# Reactions Involving Transition Metals. Part 13.[1,†] Reaction of Hydroperoxides with Complexes of the Type *trans*-$[IrX(CO)L_2]$ (X = Halogen, L = Phosphine or Arsine)

By **Brian L. Booth,* Robert N. Haszeldine,** and **Geoffrey R. H. Neuss,** Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Bis(alkylperoxy)iridium(III) complexes $[IrX(O_2Bu^t)_2(CO)L_2]$ (X = Cl, L = $PPh_3$, $AsPh_3$, or $PPh_2Me$; X = Br, L = $PPh_3$ or $AsPh_3$) and $[IrX(O_2CPhMe_2)_2(CO)L_2]$ (X = Cl, L = $PPh_3$ or $AsPh_3$; X = Br, L = $PPh_3$) have been isolated from the reactions of $Bu^tO_2H$ or $PhMe_2CO_2H$ with the respective *trans*-$[IrX(CO)L_2]$ complexes. The similar reactions of $Bu^tO_2H$ and $PhMe_2CO_2H$ with *trans*-$[IrI(CO)(PPh_3)_2]$ yield $[IrI_2(O_2R)(CO)(PPh_3)_2]$ (R = $Bu^t$ or $PhMe_2$). The bis(t-butylperoxy)iridium(III) complexes do not themselves catalyse the decomposition of hydroperoxides, polymerisation of styrene, or auto-oxidation of alkenes, but in certain solvents, particularly benzene, a light-induced decomposition reaction occurs to generate radical species which can initiate such reactions.

AUTO-OXIDATION reactions of alkenes catalysed by homogeneous $d^8$ and $d^{10}$ transition-metal complexes have aroused a great deal of interest in recent years. There is still considerable doubt as to the mechanism, or, more probably, mechanisms, of these reactions. There is some evidence, certainly for $Rh^I$ complexes, that activation of molecular oxygen is a prerequisite for auto-oxidation,[2-7] while in many reactions the transition-metal complex appears to initiate a free-radical auto-oxidation process by catalysing the homolysis of traces of hydroperoxides present in the unsaturated hydrocarbons.[8-11] In an attempt to gain more insight into the importance of hydroperoxides, and other peroxides, in such oxidation reactions and the nature of their interaction with low-valent transition-metal complexes we have investigated some reactions of peroxides with $Rh^I$ and $Ir^I$ complexes. In this paper full details of the reactions of t-butyl and cumyl ($\alpha,\alpha$-dimethylbenzyl) hydroperoxides with the iridium(I) complexes *trans*-$[IrX(CO)L_2]$ (X = Cl, Br, or I; L = $PPh_3$, $AsPh_3$, or $PPh_2Me$) are presented together with some previously unpublished information about these and related reactions.

## RESULTS

Addition of an approximate six-fold excess of $Bu^tO_2H$ to solutions of the complexes *trans*-$[IrX(CO)L_2]$ (X = Cl, L = $PPh_3$, $PPh_2Me$, or $AsPh_3$; X = Br, L = $PPh_3$ or $AsPh_3$) in toluene at room temperature under nitrogen caused an immediate colour change from yellow to deep blue-green, and after stirring for 30 min chromatographic separation of the mixture gave the bis(t-butylperoxy)iridium(III) complexes (1)—(5) (see Table 1) as crystalline yellow solids. In each case a blue or blue-green amorphous solid was also obtained. The crystals of complex (1) from toluene could not be obtained free from solvent, but a solvent-free sample was prepared by repeating the reaction in bezene or dichloromethane, although the yield was lower. When this same reaction was attempted in tetrahydrofuran (thf) only starting materials were recovered after 2 h at room temperature and there was no colour change. This solvent possibly co-ordinates to the vacant site on the iridium(I) complex preventing any interaction with the hydroperoxide.[12] The low yield of the diphenylmethylphosphine complex (3) stems in part from the higher solubility in organic solvents, and also from the increased susceptibility of the phosphine ligand to oxidation. This complex could only be characterised from spectroscopic data. For similar reasons the reaction between $[IrCl(CO)(PPhMe_2)_2]$ and $Bu^tO_2H$ in toluene gave only a trace of a yellow oil [$\nu$(CO) 2 050 $cm^{-1}$], which may be the expected product, $[IrCl(O_2Bu^t)_2(CO)(PPhMe_2)_2]$.

Addition of an excess of cumyl hydroperoxide to solutions of *trans*-$[IrX(CO)L_2]$ (X = Cl or Br, L = $PPh_3$; X = Cl, L = $AsPh_3$) in toluene at room temperature gave deep green solutions from which the yellow bis(cumylperoxy)iridium(III) complexes (6)—(8) (see Table 1) were isolated by chromatography. Other products from these reactions included 2-phenylpropan-2-ol, acetophenone, the phosphine or arsine oxide, and green, amorphous chloro(phosphine)iridium complexes.

The bis(alkylperoxy)iridium(III) complexes (1)—(8) all show a strong, single metal–carbonyl stretching vibration in the region 2 035—2 043 $cm^{-1}$ of the i.r. spectrum, indicative of an iridium(III) complex (see Table 2). In addition, there is a band of weak-medium intensity either in the region 881—889 $cm^{-1}$ (t-butylperoxy complexes) or 870—871 $cm^{-1}$ (cumylperoxy complexes) attributable to $\nu$(O–O). This compares favourably with the weak band in the region 850—950 $cm^{-1}$ observed in the spectra of cobaloxime complexes of the type $[Co(O_2R)(Hdmg)_2L]$ ($H_2dmg$ = dimethylglyoxime, L = $H_2O$ or pyridine).[13] The chloro-complexes also show a band of medium intensity at 303—304 $cm^{-1}$ [$\nu$(Ir–Cl)], which is absent from spectra of the bromo-complexes. The $^1H$ n.m.r. spectra (Table 2) of the t-butylperoxy complexes (1)—(5) show two sharp singlets in the region $\delta$ 0.7—0.92 implying that the two $Bu^tO_2$ ligands are mutually *cis*. Two methyl signals for non-equivalent cumyl groups are also observed in the spectra of the complexes (6)—(8) but the chemical shift difference is smaller, and in the spectrum of compound (6) these could not be resolved. The 'virtual coupling' of the two $^{31}P$ nuclei observed in the spectrum of complex (3) may imply [14] that the two phosphine ligands are *trans* in this complex. This evidence must be treated with some caution as cases of strong P–P coupling between *cis* phosphine ligands are known.[15-18] Further circumstantial evidence for a *trans* arrangement comes from the relative intensities of the two

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† Preliminary communication, B. L. Booth, R. N. Haszeldine, and G. R. H. Neuss, *J. Chem. Soc., Chem. Commun.*, 1972, 1074.

TABLE 1

Physical and analytical data for the (alkylperoxy)iridium(III) complexes

| Complex | M.p. [a]/°C | Analysis [b] (%) C | H | P | Halogen |
|---|---|---|---|---|---|
| $[IrCl(O_2Bu^t)_2(CO)(PPh_3)_2]$ (1) | 110 | 56.3(56.4) | 4.9(5.0) | | |
| $[IrBr(O_2Bu^t)_2(CO)(PPh_3)_2]$ (2) | 131—134 | 53.9(53.9) | 4.8(4.8) | 6.10(6.20) | 8.05(7.95) |
| $[IrCl(O_2Bu^t)_2(CO)(PPh_2Me)_2]$ (3) | 140—141 | | | | |
| $[IrCl(O_2Bu^t)_2(CO)(AsPh_3)_2]$ (4) | 141—144 | 52.0(51.7) | 4.6(4.6) | | 3.5(3.4) |
| $[IrBr(O_2Bu^t)_2(CO)(AsPh_3)_2]$ (5) | 146 | 49.5(49.5) | 4.7(4.4) | | |
| $[IrCl(O_2CMe_2Ph)_2(CO)(PPh_3)_2]$ (6) | 108—112 | 60.7(61.0) | 4.8(4.8) | | |
| $[IrBr(O_2CMe_2Ph)_2(CO)(PPh_3)_2]$ (7) | 125—127 | 58.3(58.6) | 4.7(4.7) | | |
| $[IrCl(O_2CMe_2Ph)_2(CO)(AsPh_3)_2]$ (8) | 106—110 | 55.7(56.4) | 4.2(4.5) | | 3.8(3.0) |
| $[IrI_2(O_2Bu^t)(CO)(PPh_3)_2]$ (9) | 134 | 45.6(45.3) | 3.9(3.6) | 5.60(5.70) | 23.15(23.35) |
| $[IrI_2(O_2CMe_2Ph)(CO)(PPh_3)_2]$ (10) | | 51.6(48.2) | 4.3(3.6) | | |

[a] With decomposition. [b] Calculated values are given in parentheses.

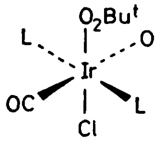
TABLE 2

Spectroscopic data for the (alkylperoxy)iridium(III) complexes

| Complex | I.r. spectrum [a]/cm$^{-1}$ $\nu$(CO) [b] | $\nu$(Ir–Cl) | $\nu$(O–O) | $^1$H N.m.r. [c] $\delta$/p.p.m. |
|---|---|---|---|---|
| (1) | 2 043 | 303 | 889 | 8.00 (m, 12), 7.35 (m, 18), 0.85 (s, 9), 0.70 (s, 9) |
| (2) | 2 038 | | 881 | 7.93 (m, 12), 7.37 (m, 18), 0.92 (s, 9), 0.71 (s, 9) |
| (3) | 2 040 | 318 | *d* | 7.70 (m, 8), 7.33 (m, 12), 2.19 (t, $J$ = 4.35 Hz,[e] 6), 1.09 (s, 9), 0.83 (s, 9) |
| (4) | 2 035 | 304 | 888 | 7.88 (m, 12), 7.35 (m, 18), 0.85 (s, 9), 0.75 (s, 9) |
| (5) | 2 038 | | 882 | 7.88 (m, 12), 7.38 (m, 18), 0.90 (s, 9), 0.76 (s, 9) |
| (6) | 2 043 | 303 | 870 | 7.80 (m, 12), 7.24 (m, 28), 1.11 (s, 12) |
| (7) | 2 043 | | 871 | 7.8 (m, 12), 7.22 (m, 28), 1.17 (s, 6), 1.14 (s, 6) |
| (8) | 2 035 | 302 | 871 | 7.72 (m, 12), 7.32 (m, 28), 1.03 (s, 6), 1.00 (s, 6) |
| (9) | 2 054 | | 876 | 8.07 (m, 12), 7.28 (m, 23), 1.29 (s, 9) |
| (10) | 2 040 | | 872 | 7.99 (m, 12), 7.35 (m, 23), 1.60 (s, 6) |

[a] Recorded as Nujol mulls. [b] Separately recorded on solutions in $CH_2Cl_2$ with 10 times expansion. [c] $CCl_4$ solutions with $SiMe_4$ internal reference, s = singlet, m = multiplet, t = triplet; relative intensities are given in parentheses. [d] Band due to $\nu$(O–O) obscured by a strong band at 888 cm$^{-1}$ attributed to the phosphine ligand. [e] Measured apparent coupling constant for the $X_6AA'X'_6$ pattern.

bands at 1 585vw and 1 568w cm$^{-1}$ in the i.r. spectra of complexes (1) and (2) due to the C–C skeletal modes of the phosphine ligands. Empirical observations [19] indicate that the relative intensities of these two bands would be reversed for a *cis* arrangement. Problems of crystal twinning have prevented all attempts * to establish the structure of complexes (2) and (7) by *X*-ray crystallography. The available spectroscopic data indicate that complex (3) probably has $C_s$ symmetry and the structure (I). The close similarity between the spectra of complex (3) and those of the other bis(alkylperoxy)iridium(III) complexes suggests that these also have a similar structure.



(I)

In each of the reactions leading to the complexes (1)—(8) the major products were blue-green, amorphous solids formed together with the corresponding phosphine or arsine oxide. In the majority of reactions these solids were not isolated but they remained on the chromatography column. The solids from the reactions of $[IrCl(CO)L_2]$ (L = $PPh_3$, $PPhMe_2$, and $PPh_2Me$) with $Bu^tO_2H$ were isolated, and were found to be partially soluble in toluene, $CHCl_3$, and $CH_2Cl_2$. Their i.r. spectra showed only broad, poorly resolved bands, and there was no evidence for a t-butyl or cumyl residue, a metal carbonyl absorption, or $\nu$(O–O) vibration. The spectrum of the triphenylphosphine complex showed a broad band of medium intensity at 320 cm$^{-1}$ possibly indicative of an Ir–Cl bond. The $^1$H n.m.r. spectrum for the product from $[IrCl(CO)(PPh_3)_2]$ showed only a singlet at $\delta$ 7.30 for $PPh_3$ ligands. The elemental analysis (C and H) for this complex did not fit any simple ratio of Ir : $PPh_3$ : Cl : O, although the Ir : $PPh_3$ : Cl ratio of approximately 1 : 1 : 1 reported by Harvie and McQuillin [20] is not unreasonable. The $^1$H n.m.r. spectra of the blue-green solids from the reactions of the methyldiphenylphosphine and dimethylphenylphosphine complexes showed only broad resonances at $\delta$ 7.30 and $\delta$ 1.0—2.0 ($PPhMe_2$), and $\delta$ 7.30 and $\delta$ 1.2—2.1 ($PPh_2Me$) in approximately the expected ratios for phenyl : methyl protons. We have been unable to characterise fully these blue-green solids, and can only speculate that they are possibly dimeric or polymeric iridium oxide complexes $[\{Ir(O)Cl(PPh_3)\}_n]$, or perhaps, (phosphine oxide)iridium complexes. It is interesting that an oxide complex reported to be $[\{Rh(O)Cl(PPh_3)(OH_2)\}_2]$ has been isolated during the auto-oxidation of ethylbenzene by $[RhCl(PPh_3)_3]$.[21]

It was expected that the iodo-complex *trans*-$[IrI(CO)(PPh_3)_2]$ would react with t-butyl and cumyl hydroperoxide to give similar bis(alkylperoxy)iridium(III) complexes. Instead, addition of an excess of $Bu^tO_2H$ caused formation of the complex $[IrI_2(O_2Bu^t)(CO)(PPh_3)_2]$ (9) (see Table 1) isolated as a red, crystalline solid, together with a blue-green

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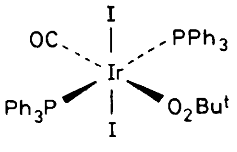
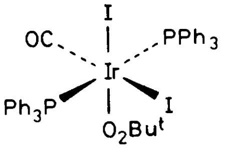
* We record our grateful thanks to Professor J. A. Ibers and Dr. R. Kirschner for their efforts to obtain satisfactory crystallographic data.

residue which remained on the column after chromatography. An analogous product (10) was obtained from the reaction with cumyl hydroperoxide, although this could not be obtained analytically pure. The i.r. and $^1H$ n.m.r. spectra (Table 2) of these mono(alkylperoxy)iridium(III) complexes are fully consistent with the assigned molecular formulae. The relative intensities of the two i.r. absorptions at 1 582vw and 1 568w cm$^{-1}$ in the spectrum of complex (9) suggest that the two phosphine ligands are *trans*,[19] and it has either structure (II) or (III).



(II)



(III)

Attempts to extend these reactions of hydroperoxides to other iridium(I) complexes have met with little success. Addition of $Bu^tO_2H$ to a toluene solution of [Ir(dppe)$_2$]Cl at room temperature caused complete decomposition to a turquoise solid, which gave only a poorly resolved i.r. spectrum having no bands due to $Bu^tO_2^-$ or CO ligands [dppe = 1,2-bis(diphenylphosphino)ethane]. Under analogous conditions, reaction between an excess of $Bu^tO_2H$ and [IrH(CO)(PPh$_3$)$_3$] caused immediate formation of a deep blue solution from which a blue, amorphous solid was isolated. The i.r. spectrum of this solid showed only the presence of phosphine ligands; there was no evidence for metal–hydride, –carbonyl, or –$O_2Bu^t$ moieties. This reaction appears to be similar to that reported to occur on progressive addition of $Bu^tO_2H$ to [RhH(CO)(PPh$_3$)$_3$] in benzene, which resulted in loss of the hydride and carbonyl ligands, and formation of $PPh_3O$.[22] Addition of $Bu^tO_2H$ to the dihydridoiridium(III) complex [IrH$_2$Cl(CO)(PPh$_3$)$_2$] in benzene gave, after an induction period of 5 min, an exothermic reaction with the formation of [IrCl(O$_2$Bu$^t$)$_2$(CO)(PPh$_3$)$_2$] (13%) and a blue-green solid. This reaction undoubtedly results from the reversible formation of [IrCl(CO)(PPh$_3$)$_2$] on dissolving the dihydrido-complex in benzene. The monohydridoiridium(III) complex [IrHCl$_2$(CO)(PPh$_3$)$_2$], which does not dissociate in benzene, failed to react with $Bu^tO_2H$ after 1 week at room temperature.

All the mono- and bis-(alkylperoxy)iridium(III) complexes (1)—(10) are soluble in benzene, toluene, thf, dichloromethane, and chloroform. They are also slightly soluble in carbon tetrachloride, diethyl ether, and acetone, but insoluble in n-hexane and methanol. In the solid state these compounds are stable in air for several weeks, but solutions in toluene, chloroform, dichloromethane, and thf gradually darken over several days. Solutions in benzene are particularly sensitive even in the absence of air. A benzene solution of complex (1) sealed under vacuum in an n.m.r. tube but left in diffuse daylight soon turned green, and after 24 h had undergone substantial decomposition, without gas evolution, to product $Bu^tOH$ and an amorphous, green solid. The latter had a similar i.r. spectrum to that of the blue-green solid obtained from the reaction between $Bu^tO_2H$ and [IrCl(CO)(PPh$_3$)$_2$] except for a broad ν(CO) band at 2 030 cm$^{-1}$ which does not correspond to that of either [IrCl(CO)(PPh$_3$)$_2$] or [IrCl(O$_2$)(CO)(PPh$_3$)$_2$]. This reaction appears to be initiated by light as a benzene solution sealed under vacuum, but kept in the dark, showed no signs of decomposition even after 1 week at room temperature. It seems reasonable to suppose that the initial step in this decomposition is homolysis of the O–O bond of the peroxy ligands to form t-butoxyl radicals, which abstract hydrogen atoms from the triphenylphosphine ligands or, perhaps less likely, from the benzene solvent. Support for this breakdown pathway comes from the observation that in benzene the bis(t-butylperoxy)iridium(III) complexes can be used to initiate radical reactions. So, for example, although addition of a large excess of $Bu^tO_2H$ to crystals of complex (1) does not cause decomposition of the hydroperoxide, when the same reaction is carried out in benzene the solution turns green after a few minutes and slow evolution of oxygen is observed. Decomposition of the hydroperoxide is complete after 2 h to give a total yield of oxygen of 84%. Similarly, a solution of a catalytic quantity of complex (2) in a large excess of styrene stored under nitrogen, but exposed to diffuse daylight, gradually turned green at room temperature with the formation of polystyrene. The rate of polymerisation is slightly faster than that observed on stirring together a catalytic amount of [IrCl(CO)(PPh$_3$)$_2$] (0.13 mmol) and $Bu^tO_2H$ (*ca.* 7.8 mmol) with a large excess of styrene under similar conditions. Polymer formation did not take place in control experiments carried out with styrene in the presence of either [IrCl(CO)(PPh$_3$)$_2$] or $Bu^tO_2H$ separately.

When styrene was stirred with catalytic amounts of $Bu^tO_2H$ and [IrCl(CO)(PPh$_3$)$_2$] under an atmosphere of oxygen at room temperature, after 10 d the mixture was found to contain benzaldehyde (1%), and polymeric material (59%). Under similar conditions, styrene in the presence of a catalytic amount of [IrBr(O$_2$Bu$^t$)$_2$(CO)(PPh$_3$)$_2$] gave an almost identical product distribution. Although in both cases there is some evidence for auto-oxidation, the major reaction under these conditions appears to be styrene polymerisation. In order to avoid competition from the polymerisation reaction the oxidation was repeated with oct-1-ene, $Bu^tO_2H$, and [IrCl(CO)(PPh$_3$)$_2$]. After 6 d at room temperature an i.r. spectrum of the mixture indicated appreciable formation of alcohols and carbonyl compounds (bands at 3 400 and 1 700 cm$^{-1}$), and g.l.c. analysis revealed at least eleven products in addition to $Bu^tOH$ and $Bu^tO_2Bu^t$, but these were not characterised. Under similar conditions there was no reaction between oct-1-ene and a catalytic amount of [IrBr(O$_2$Bu$^t$)$_2$(CO)(PPh$_3$)$_2$] over 6 d at room temperature, until a small quantity of benzene was added whereupon the solution gradually turned green with concomitant growth of i.r. absorptions at 3 400 and 1 700 cm$^{-1}$. After 4—5 d, g.l.c. analysis of the reaction mixture showed that it contained a similar range and distribution of products as observed for the reaction carried out with [IrCl(CO)(PPh$_3$)$_2$] and $Bu^tO_2H$.

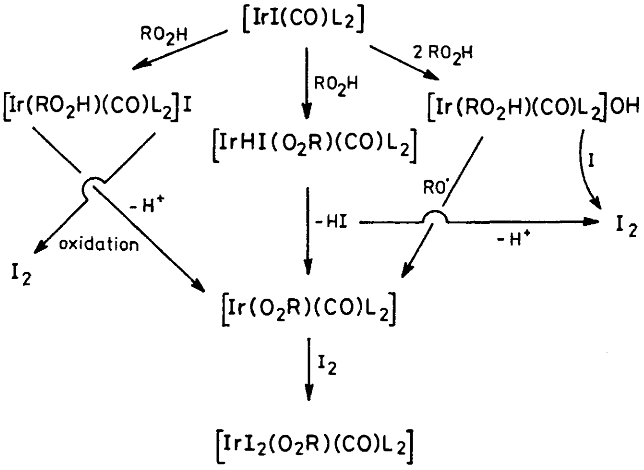
These qualitative experiments demonstrate that the bis(t-butylperoxy)iridium(III) complexes themselves are not catalysts for the breakdown of hydroperoxides, polymerisation of styrene, or auto-oxidation of alkenes, but in certain solvents, particularly benzene, they undergo a light-induced decomposition probably to produce t-butoxyl radicals which can initiate such reactions. The possibility that an iridium-containing species resulting from this decomposition may also be capable of initiating radical reactions can not be ignored. The interaction of $Bu^tO_2H$ with [IrCl(CO)(PPh$_3$)$_2$] also appears to generate t-butoxyl or t-butylperoxy radicals, although not necessarily by intermediate formation of [IrCl(O$_2$Bu$^t$)$_2$(CO)(PPh$_3$)$_2$].

## DISCUSSION

Three types of interaction between an iridium(I) complex and a hydroperoxide can be envisaged. These are (*a*) an electron-transfer process according to the general Haber-Weiss equation (1), (*b*) an oxidative addition process, either (2) or (3), and (*c*) co-ordination

$$\begin{aligned} RO_2H + Ir^{I} &\longrightarrow RO\cdot + HO^- + Ir^{II}; \\ RO_2H + Ir^{II} &\longrightarrow RO_2\cdot + H^+ + Ir^{I} \qquad (1) \\ RO_2H + Ir^{I} &\longrightarrow Ir^{III}(OR)(OH) \qquad (2) \\ RO_2H + Ir^{I} &\longrightarrow Ir^{III}(O_2R)H \qquad (3) \\ RO_2H + Ir^{I} &\longrightarrow Ir^{I}(RO_2H) \qquad (4) \end{aligned}$$

at a vacant site. While (*a*) does not necessarily require co-ordination of the hydroperoxide to the metal atom, such a co-ordination may be required in the oxidative addition processes in (*b*) and, indeed, may be a consequence of (*c*). An alternative consequence of (*c*) could be oxygen transfer to a phosphine, arsine, or carbonyl ligand. Harvie and McQuillin [20] have implied that the presence of co-ordinating ligands such as $HC(O)NMe_2$, $NEt_3$, or CO during the reaction of $[IrCl(CO)(PPh_3)_2]$ and $Bu^tO_2H$ suppresses formation of the blue complex but not that of $[IrCl(O_2Bu^t)_2(CO)(PPh_3)_2]$. It is suggested further that these two products arise by entirely different pathways, of which, only the one leading to the blue complex requires co-ordination of the hydroperoxide to the iridium atom. In our hands, the presence of phenols and *N*-heterocycles [12] and the use of thf as a solvent in this reaction supresses formation of both products. The blue complex may arise by oxidation of the phosphine ligand as suggested earlier,[20] as triphenylphosphine oxide is certainly one of the products of this reaction, but whether the precursor to the blue material is a simple iridium(I) hydroperoxide [as shown in (*c*)] or an alkylperoxyiridium(I) complex remains to be settled. Slight support for the latter comes from the observation that in certain solvents the bis(t-butylperoxy)iridium(III) complexes undergo a light-induced decomposition to give similar blue-green solids. There seems little doubt from our work and that of Harvie and McQuillin [20] that alkylperoxyl radicals are involved in the formation of the yellow bis(alkylperoxy)iridium(III) complexes. It is our contention that generation of these alkylperoxyl radicals, possibly by the electron-transfer processes shown in (*a*), requires prior co-ordination of the hydroperoxide to the iridium atom. The fact that these bis(alkylperoxy)iridium(III) complexes invariably have a single structure and are not mixtures of isomers suggests that either both alkylperoxyl radicals add simultaneously, perhaps within a solvent cage, or reaction involves oxidative addition of a tetraoxide intermediate, ROOOOR, a known product [23,24] of the bimolecular coupling of alkylperoxyl radicals at room temperature. The reactions of $[IrI(CO)(PPh_3)_2]$ are rather different in that they result only in the formation of the mono(alkylperoxy)iridium(III) complexes $[IrI_2(O_2R)(CO)(PPh_3)_2]$. This can be explained if, in the presence of a hydroperoxide, the iodide ligand is oxidised to iodine. Several pathways are possible for this process including nucleophilic displacement of iodide ion by the hydroperoxide, oxidative addition of hydroperoxide and reductive elimination of HI, and an electron-transfer process leading to iodine atoms (see Scheme). Each of these reactions could give rise to a common mono(alkylperoxy)iridium(I) intermediate, and hence the observed product by oxidative-addition of iodine.



SCHEME

## EXPERIMENTAL

The t-butyl hydroperoxide was a commercial sample containing 30% $Bu^tO_2Bu^t$, and was dried before use. Cumyl hydroperoxide, which contained *ca.* 17% cumene, was filtered to remove stabilizer and dried. I.r. spectra were recorded on a Perkin–Elmer 621 spectrophotometer, and $^1H$ n.m.r. spectra were recorded at 100 MHz on a Varian Associates HA100 instrument. Analyses for phosphorus and some halogens were performed by Alfred Bernhardt, Microanalytisches Laboratorium, Elbach über Engelskirchen, West Germany. Chromatographic separations were carried out on Florisil. Except where stated, all reactions were carried out under an atmosphere of dry nitrogen.

*Reactions of t-Butyl Hydroperoxide.*—(*a*) *With trans*-$[IrCl(CO)(PPh_3)_2]$. Addition of the hydroperoxide (2.00 g, *ca.* 15.6 mmol) to a rapidly stirred solution of *trans*-$[IrCl(CO)(PPh_3)_2]$ (2.00 g, 2.56 mmol) in toluene (100 cm³) at room temperature caused immediate colour change to an intense green. After 30 min chromatography ($Et_2O$ eluant) gave (1) (1.01 g, 1.01 mmol, 39%) containing 3/8 mol of toluene of crystallisation. A blue residue remained on the chromatography column.

A repeat of this reaction in benzene (100 cm³) gave an intense blue solution, which was reduced in volume and addition of diethyl ether (150 cm³) precipitated a blue, amorphous solid (0.81 g) (Found: C, 39.0; H, 3.8%); $\nu_{max.}$ 3 050m, 1 600br, 1 480s, 1 431s, 1 186m, 1 156w, 1 115m, 1 094s, 1 050w, 1 027w, 997m, 848w, 782m, 742s, 690vs, 616w, 538s, 522s, 510s, 501 (sh), and 320m cm$^{-1}$. Chromatography of the filtrate gave (1) (0.28 g, 0.29 mmol, 11%). Under similar conditions reaction in dichloromethane gave a 25% yield of (1).

(*b*) *With trans*-[IrBr(CO)(PPh$_3$)$_2$]. Using a similar procedure to that above, reaction between *trans*-[IrBr(CO)(PPh$_3$)$_2$] (2.00 g, 2.42 mmol) and Bu$^t$O$_2$H (2.00 g, *ca.* 15.6 mmol) gave (2) (0.87 g, 0.87 mmol, 36%).

(*c*) *With trans*-[IrCl(CO)(PPh$_2$Me)$_2$]. Chromatography (Et$_2$O eluant) of the intense green solution from addition of Bu$^t$O$_2$H (2.00 g, *ca.* 15.6 mmol) to *trans*-[IrCl(CO)(PPh$_2$Me)$_2$] (3.00 g, 4.57 mmol) in toluene gave (3) (0.02 g, 0.024 mmol, 0.5%). Further elution with methanol gave an amorphous blue-green solid (1.80 g); $\nu_{max.}$ 3 050m, 1 600m, 1 480m, 1 430ms, 1 180s, 1 100s, 1 027m, 1 000m, 890vs, 740vs, and 692vs cm$^{-1}$.

(*d*) *With trans*-[IrCl(CO)(PPhMe$_2$)$_2$]. Under similar conditions Bu$^t$O$_2$H (1.50 g, *ca.* 11.7 mmol) and *trans*-[IrCl(CO)(PPhMe$_2$)$_2$] (2.00 g, 3.76 mmol) in toluene (50 cm$^3$) gave a trace of a yellow oil, and an amorphous, blue-green solid (1.13 g); $\nu_{max.}$ 3 000m, 2 050w, 1 600s, 1 440s, 1 300m, 1 190s, 1 070w, 1 030w, 1 003w, 950s, 918vs, 850s, 745s, 720s, and 695vs cm$^{-1}$.

(*e*) *With trans*-[IrCl(CO)(AsPh$_3$)$_2$]. Yellow crystals of (4) (0.71 g, 0.69 mmol, 24%) were obtained from Bu$^t$O$_2$H (2.00 g, *ca.* 15.6 mmol) and *trans*-[IrCl(CO)(AsPh$_3$)$_2$] (2.50 g, 2.88 mmol).

(*f*) *With trans*-[IrBr(CO)(AsPh$_3$)$_2$]. Reaction between Bu$^t$O$_2$H (1.50 g, *ca.* 11.7 mmol) and the iridium complex (2.00 g, 2.19 mmol) gave (5) (0.64 g, 0.59 mmol, 27%).

(*g*) *With trans*-[IrI(CO)(PPh$_3$)$_2$]. Chromatography (Et$_2$O eluant) of the intense blue-green solution obtained on addition of Bu$^t$O$_2$H (2.00 g, *ca.* 15.6 mmol) to a stirred solution of *trans*-[IrI(CO)(PPh$_3$)$_2$] (2.00 g, 2.29 mmol) in toluene (100 cm$^3$) gave red crystals of (9) (0.75 g, 0.69 mmol, 30%). A blue residue remained on the chromatography column.

(*h*) *With* [Ir(dppe)$_2$]Cl. Reaction between Bu$^t$O$_2$H (1.00 g, *ca.* 7.8 mmol) and [Ir(dppe)$_2$]Cl (1.00 g, 0.98 mmol) in toluene (40 cm$^3$) at room temperature gave an intense turquoise solution. Addition of n-hexane precipitated an amorphous, turquoise solid (0.82 g); $\nu_{max.}$ 3 050m, 2 990m, 1 582w, 1 567w, 1 480m, 1 434s, 1 190vs, 1 120m, 1 100s, 1 070w, 1 028m, 1 000m, 882m, 826m, 742vs, and 693vs cm$^{-1}$.

(*i*) *With* [IrH(CO)(PPh$_3$)$_3$]. Addition of n-hexane (100 cm$^3$) to the intense blue solution obtained on addition of Bu$^t$O$_2$H (1.50 g, *ca.* 11.7 mmol) to a rapidly stirred solution of [IrH(CO)(PPh$_3$)$_3$] (1.50 g, 1.49 mmol) in toluene (60 cm$^3$) gave an amorphous, blue solid (0.91 g) (Found: C, 51.0; H, 4.3%); $\nu_{max.}$ 3 052m, 2 030vw, 1 605vs, 1 480m, 1 433s, 1 372m, 1 321m, 1 270vw, 1 238w, 1 186m, 1 158m, 1 116m, 1 091s, 1 070w, 1 025m, 997m, 970vw, 921w, 845w, 812w, 744s, 720m, 692vs, 616w, 540s, 520vs, 458w, 392w, and 350w cm$^{-1}$.

*Reactions of Cumyl Hydroperoxide*.—(*a*) *With trans*-[IrCl(CO)(PPh$_3$)$_2$]. Addition of the hydroperoxide (2.50 g, *ca.* 11.5 mmol) to a rapidly stirred solution of *trans*-[IrCl(CO)(PPh$_3$)$_2$] (2.00 g, 2.56 mmol) in toluene (100 cm$^3$) gave, after chromatography (Et$_2$O eluant), yellow crystals of (6) (0.99 g, 0.91 mmol, 36%); a blue compound remained on the chromatography column.

(*b*) *With trans*-[IrBr(CO)(PPh$_3$)$_2$]. Under similar conditions PhMe$_2$CO$_2$H (2.50 g, *ca.* 11.5 mmol) and *trans*-[IrBr(CO)(PPh$_3$)$_2$] (2.10 g, 2.56 mmol) gave (7) (1.29 g, 1.14 mmol, 45%).

(*c*) *With trans*-[IrCl(CO)(AsPh$_3$)$_2$]. Yellow crystals of (8) (0.53 g, 0.45 mmol, 28%) were obtained from PhMe$_2$CO$_2$H (2.00 g, *ca.* 9.2 mmol) and *trans*-[IrCl(CO)(AsPh$_3$)$_2$] (1.40 g, 1.61 mmol).

(*d*) *With trans*-[IrI(CO)(PPh$_3$)$_2$]. Chromatography (Et$_2$O) of the intense blue-green solution obtained by addition of PhMe$_2$CO$_2$H (2.50 g, *ca.* 11.5 mmol) to *trans*-[IrI(CO)(PPh$_3$)$_2$] (2.00 g, 2.29 mmol) in toluene (100 cm$^3$) gave impure red crystals of (10) (0.59 g, 0.51 mmol, 22%). Repeated recrystallisation from a 1 : 2 mixture of toluene and methanol failed to give an analytically pure sample.

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