis(triphenylarsine)iridium*(III) (3) as yellow crystals (64%); *bromobis(3-chlorobenzoato)bis(triphenylphosphine)iridium*(III) (4) as pink crystals (43%); *bis(acetato)chlorobis(triphenylphosphine)iridium*(III) (5) as pink crystals (36%); *bis(benzoato)chlorobis(triphenylphosphine)iridium*(III) (6) as pink crystals (58%); *bis(benzoato)chlorobis(triphenylarsine)iridium*(III)*–dichloromethane* (4/3), (7), as yellow crystals (71%).

(b) *With di(3-chlorobenzoyl) peroxide*.—A solution of the peroxide (0.81 g, 2.6 mmol) in benzene (25 cm^3) was added to the iridium complex (1.0 g, 1.28 mmol) in benzene (70 cm^3) and the mixture was stirred at room temperature for 1.5 h. The volume of the solution was reduced and methanol was added to precipitate *carbonylchlorodi(3-chlorobenzoato)bis(triphenylphosphine)iridium*(III)*–dichloromethane* (20/13), (11) (1.15 g, 1.0 mmol, 78%), as light yellow crystals, m.p. 148—152 °C, recrystallised from a mixture of dichloromethane and methanol (1 : 1 v/v).

(c) *With dibenzoyl peroxide*. Using a similar procedure, reaction between dibenzoyl peroxide (0.80 g, 3.30 mmol) and the iridium complex (0.40 g, 0.51 mmol) gave *dibenzoato(carbonyl)chlorobis(triphenylphosphine)iridium*(III) (10) (0.42 g, 0.41 mmol, 80%) as a white solid, m.p. 154 °C, recrystallised from dichloromethane–methanol (1 : 1 v/v).

(d) *With acetyl benzoyl peroxide*. Reaction between acetyl benzoyl peroxide (0.69 g, 3.83 mmol) and the iridium complex (2.0 g, 2.56 mmol) gave dibenzoato(carbonyl)chlorobis(triphenylphosphine)iridium(III)–dichloromethane (10/7) (1.83 g, 1.84 mmol, 66%).

Reactions of $[IrI(CO)(PPh_3)_2]$.—(a) *With 3-chloroperoxybenzoic acid*. Addition of 3-chloroperoxybenzoic acid (1.5 g, 8.72 mmol) to $[IrI(CO)(PPh_3)_2]$ (1.0 g, 1.14 mmol) in toluene (40 cm^3) at room temperature gave a deep red solution, which after 0.5 h was chromatographed (Florisil, hexane eluant, then CH_2Cl_2) to give light yellow crystals of *tris(3-chlorobenzoato)bis(triphenylphosphine)iridium*(III) (8) (0.75 g, 0.63 mmol, 55%). A fawn yellow solid remained on the column.

(b) *With peroxybenzoic acid*. Using a similar procedure peroxybenzoic acid gave *tris(benzoato)bis(triphenylphosphine)iridium*(III)*–dichloromethane* (4/1) (9) (51%), as yellow crystals, m.p. 208—210 °C (lit.,[4] 186—187 °C).

(c) *With dibenzoyl peroxide*. A solution of dibenzoyl peroxide (0.43 g, 1.77 mmol) in benzene (20 cm^3) added to $[IrI(CO)(PPh_3)_2]$ (1.03 g, 1.18 mmol) in the same solvent at room temperature gave an orange solution. After 1 h the volume of the solution was reduced to 25 cm^3 and methanol added to give [$IrI_3(CO)(PPh_3)_2$] (0.32 g, 0.28 mmol, 24%). Reduction of the filtrate to 15 cm^3 and addition of light petroleum (b.p. 40—60 °C) gave [$Ir(O_2CPh)_3(PPh_3)_2$] (0.7 g, 0.65 mmol, 55%). Both compounds were identified by comparison of their i.r. spectra with those of authentic samples.

Reaction of [$Ir(O_2CC_6H_4Cl\text{-}3)(CO)(PPh_3)_2$] *with 3-Chloroperoxybenzoic acid.*—A solution of 3-chloroperoxybenzoic acid (0.52 g, 3.0 mmol) in dichloromethane (10 cm^3) was added to [$Ir(O_2CC_6H_4Cl\text{-}3)(CO)(PPh_3)_2$]$\cdot 0.6CH_2Cl_2$ (0.88 g, 0.93 mmol) in dichloromethane (15 cm^3) at room temperature gave a dark green solution. Chromatography after 20 min gave tris(3-chlorobenzoato)bis(triphenylphosphine)-iridium(III) (0.56 g, 0.47 mmol, 51%).

Reactions of [$IrCl(N_2)(PPh_3)_2$].—(a) *With dibenzoyl peroxide.* Addition of a solution of dibenzoyl peroxide (0.27 g, 1.1 mmol) in benzene (10 cm^3) to the iridium complex (0.61 g, 0.79 mmol) in benzene (15 cm^3) at room temperature gave a deep red solution with gas evolution. After 20 min, evaporation of most of the solvent and addition of methanol gave dibenzoatochlorobis(triphenylphosphine)iridium(III) (0.52 g, 0.52 mmol, 66%), identified by comparison of its i.r. and ^{1}H n.m.r. spectrum with that of an authentic sample.

(b) *With diacetyl peroxide.* Using a similar procedure, addition of diacetyl peroxide (1.42 g, 3.0 mmol) and the iridium complex (0.78 g, 1.0 mmol) gave pink crystals of diacetatochlorobis(triphenylphosphine)iridium(III) (0.48 g, 0.55 mmol, 55%).

(c) *With di(3-chlorobenzoyl) peroxide.* Reaction between the iridium complex (0.64 g, 0.82 mmol) and di(3-chlorobenzoyl) peroxide (0.37 g, 1.2 mmol) in benzene at room temperature gave pink crystals of chlorodi(3-chlorobenzoato)-bis(triphenylphosphine)iridium(III) (0.64 g, 0.6 mmol, 73%).

Reactions of [$Pt(PPh_3)_4$].—(a) *With acetyl benzoyl peroxide.* A solution of the peroxide (0.9 g, 5.0 mmol) in benzene (10 cm^3) was added to a solution of [$Pt(PPh_3)_4$] (3.1 g, 2.48 mmol) in the same solvent (50 cm^3) at room temperature causing an immediate colour change from deep yellow to pale green. After 30 min the volume of the solvent was reduced, and light petroleum (b.p. 40—60 °C) added to precipitate white crystals of *cis*-dibenzoatobis(triphenylphosphine)platinum(II) (1.7 g, 1.81 mmol, 73%), which were recrystallised from a mixture of dichloromethane and light petroleum (b.p. 40—60 °C; 1 : 1 v/v) and dried under vacuum (Found: C, 62.0; H, 4.7; P, 6.4. Calc. for $C_{50}H_{40}O_4P_2Pt$: C, 62.4; H, 4.2; P, 6.4%).

(b) *With t-butyl peroxybenzoate.* When t-butyl peroxybenzoate (0.58 g, 2.6 mmol) in dichloromethane (10 cm^3) was added with stirring to the platinum complex (1.2 g, 0.96 mmol) in the same solvent (50 cm^3) the yellow solution turned colourless, and *cis*-dibenzoatobis(triphenylphosphine)platinum(II) (0.60 g, 0.64 mmol, 66%) was isolated by precipitation with methanol.

(c) *With di-t-butyl peroxide.* Addition of a dichloromethane solution of di-t-butyl peroxide (0.43 g 2.9 mmol) to a solution of the platinum complex (1.2 g, 1.05 mmol) in the same solvent at room temperature gave a pale orange solution. Reduction of the volume of the solution under vacuum and addition of methanol gave a pale orange solid (0.5 g) thought to be *cis*-di-t-butoxobis(triphenylphosphine)-platinum(II)–dichloromethane (2/1) on the basis of i.r. and ^{1}H n.m.r. spectroscopy. This solid was unstable at room temperature and the elemental analysis results were poor (Found: C, 58.6; H, 4.3; P, 8.7. Calc. for $C_{44}H_{48}O_2P_2Pt\cdot 0.5CH_2Cl_2$: C, 58.8; H, 5.4; P, 6.85%).

Reaction of [$Pd(PPh_3)_4$] *with Dibenzoyl Peroxide.*—When a solution of dibenzoyl peroxide (0.72 g, 2.63 mmol) in dichloromethane (10 cm^3) was added to a solution of the palladium complex (1.15 g, 1.0 mmol) in the same solvent at room temperature the yellow solution turned light green. After 45 min the volume of the solution was reduced and addition of methanol gave white crystals of *dibenzoatobis(triphenylphosphine)palladium*(II) (13) (0.55 g, 0.63 mmol, 63%).

Reaction of [$Pd(Ph_2PCH_2CH_2PPh_2)_2$].—(a) *With dibenzoyl peroxide.* Addition of dibenzoyl peroxide (0.72 g, 2.63 mmol) to the palladium complex (0.90 g, 1.0 mmol) in dichloromethane (60 cm^3) at room temperature, followed after 1 h by removal of most of the solvent and addition of methanol, gave white crystals of *dibenzoato[1,2-bis(diphenylphosphino)ethane]palladium*(II) (14) (0.48 g, 0.65 mmol, 65%).

(b) *With t-butyl peroxybenzoate.* Under similar conditions reaction between the palladium complex (0.90 g, 1.0 mmol) and t-butyl peroxybenzoate (0.58 g, 2.6 mmol) in dichloromethane gave complex (14) (0.45 g, 0.61 mmol, 61%).

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