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OBSERVATIONS ON OLEFIN OXIDATION BY NEUTRAL AND CATIONIC PHOSPHINEIRIDIUM COMPLEXES *

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Summary

The ethyleneiridium oxygen complex $ClIr(PPh_3)_2(O_2)(C_2H_4)$ previously prepared by Van der Ent, decomposes in solution forming some Ph_3PO and CH_3CHO, in the absence of excess ethylene. It promotes the oxidation of 1-octene and styrene by O_2 and factors affecting the rate and efficiency of oxidation have been examined. Tetrastyrene di-μ-chlorodiiridium is only oxidised effectively by O_2 in the presence of PPh_3. The 1-octene complex $ClIr(PPh_3)_2(C_8H_{16})$ reacts very rapidly with oxygen at low temperatures but 2-octanone is not found in the decomposition products. The cationic complex $(C_2H_4)_3\overset{+}{Ir}(PPh_3)_2$ promotes the oxidation of 1-octene and styrene but low yields of products are formed, including phenyloxirane and benzaldehyde.

Complexes of 5-phenyldibenzophosphole were examined. They are not effective in promoting oxidation and display a strong tendency to form stable five-coordinate complexes and a greater propensity for *cis*-biphosphine coordination.

Introduction

Despite the early observation by Read and co-workers [1] that terminal olefins are oxidised to methyl ketones in the presence of phosphine complexes of rhodium with concomitant formation of phosphine oxide, the reaction has not been developed into a useful catalytic synthesis [2]. On the basis of an initial suggestion by Read [1], and its enthusiastic development by Mimoun and co-workers [2], it is generally considered that oxidation proceeds through a metalladioxacyclopentane (Scheme 1) which decomposes by an undefined pathway to give the methyl ketone and a metal oxide which in turn fragments to form phosphine oxide. This mechanism explains a number of features of the reaction satisfactorily, including the catalytic turnover

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* This paper dedicated to Professor J. Halpern on the occasion of his 60th birthday: "The great tragedy of science is the slaying of beautiful hypotheses by ugly facts" T.H. Huxley, d. 1895.

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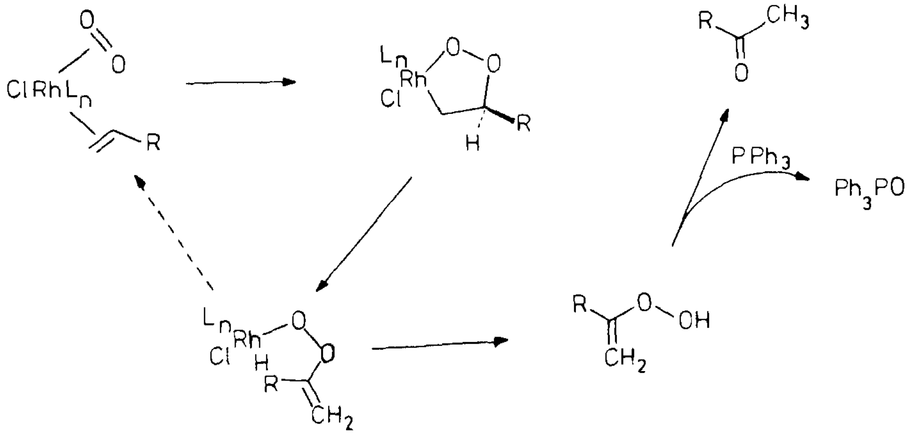


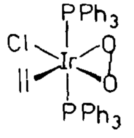
SCHEME 1. Olefin oxidation mechanism involving a metalladioxacyclopentane

observed in the presence of excess phosphine, and the high selectivity towards terminal olefins. The putative intermediate has never been observed, and difficulties arise when the precise pathway by which it might decompose to ketone are considered. Firstly, a β-elimination in a five-membered ring is stereoelectronically difficult because of the poor overlap between α-M–C and β-C–H bonds [3]. Stable platinum metallocycles of this structure are known [4] and show no tendency to decompose by this mechanism. On the basis of labelling experiments [5] employing $^{18}O_2$ or $^{18}OH_2$, it has been established that the phosphine-promoted oxidation cannot be a Wacker-type reaction (i.e. involving exometallic attack by OH^-) but that oxidation of 1,7-octadiene in a phosphine-free system; $RhCl_3$; $Cu(ClO_4)_2$, may involve a contribution from this pathway [5].

Iridium complexes have been less widely employed in olefin oxidation, although a slow catalytic turnover has been achieved [6] for oxidation of cyclooctene by H_2/O_2 mixtures employing $[(C_8H_{14})_2IrCl]_2$, the function of H_2 being to reduce H_2O_2 to H_2O. It was of some interest that the co-complexation of oxygen and ethylene to iridium was observed several years ago [7]. Complex **1** is stable in the solid state and in solution in the presence of excess ethylene, showing no tendency to rearrange to the metallocycle or to oxidise ethylene. We decided to investigate its reactivity in the promotion of olefin oxidation.

Results and discussion

(a) Reactions involving the Van der Ent complex (1): Dissolution of complex **1** in CH_2Cl_2 and regular monitoring by ^{31}P NMR showed that the sample was quite stable under an ethylene atmosphere. In the absence of excess ethylene the solution rapidly turns green, and ^{31}P NMR shows that Ph_3PO is formed concomitant with the disappearance of the resonance of **1** at -5.3 ppm and the growth of a new broad absorbance at -27.3 ppm (Fig. 1). Addition of 2,4-dinitrophenylhydrazine (as Brady's reagent) to the green solution produced after complete decomposition of **1** showed that acetaldehyde had been formed which was identified by the TLC of its 2,4-DNP derivative.



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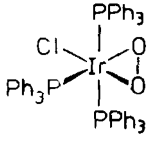

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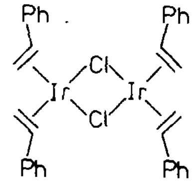

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The reaction between **1** and a 5-molar excess of oct-1-ene or styrene may be monitored by GLC (15% OV17 on diatomite C-AW 100–120 mesh, 121°C). It was first observed that an apparent rapid burst of oxidation occurred in the initial phases, consistent with observations recorded by Read and Walker [1]. This was traced to reaction taking place in the inlet of the gas-chromatograph and did not occur if aliquots from the reaction mixture were first quenched in excess isopentane at −30°C. The latter technique was carried out exclusively in all subsequent experiments. The presence of oct-1-ene does not inhibit decomposition of the complex in the absence of excess ethylene to any marked extent (Fig. 1). When this decomposition is permitted to go to completion before oct-1-ene is added, then the resulting green solution is ineffective for olefin oxidation. Although oxidation did proceed under an argon atmosphere, yields were higher in an oxygen atmosphere. Note the complete regioselectivity in oxidation of penta-1,3-diene (Table 1).

(b) Reactions involving dioxygen (tris(triphenylphosphine))iridium chloride. Since ethylene dissociation appeared to be a prerequisite to olefin oxidation, it was decided to examine reactions of the corresponding tris(triphenylphosphine) complex **2**. Oxidation of oct-1-ene proceeded rapidly (Fig. 2), and by simultaneous monitoring by both GLC and ^{31}P NMR it proved possible to show that the decomposition of complex **2** and formation of octan-2-one are closely linked. Again, product yields are higher in an oxygen atmosphere.

(c) Preformed complexes of styrene and oct-1-ene. The reaction between tetracyclooctenedi-μ-chlorodiiridium and styrene gave the corresponding styrene complex **3**, isolated as a red solid. This was stirred under oxygen in CH_2Cl_2 and the course of

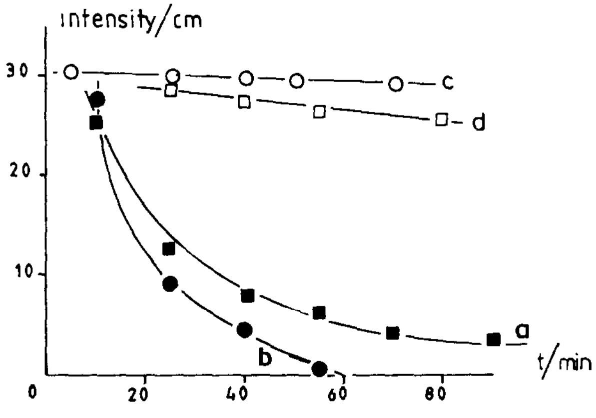


Fig. 1. Decay of the ^{31}P NMR singlet of $ClIr(PPh_3)_2(C_2H_4)(O_2)$ (50 mM in CH_2Cl_2) (a) under argon ■; (b) under argon in the presence of oct-1-ene (250 mM) ●; (c) under ethylene ○ and (d) under ethylene in the presence of oct-1-ene (250 mM), □.

TABLE 1

YIELDS (based on [Ir]) OF METHYL KETONE IN OLEFIN OXIDATIONS (CH_2Cl_2, 10 h, 40°C); GLC ESTIMATION

Olefin	Complex	Ketone (Ar) (%)	Ketone (O_2) (%)
Oct-1-ene	**1**	42	72
Oct-1-ene	**2**	48	93 (77) [a]
Oct-1-ene	**7**	–	0
Styrene	**1**	51	80
Penta-1,3-diene	**1**	52	–

[a] 5 *M* excess PPh_3.

reaction followed by GLC. Only a very small quantity of acetophenone was produced and it was accompanied by a comparable amount of benzaldehyde. Experiments carried out in the presence of added PPh_3 revealed that the proportion of acetophenone increased to a plateau (Fig. 3) whilst the proportion of benzaldehyde diminished. Benzaldehyde has previously been observed in oxidation of styrene by $ClRh(PPh_3)_3$ [8] and is thought to be a consequence of free-radical reaction pathways [9], for which Scheme 2 records one possibility.

Attempts to form a mixed olefin/phosphine complexes (other than the ethylene complex) proved to be unsuccessful. For this reason the iridium dinitrogen compound **4** was prepared [10] and reacted with oct-1-ene in CD_2Cl_2 solution at −60 °C. The changes which occurred in the ^{31}P NMR spectra were entirely consistent with formation of the monoolefin complex **5** (Table 2), displacement of

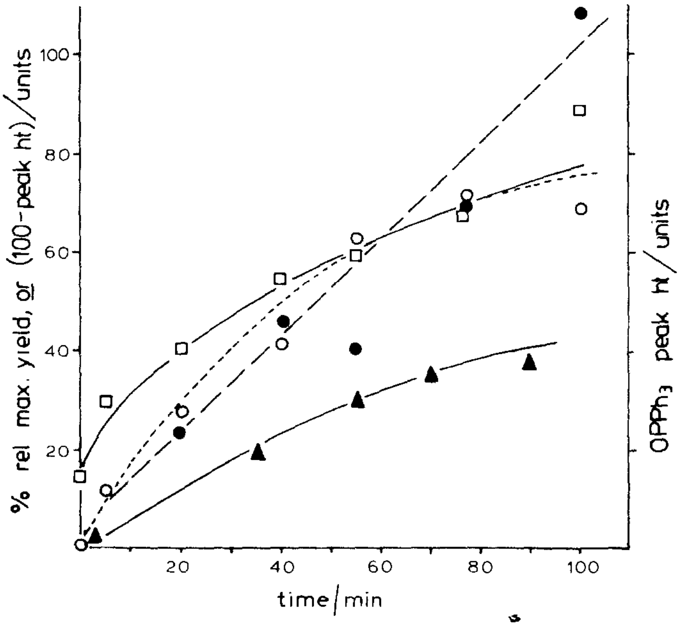
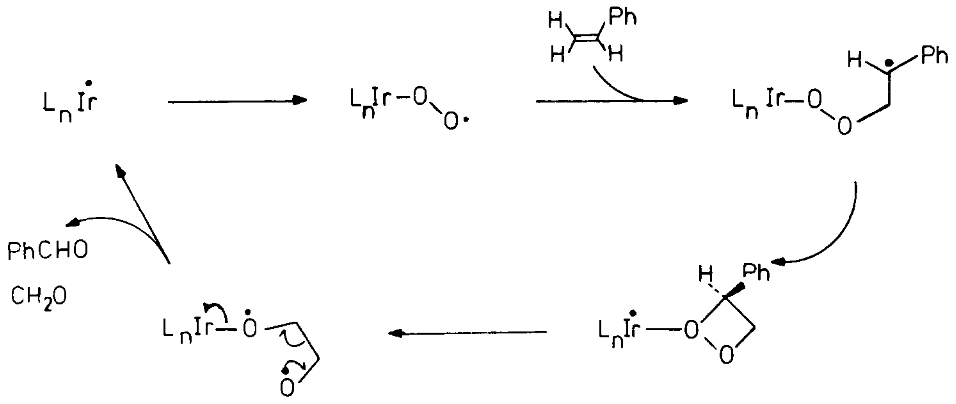


Fig. 2. Monitoring of the oxidation of oct-1-ene and decomposition of $ClIr(PPh_3)_3(O_2)$ in CH_2Cl_2 (54 m*M*) thus: (a) Decay of complex under argon, ^{31}P NMR ▲; (b) Decay of complex under argon in the presence of oct-1-ene (271 m*M*) ○; (c) experiment b, monitoring the formation of octan-2-one by GLC ●; (d) experiment b, monitoring formation of PPh_3O by ^{31}P NMR, □.



SCHEME 2. Free-radical metal catalysed oxidation of styrene.

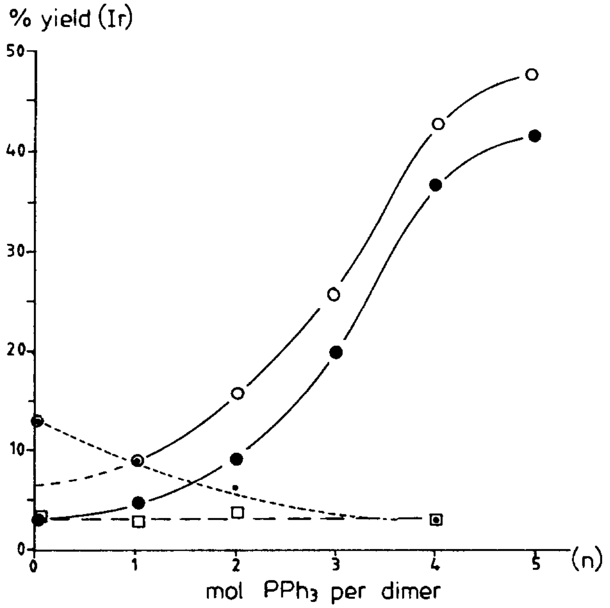
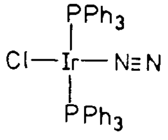


Fig. 3. Effect of added triphenylphosphine on the oxidation of styrene (280 mM) in the presence of $[(PhCH{=}CH_2)_2IrCl]_2$ (28 mM) under an oxygen atmosphere. Acetophenone, 2 h, ●; 10 h, ○; Benzaldehyde 2 h □; 10 h, •.

nitrogen taking place over a period of several days. The product was stable in solution at low temperatures but reacted rapidly on exposure to oxygen at −65 °C such that the singlet at +26.4 ppm disappeared without the appearance of new



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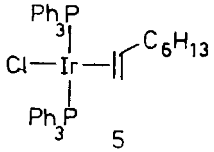

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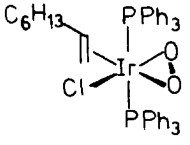

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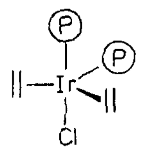
peaks. Quenching at that stage and GLC analysis revealed that only very slight traces of 2-octanone had been produced in the decomposition, the major volatile component being oct-1-ene. Thus oxygenation of a preformed olefin complex leads to displacement rather than oxidation as the likely fate of intermediate (**6**).

(d) Experiments with 5-phenyldibenzophosphole. It was of interest to examine reactions with a phosphine of slightly different steric demand, and the related phosphole is known to form catalytically active rhodium complexes [11] with a tendency to higher coordination numbers and a lower degree of ligand dissociation [12]. Reaction of the phosphole with tetraethylenedi-μ-chlorodiiridium led to a new complex (7) whose ^{31}P NMR revealed an AB quartet ($^2J_{cis}$ 12 Hz). The relative orientation of the ethylene ligands was apparent from the temperature-independent ($-80 \rightarrow +30$°C) ^{1}H NMR spectrum displaying four separate vinyl-H environments between 2.5 and 3.2 ppm (Fig. 4). This is consistent only with the conformation illustrated in 7.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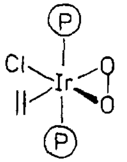
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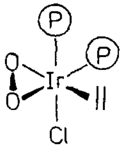
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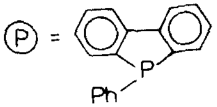

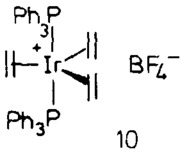
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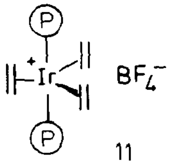
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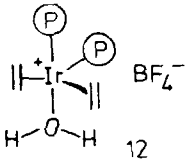
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Addition of oxygen to the diethylene adduct 7 may be followed by ^{1}H and ^{31}P NMR in CD_2Cl_2 solution, and simultaneous formation of two new species is then observed. The minor isomer exhibits a singlet in the ^{31}P NMR spectrum at -13.8 ppm and a sharp triplet in the ^{1}H NMR at 2.9 ppm. These observations are

TABLE 2

^{31}P NMR DATA FOR OLEFIN COMPLEXES OF IRIDIUM RELATED TO THE OCT-1-ENE DERIVATIVE (5)

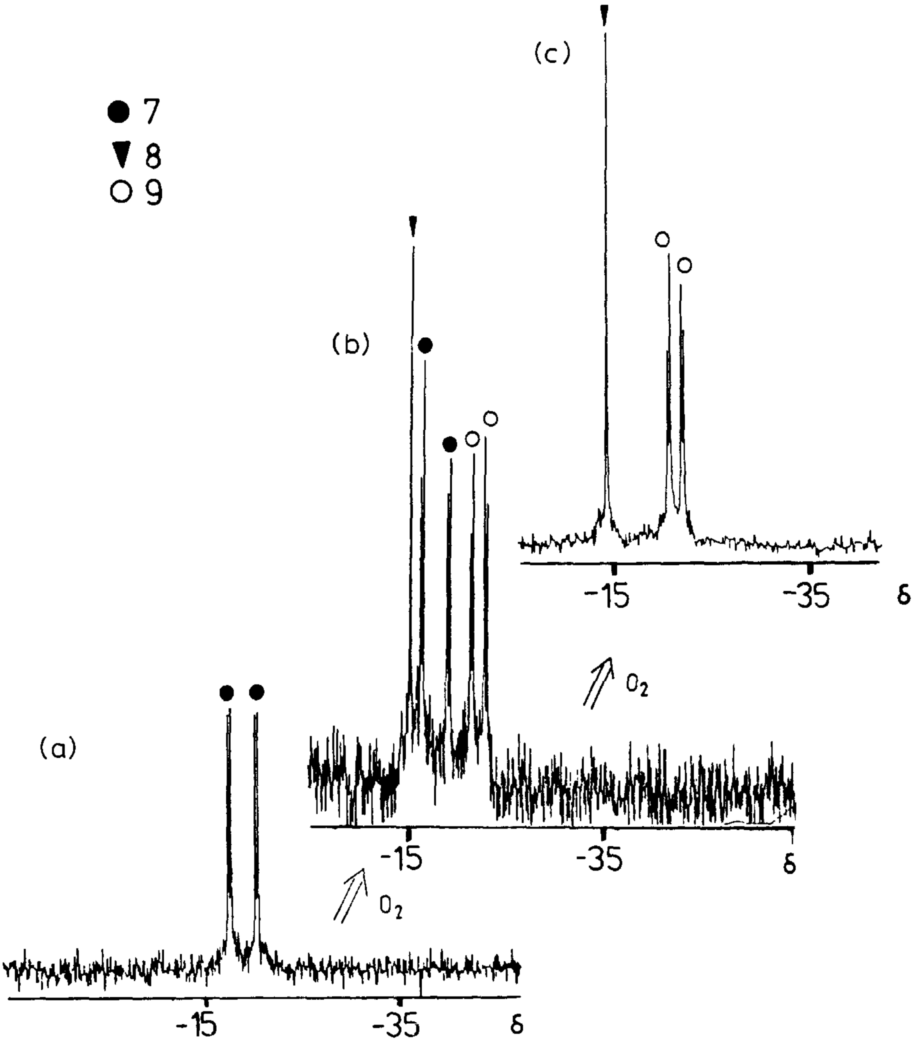
Complex	δ(ppm rel. 85% H_3PO_4)	Solvent
$ClIr(PPh_3)_2(N_2)$ [10]	$+22.3$ [a]	C_7H_8
$ClIr(PPh_3)_2(N_2)$	$+20.9$ [b]	$CHCl_3$
$ClIr(PPh_3)_2(N_2)(ol)$ [c]	-18.3 [a,c]	C_7H_8
$ClIr(PPh_3)_2$(oct-1-ene)	$+26.4$ [a]	C_7H_8
$ClIr(PPh_3)_2(C_2H_4)$	$+25.5$ [b]	$CHCl_3$

[a] This work. [b] K.D. Schramm, T.H. Tulip and J.A. Ibers, Inorg. Chem., 19 (1980) 3183. [c] Diethyl maleate.

consistent with structure **8**. The major isomer showed an AB quartet in the ^{31}P NMR at δ 20.3, 21.6 ppm ($^2J_{cis}$ 10 Hz) and two broad doublets in the ^{1}H NMR at δ 3.75 and 3.5 ppm, now consistent with structure **9**. The two isomers do not interconvert on the NMR time scale, and are stable over long periods in solution. In accordance with this neither of the phosphole complexes **7**, or **8** $\rightleftharpoons$ **9**, demonstrates any reactivity in oxygenation of oct-1-ene.

(e) Reactions of cationic complexes. Treatment of the complex ClIr(PPh$_3$)$_2$-(C$_2$H$_4$) with silver tetrafluoroborate in ethylene-saturated CH$_2$Cl$_2$ leads to precipitation of AgCl. The filtered solution is colourless under ethylene (^{31}P, δ 2.9 ppm) but goes orange when argon is passed through. The cycle may be repeated two or three times before decomposition occurs but the complex, of presumed structure **10** cannot be stored without decomposition, even at −30°C under C$_2$H$_4$.

The corresponding reaction of complex **7** with AgBF$_4$ in ethylene-saturated CH$_2$Cl$_2$ gives a more stable analogue **11** exhibiting a singlet at −15.5 ppm in its ^{31}P



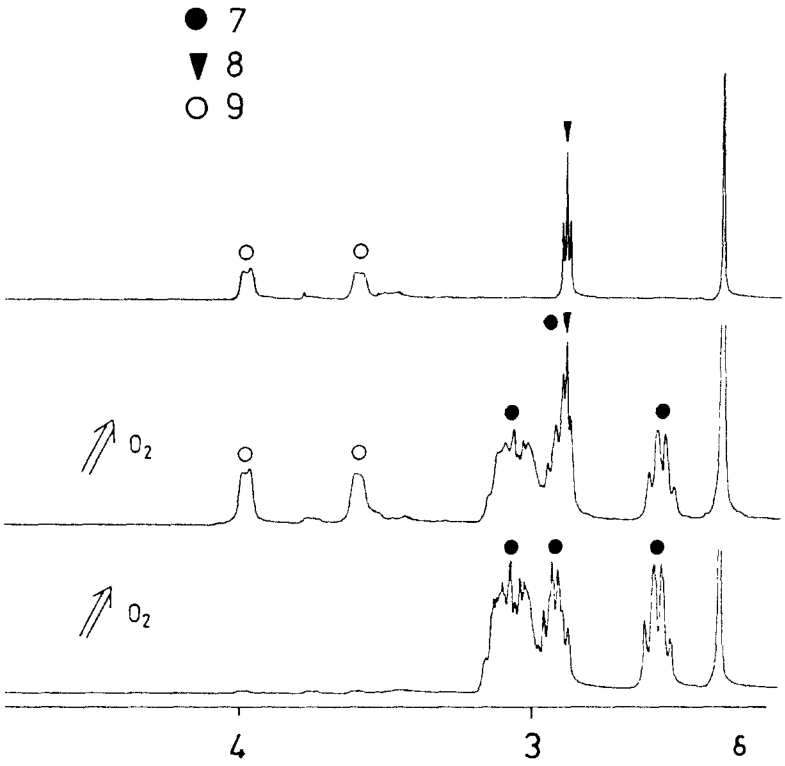


Fig. 4. Monitoring of the reaction between complex 7 and dioxygen in CD_2Cl_2 (i) (a) ^{31}P NMR spectrum of starting material (b) at intermediate time and (c) on completion of reaction; (ii) (a) ^1H NMR spectrum of starting material (b) at intermediate times and (c) on completion of reaction.

NMR. After isolation an impurity was apparent in both the ^{31}P and ^1H NMR spectra. This was shown to be the aquo-complex **12**, and addition of 1 mole of D_2O to the solution led to its becoming the predominant species. Displacement of one ethylene by water occurred with a change in biphosphine geometry from *trans* to *cis*.

When excess styrene was added to an initially colourless solution of cation **10** in CH_2Cl_2, a red colouration was produced over several minutes. When oxygen was introduced the colour changed to brown and then green over the course of an hour. GLC analysis then demonstrated that acetophenone, benzaldehyde and phenyloxirane had been produced in comparable proportions. Yields were low and the reaction proved to be irreproducible. Similarly, 1-hexyloxirane was one of the products of octene oxidation in the presence of complex **10**.

(f) Summary and conclusions. The reaction of Van der Ent's complex **1** with oxygen and terminal olefins requires that ethylene dissociate before oxidation of the olefin can occur. An endometallic pathway involving the metalladioxacyclopentane, analogous to that outlined in Scheme 1 would then require coordination of the olefin, presumably to first form complex **6** or its congeners. Nevertheless, when the synthesis of complex **6** is attempted by addition of oxygen to the olefin complex **5** irreversible decomposition occurs at low temperatures without any evidence for the presence of 2-octanone among the products.

Taken together this evidence rather suggests that the oxygen is in place before olefin adds in the cycle of catalytic oxidation. If a metalladioxacyclopentane is involved then it is unlikely to be formed by intracomplex reaction of an olefin dioxygen complex such as **6**. One alternative might be direct cyclofin addition of an $\overset{+}{\text{M}}\text{–O–O}^-$ moiety to free olefin but other possibilities must be considered. The selectivity towards terminal olefins and specificity (at least in oxidations promoted by neutral complexes) rule out pathways involving the oxidation of free olefin by adventitious reagents such as H_2O_2 [13] or metal hydroperoxides, which would exhibit a different spectrum of selectivity [14]. An attractive alternative involves oxygen-induced decomposition of the starting complex and transfer of one oxygen atom to PPh_3. The resulting iridium oxide is then the true oxidising agent towards olefin. Since this and other related pathways are equally in accord with the assembled experimental evidence, they must be given comparable status pending more direct information on the true reaction intermediates.

Experimental

Solvents were purified by standard procedures before use, and distilled under argon. Oct-1-ene was distilled off a small pellet of sodium and used immediately; styrene was distilled off its stabiliser and then stored at −30 °C.

^{1}H NMR spectra were obtained on a Bruker WH300 instrument, along with some ^{31}P NMR spectra at 121.4 MHz. Others were recorded at 36.43 MHz on a Bruker WH90 instrument. ^{31}P chemical shifts are quoted in ppm downfield from external 85% H_3PO_4. Infrared spectra were recorded in KBr discs using a Perkin–Elmer 257 or Unicam SP1000 spectrometer. Mass spectra were obtained on a Micromass ZAB 2F by field-desorption. Melting points were recorded on a Reichert–Kofler block, and are uncorrected. Microanalyses were performed by Dr. F.B. Strauss and his staff.

All reactions were carried out in a vacuum-line controlled atmosphere using Schlenk-tube techniques. Known compounds were prepared according to literature procedures which are indicated where appropriate.

Di-μ-chlorotetrakis(1,2-η)(1-phenylethene)iridium(I)

Di-μ-chlorotetrakis(ethylene)iridium(I) [15] (300 mg, 0.33 mmol) was suspended in 5 ml isopentane. Styrene (600 μl, 6 mmol) was added and the suspension stirred under argon. The yellow suspension disappeared in seconds to give a deep red solution which deposited a red solid in minutes. The solid was collected by filtration and washed with cold isopentane (in which it is slightly soluble) to remove excess styrene (2 × 5 ml). A red solid (222 mg, 77%) was collected and dried in vacuo. This was recrystallised by dissolving in minimum chloroform and then adding isopentane until cloudiness was observed. The solution was left to stand at 4°C and red crystals were collected by decanting the supernatant and washing with minimum isopentane. M.p. 130°C (dec).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.5–7.2 (m, 5H), 3.6 (d, 1H), 3.2 (dd, 1H), 2.4 ppm (d, 1H). Mass spectrum (field-desorption) m/z 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879 with intensities in agreement with isotopic patterns in Ir and Cl. Microanalysis: Found C, 43.79, H, 3.72. $C_{32}H_{32}Cl_4Ir_2$ calcd.: C, 44.0, H, 3.67%.

Preparation and oxygenation of chlorooct-1-enebis(triphenylphosphine)iridium(I)

Chlorodinitrogen bis(triphenylphosphine)iridium (0.020 g, 0.026 mmol) [10] was dissolved in deoxygenated toluene (1.5 ml) under argon in an 8 mm NMR tube. To this was added oct-1-ene (25μl, 0.015 mmol) and the tube stored at −30°C. After 24 h a new peak was observed in the ^{31}P NMR spectrum at δ 26.4 ppm which became the dominant species (> 75%) after 7 days. The new species was stable in solution under argon below 0°C, and was unreactive towards nitrogen. A similar experiment using 3,3-dimethylbut-1-ene showed only unreacted starting material.

A solution of the oct-1-ene complex, prepared as above in an 8 mm NMR tube, was cooled to −65°C, and oxygen (2 ml, 0.09 mmol) injected by gas syringe. The reaction was followed by ^{31}P NMR at −65°C. After 10 min approximately 60% of the signal due to the oct-1-ene complex had disappeared with no new peaks being observed. The reaction proceeded to completion at that temperature, and was then added to hexane to precipitate inorganic compounds. Analysis of the supernatant by GLC revealed substantial quantities of recovered oct-1-ene, and no more than traces of octan-2-one or other oxidation products.

Reaction of ethylene and $AgBF_4$ with chloro(ethylene)bis(triphenylphosphine)iridium(I)

The starting complex **7** (0.1 g, 0.13 mmol) was dissolved in ethylene-saturated dichloromethane (0.5 ml) and $AgBF_4$ (0.025 g, 0.13 mmol) added whilst ethylene was bubbled through the solution. The orange colour was quickly discharged to give a white precipitate and off-white solution, and the precipitate of AgCl was then removed by centrifugation. The volume of solvent was reduced by blowing a stream of ethylene over the solution and white needle-like crystals appeared. Addition of toluene ensured full crystallisation. The crystals were isolated by decantation of the supernatant and washed with hexane. The white crystals obtained, 76 mg (65%) were soluble in dichloromethane to give an orange solution which turned colourless on addition of ethene. They were unstable and decomposed slowly under ethene at −30°C.

^{31}P NMR (CH_2Cl_2, ethene, 36.43 MHz) −2.9 ppm (s). ^1H NMR (CD_2Cl_2, 90 MHz, −32°C), δ 7.5 (36H) 5.5 (free $CH_2{=}CH_2$, present in excess) 3.2 (12 H, br) ppm.

Preparation of chlorobis(5-phenyl-5H-dibenzophosphole)bis(1,2-η)ethyleneiridium(I)

Di-μ-chlorotetraethylenediiridium(I) (0.1 g, 0.18 mmol) was dissolved in toluene (2 ml) under ethylene to give a pale yellow solution. 5-Phenyl-5*H*-dibenzophosphole 121 (400 mg, 0.65 mmol) was added to give a crude solid which was washed with toluene (5 ml) and hexane (2 × 10 ml) and dried in vacuo to give 420 mg of the complex (60%) pale yellow solid, m.p. 170 °C (dec.).

^{31}P NMR (CH_2Cl_2, argon; 36.43 MHz) −14.8 (d, *J*(PP) 12 Hz), −17.6 ppm (d, *J*(PP) 12 Hz). ^1H NMR (CD_2Cl_2, 300 MHz) 7.8–7.0 (m, 26H), 3.13 (m, 2H), 3.02 (m, 2H), 2.78 (m, 2H), 2.52 ppm (m, 2H). IR (KBr): 3020(m), 2900(w), 1480(w), 1415(vs), 1180(m), 1150(s), 1120(m), 1090(m), 1175(m), 1160(w), 760(s), 725(s), 700(s) cm^{-1}. Mass spectrum (field-desorption) *m/z* 774, 775, 776 (main peaks). Analysis: Found: C, 61.47, H, 4.48. $C_{40}H_{34}P_2IrCl$; 0.5 C_7H_8 calcd.: C, 61.43, H, 4.47%.

Reaction of chlorobis(5-phenyl-5H-dibenzophosphole)diethyleneiridium(I) with ethylene and $AgBF_4$

The title complex (100 mg, 0.12 mmol) was dissolved in ethene-saturated dichloromethane (10 ml). Silver tetrafluoroborate (30 mg, 0.15 mmol) was added with vigorous agitation. A bright, white precipitate of silver chloride was removed by centrifugation to give a colourless solution. The volume of solvent was reduced to about 2 ml by blowing it off with a stream of ethene, to give a bright white solid which was isolated by centrifugation and washed with toluene (5 ml) and hexane (2 × 5 ml). The white solid, 68 mg (64%), was dried in vacuo. NMR spectra demonstrated contamination by the aquo-complex, thus ^{31}P NMR (CH_2Cl_2, ethene, 36.43 MHz), −15.5 (s), −7.7[a] (d, *J*(PP) 10 Hz), −18.3 ppm[a] (d, *J*(PP) 10 Hz). ^1H NMR (CD_2Cl_2, ethene, 30 MHz) 6.0–7.0 (m, 26H), 5.5 (s, free ethene), 3.3–3.1* (m, 4H), 3.05 (t, 12H, *J*(PH) 4 Hz), 2.8–2.5* (m, 4H), 2.4 ppm* (br, s, 2H; disappears on addition of 5 μl D_2O). IR (KBr): 3400(br, m), 3020(w), 1440(s), 1100(vs), 760(s), 715(s), 700(s) cm^{-1}. A field desorption mass-spectrum could not be obtained.

Reaction of chlorobis(5-phenyl-5H-dibenzophosphole)diethyleneiridium(I) with oxygen

The title complex (0.015 g, 18 μmol) was dissolved in 1,2-dichloroethane (0.25 ml) to give a pale yellow solution. Stirring under oxygen for 3 h discharged the yellow colour, giving a pale green solution. Addition of hexane gave an off-white solid (0.01 g, 61%) spectroscopically characterised as chlorodioxygenethylenebis(5-phenyldibenzophosphole)iridium(I), mixed isomers ([a])([b]). IR (KBr): 3025(w), 1480(w), 1440(vs), 1290(w), 1285(w), 1190(w), 1160(w) 1145(w), 1100(m), 1050(w), 1000(w), 870(w), 760(s), 720(s), 700(s) cm^{-1}. ^1H NMR (C_6D_6, 300 MHz) δ 8.3–6.8 (26H, br, Ar) 3.95 (brd, [a], 2H) 3.5 (brd, [a] 2H) 2.9 (t, [b], 4H, *J*(P–H) 5 Hz) ppm. ^{31}P NMR (CH_2Cl_2, 36.43 MHz) −13.6 (s, [b]) −20.3 (d, [a], *J*(PP) 10 Hz) −21.6 (d, [a], *J*(PP) 10 Hz) ppm. Mass spectrum (field desorption, m/z) 774/775/776; $M^+ - O_2$.

Decomposition of $[Ir(PPh_3)_2(Cl)(O_2)(C_2H_4)]$

The title complex (0.05 g, 60 μmol) was placed in an 8 mm NMR tube fitted to a vacuum line. Dichloromethane (1.5 ml), previously saturated in the desired gas by the freeze-thaw method was transferred to the NMR tube by steel tube. The tube was sealed by flame under the atmosphere of choice. In the preliminary runs the tube was sealed using a rubber septum cap. The rate of decomposition of the complex under an argon, oxygen or ethylene atmosphere was monitored by ^{31}P NMR spectroscopy. The intensity of the singlet resonances at −5.3 and 27.0 ppm were measured at varying times.

Oxidation of olefins promoted by $[Ir(PPh_3)_2Cl(O_2)(C_2H_4)]$

In a typical procedure for the oxidation of oct-1-ene the title complex (10 mg, 12 μmol) in 0.25 ml dichloromethane (4.8 m*M*) was added to oct-1-ene (10 μl, 60 μmol) in a drawn 5 mm tube. The tube was flame-sealed under oxygen or argon when aliquots were not required. When samples were required to be analysed over a time course the reaction was carried out as above in a 1.5 cm tube with a rubber septum cap. For ^{31}P NMR observation the reactants were mixed in an 8 mm NMR tube which was subsequently flame-sealed under the chosen atmosphere.

GLC analysis: (15% OV17 on diatonite C-AW 100-120 mesh, 121°C). Samples of oxidation reactions were removed by microsyringe (100 μl) and injected into 2 ml cold isopentane. The mixture was stored at $-30\,^\circ C$ and the supernatant pipetted from the precipitate. This solution was used for GLC analysis. In runs employing an internal calibrant, 5 μl 10% 1,2-dichlorobenzene in dichloromethane were added to the reaction mixture before sealing the tube. The internal standard was calibrated using accurately measured solutions of octan-2-one. Retention times (121°C), dichlorobenzene 6.1 min, octan-2-one 4.2 min. For analysis of styrene oxidation products a column oven temperature of 161°C was employed. Retention times (161°C): acetophenone 6.1 min, 1,2-dichlorobenzene 3.9 min.

^{31}P NMR analysis was performed in the manner previously described, for example: The title complex (10 mg, 13 μmol) in dichloromethane under argon was added to penta-1,3-diene (10 μl, 62 μmol) in an NMR tube. The tube was flame-sealed and the reaction observed by ^{1}H NMR (90 MHz). The resonance corresponding to coordinated ethylene in **1** was observed to diminish in intensity with concomitant growth of a singlet at 2.25 ppm and a doublet at 1.9 ppm (J(HH) 7.5 Hz), assignable to pent-3-en-2-one (confirmed by an authentic sample, R.N. Emanuel). The above oxidations were unaffected by the presence of 4-methyl-2,6-di-t-butylphenol in a concentration 10% that of Ir complex.

Oxidation of olefins by $[Ir(PPh_3)_3(O_2)Cl]$

Typically the title complex **16** (13.2 mg, 12 μmol) in dichloromethane (0.25 ml) under either an argon or ethylene atmosphere was added to the olefin e.g. oct-1-ene (10 μl, 60 μmol) in a drawn and heat-sealed 5 mm tube, when aliquots were not required. When the reaction was monitored against a time course the reactants were mixed under the desired atmosphere in a 1.5 cm tube fitted with a rubber septum cap. Samples which were monitored by ^{31}P NMR were made up as previously described. GLC analysis: aliquots were removed by microsyringe (100 μl) and added to cold isopentane. The estimation of octan-2-one yield was determined as previously described. For runs in which the yield of oxidation products was estimated by GLC with simultaneous observation of the ^{31}P NMR spectrum, samples were removed from the NMR probe, an aliquot was taken through the septum cap and the sample replaced in the probe immediately. Each aliquot was added to 2.5 ml cold isopentane. The rate of breakdown of the complex was monitored by measuring the absolute intensity of the doublet resonance at -17.4 ppm.

Oxidation of styrene by $[Ir(CH(Ph)CH_2)_2Cl]_2$

Dichloromethane (0.5 ml) was added to a mixture of the title complex (25 mg, 29 μmol), triphenylphosphine (8 mg, 30 μmol; 16 mg, 60 μmol; 24 mg, 90 μmol; 32 mg, 120 μmol; 40 mg, 150 μmol), 1,2-dichlorobenzene (2 μl) and styrene (37 μl, 290 μmol) in five experiments. Similarly triphenylphosphine was omitted from one sample. The reaction tubes (5 mm) were flame-sealed under an oxygen atmosphere. Samples containing phosphine changed colour from bright red to brown within minutes. The solution containing no excess triphenylphosphine maintained its red colour over the time period of the experiment. The reaction tubes were allowed to stand at 21°C for 2 h when the seal was broken and an aliquot removed for GLC analysis, vide supra. The tubes were resealed under oxygen and a second aliquot taken after 10 h. The oxidation products were estimated against the internal standard. Benzaldehyde was identified by comparison with an authentic sample (GLC; retention time 3.6 min (161°C). TLC; silica, dichloromethane, positive test with Brady's reagent.

Attempted oxidation of oct-1-ene by [Ir(5-phenyl-5H-dibenzophosphole)$_2$-(O_2)(C_2H_4)Cl], isomers

The isomer mixture (10 mg, 12 μmol) and oct-1-ene (10 μl, 60 μmol) were stirred under oxygen for 18 h at 40°C. Less than 2% (based on Ir) of octan-2-one was detected by GLC analysis (vide supra) by this time.

Attempted oxidation of olefins by iridium(I) cationic complexes

The complex [Ir(PPh_3)$_2$(C_2H_4)$_3$$BF_4$], was prepared in situ (10 mg, 12 μmol) as described (vide supra) to give a colourless or pale orange solution, under an ethylene atmosphere. Addition of styrene (15 μl, 60 μmol) followed by very gentle bubbling of argon through the solution produced a deepening in colour to red over several minutes. The admission of a blanket of oxygen over this solution resulted in a loss of the bright red colour to give a brown solution. Analysis of the solution by GLC (vide supra) showed acetophenone, 2-phenyloxirane and benzaldehyde in equal proportion.

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