Reaction of Hydroperoxides with *trans*-IrX(CO)L_2 Complexes

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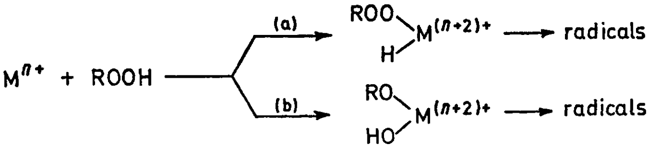
Summary The novel compounds $IrX(OOBu^t)_2(CO)L_2$ (X = Cl; L = PPh_3, $AsPh_3$, or PPh_2Me, and X = Br; L = PPh_3 or $AsPh_3$) and $IrX(OOCPhMe_2)_2(CO)(PPh_3)_2$ (X = Cl or Br) have been isolated from the reactions of Bu^tOOH or $PhMe_2COOH$ with the respective *trans*-IrX(CO)L_2 complexes; the similar reaction of Bu^tOOH with *trans*-IrI(CO)$(PPh_3)_2$ yields $IrI_2(OOBu^t)(CO)(PPh_3)_2$.

The several homogeneous autoxidation reactions catalysed by d^8 transition metal complexes reported recently[1] are believed to involve free radicals, and it has been suggested that the probable role of the metal complex is to cause the breakdown of hydroperoxide intermediates, possibly by an oxidative-addition reaction of type (a) or (b) as the initial step.



We now report some reactions of hydroperoxides with complexes of the type *trans*-IrX(CO)L$_2$ which give stable alkylperoxyiridium complexes.

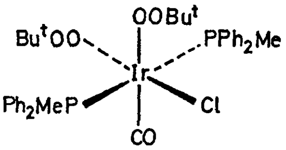
When the reaction of an excess of Bu^{t}OOH with *trans*-IrX(CO)L$_2$ (X = Cl or Br; L = PPh$_3$ or AsPh$_3$) is carried out in toluene solution at room temperature the diperoxy-complexes IrX(OOBu^t)$_2$(CO)L$_2$ are isolated by chromatography on Florisil as yellow, crystalline solids[†] in yields of 25 to 40%, together with small amounts of blue solids which did not elute from a chromatography column. These yellow complexes are stable in the solid state in air and in carbon tetrachloride solution, but some decomposition occurs in benzene solution. They are characterised by iridium carbonyl stretching frequencies in their i.r. spectra at 2035—2043 cm^{-1}, and bands of medium intensity at 880—890 cm^{-1} which could be assigned to ν (O–O); the chloro-complexes also show an Ir–Cl stretch at 303 cm^{-1} (L = PPh$_3$) or 304 cm^{-1} (L = Ph$_3$As). The presence, in the ^{1}H n.m.r. spectrum of each compound, of two singlets (9H) in the region τ 9·00—9·31 suggests that in these complexes the two Bu^{t}OO groups are mutually *cis*. The ^{1}H n.m.r. spectrum in CCl$_4$ of the complex IrCl(OOBu^t)$_2$(CO)(PPh$_2$Me)$_2$ obtained in low yield from IrCl(CO)(PPh$_2$Me)$_2$ shows bands at τ 7·81 (6H, t, apparent J_{P-H} 4·35 Hz) and 8·91 (9H, s), and 9·17 (9H, s) in addition to bands for the aromatic protons. The 'virtual coupling' of the two ^{31}P nuclei indicates that the two phosphine ligands are *trans* in this complex [see (A)].

Cumene hydroperoxide reacts similarly with IrX(CO)(PPh$_3$)$_2$ (X = Cl or Br) in benzene or toluene to give IrX(OOCPhMe$_2$)$_2$(CO)(PPh$_3$)$_2$, which have similar i.r. and ^{1}H n.m.r. spectra to the t-butyl complexes described above, together with a small amount of a blue solid.

Under similar conditions Bu^{t}OOH reacts with IrI(CO)(PPh$_3$)$_2$ to give red crystals (*ca.* 30%) of IrI$_2$(OOBu^t)(CO)(PPh$_3$)$_2$, m.p. 133—134 °C with decomposition.[†] Its i.r. spectrum shows bands at 2054 cm^{-1} [ν (CO)] and 876 cm^{-1} [ν (O–O)], and only a single band at τ 8·71 in the ^{1}H n.m.r. spectrum for the Bu^t protons.

In all these reactions complete decomposition of the hydroperoxide occurs with the evolution of oxygen. The yields of the peroxy-complexes depend upon the solvent, and lower yields are obtained in benzene or dichloromethane.

Like Pd(PPh$_3$)$_4$,[2] a catalytic amount of *trans*-IrCl(CO)(PPh$_3$)$_2$ rapidly causes the decomposition of the hydroperoxides ROOH (R = Bu^t or PhMe$_2$C) to give oxygen and the corresponding alcohol as the major products, according to the stoicheiometry $2\,ROOH \longrightarrow 2\,ROH + O_2$.



(A)

This contrasts with a previous report[3] that reaction of a catalytic amount of the chloro-iridium complex with PhMe$_2$COOH gives CO$_2$ under similar conditions. The iridium-containing residue after the reaction showed a ν (CO) i.r. band at 2043 cm^{-1} consistent with the formation of some IrCl(OOBu^t)$_2$(CO)(PPh$_3$)$_2$ during this catalytic reaction. Phenol, which itself does not react with *trans*-IrCl(CO)(PPh$_3$)$_2$, almost completely inhibits the reaction, and reaction only occurs with the hydroperoxides; t-butyl peroxide is unaffected under these conditions. Other d^8 complexes, such as [Ir(diphos)$_2$]$^+$Cl$^-$ and RhCl(PPh$_3$)$_3$ also catalyse the decomposition of the hydroperoxides.

The peroxy-iridium complexes are secondary products and not intermediates in the reaction since they do not catalyse the rapid decomposition of Bu^{t}OOH. It is probable, however, that they are structurally related to the reactive intermediates responsible for the homolytic breakdown of the hydroperoxides in these and related homogeneous autoxidation reactions catalysed by transition-metal complexes.

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[†] Satisfactory molecular weights and elemental analyses (C, H and usually P and halogen) have been obtained. A separate *X*-ray crystallographic study is in progress.

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