

ACTIVATION OF MOLECULAR OXYGEN AND SELECTIVE OXIDATION OF OLEFINS  
 CATALYZED BY GROUP VIII TRANSITION METAL COMPLEXES

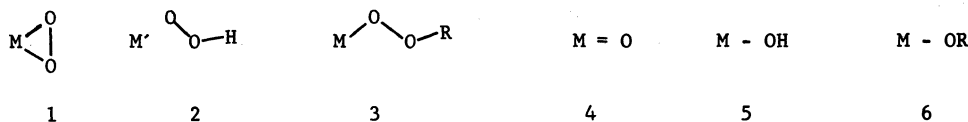
Hubert MIMOUN

Laboratoire d'Oxydation, Institut Français du Pétrole  
 92506 Rueil-Malmaison - France

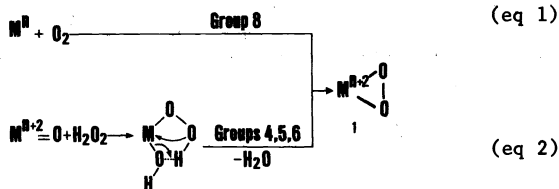
**Abstract** - A review is given on oxidation of terminal olefins to methyl ketones by O<sub>2</sub>, ROOH, or H<sub>2</sub>O<sub>2</sub> in the presence of rhodium, palladium, platinum and iridium catalysts. a) Rhodium catalysts can use both oxygen atoms of the dioxygen molecule for the oxidation of two moles of terminal olefins by the coupling of a cyclic or pseudocyclic peroxymetalation process with a Wacker-type intramolecular hydroxymetalation pathway. b) Palladium catalysts act as alkyl peroxidic (stable) or hydroperoxidic (generated from H<sub>2</sub>O<sub>2</sub> or protonation of peroxo complexes) reactive species for the oxidation of terminal olefins to methyl ketones. c) Platinum peroxo or hydroperoxidic species are generally inactive, but a stable and reactive platinum tert-butyl peroxide trifluoroacetate complex has been synthesized. d) Although iridium catalysts can coordinate both O<sub>2</sub> and olefin on the same metal center, they exhibit a different behavior with respect to rhodium complexes, and are generally poor oxidation catalysts. However IrOOH species, generated from reaction of O<sub>2</sub> with iridium hydride was found to oxidize coordinated cyclooctene to cyclooctanone. The problem of activation and transfer of molecular oxygen by the stepwise utilization of both oxygen atoms will be discussed.

INTRODUCTION

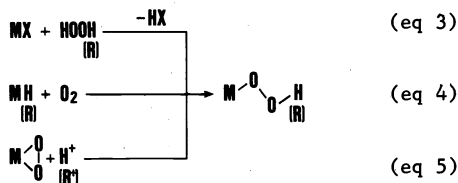
The search for transition metal catalysts capable of fixing molecular oxygen, and of transferring it selectively to organic substrates is a rewarding goal, owing to the economic impetus to develop new processes for the selective oxidation of hydrocarbons, and owing to the relevance of such catalysts to the naturally occurring oxygen-storage and transfer enzymatic systems. Reduced group VIII transition-metal complexes interact with molecular oxygen, even to the extent of forming stable reversible and irreversible dioxygen adducts (1). Since such adducts are potential oxygen donors to reactive substrates, they have been used for the oxidation of phosphines (2) and isonitriles (3), but until recently they were found quite reluctant to react with unactivated olefins by non-radical pathways (4). Potential group VIII oxygen donors involve : a) peroxidic species, i.e. peroxo 1, hydroperoxidic 2, and alkyl-peroxidic 3 complexes and b) non peroxidic species, i.e. oxo 4, hydroxo 5 and alkoxo 6 complexes.



Peroxo complexes can be obtained either from the reaction of a reduced two - electron donor metal complex with molecular oxygen (eq 1), or from the reaction of a high-valent metal-oxo complex with H<sub>2</sub>O<sub>2</sub> (eq 2) (5)



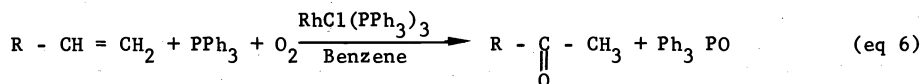
Hydro- or alkyl peroxidic complexes result from the reaction of a metal salt or complex with  $H_2O_2$  or  $ROOH$  (eq 3), from the insertion of  $O_2$  between a metal-hydrogen or metal-carbon bond (eq 4), or from the protonation or alkylation of a peroxy metal complex (eq 5) (5).



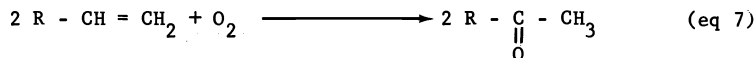
The way in which oxygen transfers from peroxy and hydro- or alkyl-peroxidic complexes is therefore relevant to oxidations involving activation and transfer of molecular oxygen (eq 1, 4 and 5), and to oxidations using  $H_2O_2$  and  $ROOH$  as the oxygen source (eq 2 and 3). Since peroxidic complexes 1 - 3 can only release one oxygen atom to a reactive substrate, oxo 4, hydroxo 5 and alkoxy 6 complexes result from the reduction of peroxy 1, hydroperoxy 2 and alkyl peroxy 3 complexes. Oxygen transfer from 4 - 6 complexes would result in the formation of reduced species which could reincorporate dioxygen, allowing the utilization of both oxygen atoms of the dioxygen molecule for the oxidation of two moles of substrate. Important questions are the following: i) What are the suitable conditions for realizing an oxygen transfer from group VIII transition metal peroxides to olefins? ii) Which metals are capable of using both oxygen atoms of the dioxygen molecule to oxidize two molecules of olefins? We will successively consider the behavior of rhodium, palladium, platinum and iridium catalysts in the selective oxidation of terminal olefins to methyl ketones by molecular oxygen, hydrogen peroxide and alkyl-hydroperoxides.

### I. RHODIUM CATALYSTS

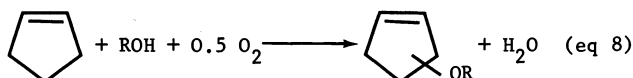
Read and coworkers have shown that rhodium complexes such as  $RhCl(PPh_3)_3$  are able to promote the co-oxygenation of terminal olefins to methyl ketones and triphenylphosphine to triphenylphosphine oxide, in conditions under which a Wacker-type oxidation (hydroxymetalation by water of the coordinated olefin) is disfavored (eq 6) (6)



In this reaction, one oxygen atom of the dioxygen molecule is incorporated into the olefin, while the phosphine acts as a coreducing agent by reacting with the second oxygen atom to produce the phosphine oxide. We have reported a different process for the catalytic oxidation of terminal olefins to methyl ketones by molecular oxygen using  $RhCl_3 + Cu(ClO_4)_3$  or  $Rh(ClO_4)_3$  alone as catalyst, and operating in alcoholic solvents in the absence of water or co-reducing agents such as phosphines (eq 7) (7).



In this reaction, both oxygen atoms are incorporated into two mol. of olefin to give two mol. of ketone with a selectivity based on consumed olefin and  $O_2$  of up to 98%. Ketones are produced only from olefins which can form  $\pi$ -complexes with rhodium (I), e.g. terminal olefins and internal olefins such as cycloheptene or cyclooctene. Instead, olefins which form  $\pi$ -allylic complexes of rhodium (III), e.g. cyclopentene, are transformed into alkenyl ethers resulting from the oxidative substitution of the alcohol used as solvent, on the saturated positions of the olefin (eq 8) (7)

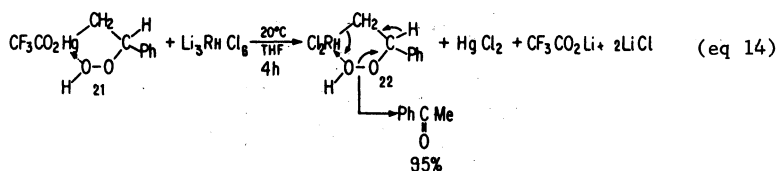


The overall catalytic oxidation of terminal olefins to methyl ketones by molecular oxygen has been interpreted as resulting from the coupling of two complementary reactions: a) an oxygen activation and transfer pathway in which the first peroxidic oxygen atom is transferred to





according to a pseudocyclic hydroperoxymetalation mechanism (*vide infra*), producing the ketone and the rhodium hydroxy complex 16. Such a process has been illustrated by the transmetalation of mercury by rhodium in  $(CF_3CO_2)_2Hg-CH_2-CH(Ph)-OOH$  21 (11), producing the unstable pseudocyclic compound 22 which decomposes to give acetophenone in 95 % yield (4h, 20°C, THF) (12) (eq 14).

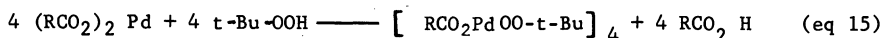


The resulting Rhodium (III) hydroxo complex 16, which can also be obtained from the protonation of the oxo complex 13, can further react with a second molecule of olefin according to an intramolecular hydroxymetalation mechanism (Wacker type) to give the hydrido complex 18. This complex 18 can directly react with  $O_2$  and regenerate the hydroperoxo complex 19 (13), making the reaction catalytic. Hence, the catalytic formation of 2 mol of methyl ketone from 2 mol of terminal olefins and one mol of dioxygen can be interpreted as resulting from a reaction step by step of each oxygen atom of  $O_2$ . The first peroxidic oxygen atom reacts by a cyclic (from peroxo complex 11), or a pseudocyclic (from hydro peroxo complex 19) peroxymetalation procedure, while the second hydroxilic oxygen atom reacts by a Wacker-type hydroxymetalation procedure.

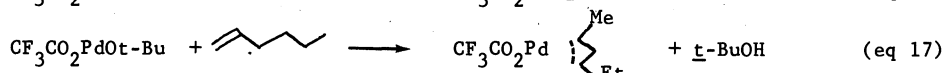
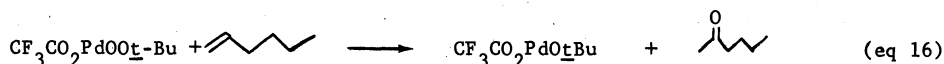
## II. PALLADIUM CATALYSTS

### 1. Oxidation of Olefins by Palladium (II) *tert*-Butyl Peroxide Carboxylates

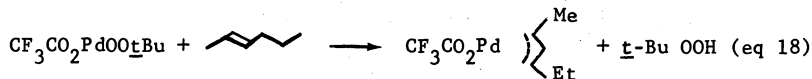
A new family of palladium (II) *tert*-butyl peroxide carboxylates of general formula  $[RCO_2Pd-OO-t-Bu]_4$  has been synthesized in high yield from the reaction of *tert*-butyl hydroperoxide with palladium carboxylates (eq 15).



These stable crystalline yellow-orange complexes have been characterized by elemental analysis, IR., NMR and X-ray crystallography. The structure of  $[CCl_3CO_2Pd-OOt-Bu]_4$  consists of four coplanar palladium atoms bonded between them alternatively by the oxygen atoms of the trichloroacetate groups and by the terminal oxygen atom of the  $OOt-Bu$  groups. These complexes are most efficient reagents for the selective oxidation of terminal olefins to methyl ketones in anhydrous and anaerobic conditions. Their reactivity toward terminal olefins decreases in the order  $R = CF_3 > C_2F_5 > CCl_3 > CH_3$ . The reaction of  $[CF_3CO_2Pd-OOt-Bu]_4$  with 1-hexene has been shown to proceed in two steps: (a) Oxygen transfer from the *tert*-butyl peroxidic complex to the olefin, producing the methylketone and the palladium *tert*-butoxy complex (eq 16) followed by (b) a rapid substitution of the  $O-t-Bu$  group by the olefin on the metal, giving rise to the formation of *tert*-butanol and the  $\pi$ -allylic complex (eq 17).

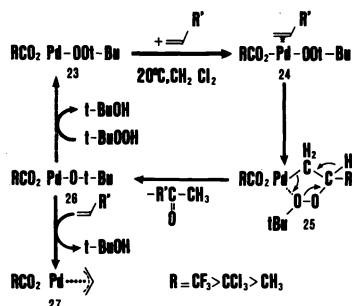


Only terminal olefins are selectively oxidized to the corresponding methylketones. Internal olefins directly produce the  $\pi$ -allylic complex upon exchange with the  $OOt-Bu$  group (eq 18)

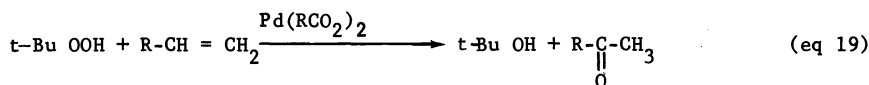


Several  $\pi$ -allylic Pd(II) trifluoroacetate complexes of general formula  $[CF_3CO_2Pd(\pi\text{-allyl})]_2$  have been isolated in this way from the reaction of  $[CF_3CO_2PdOOt-Bu]_4$  with both terminal and internal olefins (14,15). The suggested mechanism for the oxidation of terminal olefins by  $[CF_3CO_2Pd-OOt-Bu]_4$  is depicted in Scheme II. The first step consists of coordination of the terminal olefin on palladium, producing the alkyl peroxidic  $\pi$ -olefinic complex 24. The intramolecular nucleophilic attack of the  $-OOt-Bu$  group on the coordinated electrophilic olefin constitutes the *cis*-peroxy-palladation step of this mechanism and gives rise to the formation of the five membered pseudocyclic intermediate 25. The pseudocyclic nature of 25 is due to electron donation from the oxygen atom adjacent to the *tert*-butyl group to the vacant coordination site on the metal resulting from the peroxymetalation of the olefin. Decomposition of 25 occurs with the rupture of the O-O bond, followed by a  $\beta$ -hydride migration, producing the methylketone and the palladium *tert*-butoxy complex 26. The decomposition of 25 is similar to

Scheme II

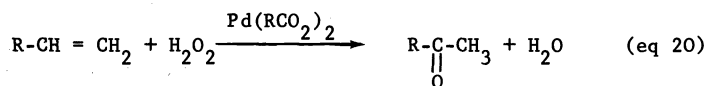


that of the closed five-membered rhodium peroxymetallo cyclic adduct previously shown in eq 9. The pseudocyclic peroxy palladation procedure has been evidenced, as previously shown in eq. 14, by the transmetalation of mercury by palladium in the reaction of  $\text{Na}_2\text{PdCl}_4$  with  $\text{CF}_3\text{CO}_2\text{HgCH}_2\text{CH}(\text{Ph})\text{-O}t\text{Bu}$ , producing acetophenone in 95 % yield (20°C, THF solution). Methylketones can be obtained on a catalytic scale when an excess of *t*-BuOOH is used for regenerating the initial *tert*-butyl peroxidic complex 23 from the *tert*-butoxy complex 26. (Scheme II). In order to avoid the formation of a  $\pi$ -allylic complex 27 causing lower selectivities, a large excess of *t*-Bu OOH with respect to olefin is required (eq 19) (16)

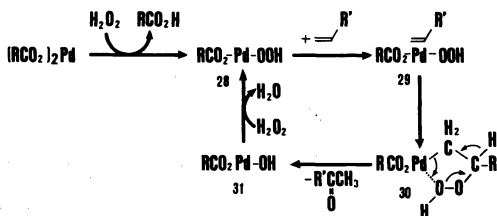


## 2. Palladium-Catalyzed Oxidation of Terminal Olefins to Methyl-Ketones by Hydrogen Peroxide

Palladium carboxylates are effective catalysts for the selective oxidation of terminal olefins to methyl ketones by hydrogen peroxide (eq 20) (17)



This reaction can be carried out at room to moderate (80°C) temperature, in biphasic (benzene or ethyl acetate) or monophasic (*tert*-butanol or acetic acid) solution. A large excess of  $\text{H}_2\text{O}_2$  with respect to olefin is required in order to prevent  $\pi$ -allylic complex formation causing isomerization of olefin. Only terminal olefins, e.g., 1-hexene, 1-octene, allyl acetate, were selectively oxidized to the corresponding methyl ketone. Internal linear or cyclic olefins were found to be unreactive. Palladium-catalyzed decomposition of  $\text{H}_2\text{O}_2$  occurs during the reaction. Oxidation of 1-octene in *t*-Bu OH by  $\text{H}_2\text{O}_2$  (16) catalyzed by  $\text{Pd}(\text{OAc})_2$ , and in the presence of a large excess of  $\text{H}_2\text{O}$  (18), only produces unlabeled 2-octanone. This indicates that the oxygen source for ketone formation is only  $\text{H}_2\text{O}_2$  and not water as in the Wacker Process. The following mechanism, similar to that previously shown for the oxidation of terminal olefins by Palladium *tert*-butyl peroxidic complexes, has been suggested (Scheme III) (17)



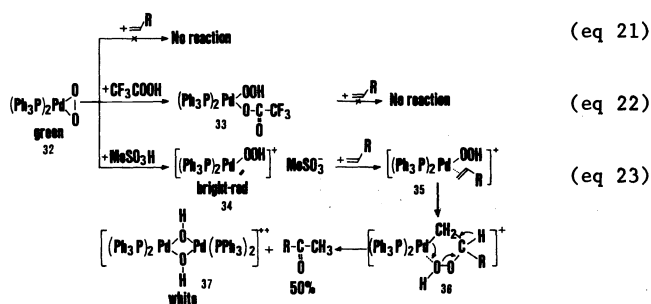
Scheme III

As a reactive intermediate, this mechanism involves the palladium hydroperoxidic compound 28 resulting from the exchange on Pd of one carboxylate by  $\text{H}_2\text{O}_2$ . This compound acts similar to the palladium *tert*-butyl peroxidic complex 23, and releases one oxygen atom to the coordinated terminal olefin according to a pseudocyclic hydroperoxypalladation procedure, producing the methylketone and a palladium hydroxo complex 31. The hydroperoxidic complex 28 is regenerated from 31 upon reaction with  $\text{H}_2\text{O}_2$ , liberating water. Despite many attempts, and due to

extensive  $H_2O_2$  decomposition, the isolation of such palladium hydroperoxidic species failed. However, the existence of such complexes as reactive intermediates will be justified in the next paragraph.

### 3. Oxidation of Terminal Olefins to Methyl Ketones by Palladium Dioxygen Complexes Induced by Strong Non-Coordinating Acids and Alkylating Agents

Contrary to rhodium dioxygen complexes, palladium compounds such as  $L_2PdO_2$  ( $L =$  phosphine) do not react with terminal olefins (eq 21). Since hydroperoxidic and alkylperoxidic palladium species are potential oxidizing reagents, we have tried to generate such compounds by protonating or alkylating inactive palladium peroxy compounds by strong non-coordinating acids and alkylating agents (18). Hydroperoxidic species have been previously shown to be involved as intermediates in the acid hydrolysis of Pd and Pt dioxygen complexes, yielding  $H_2O_2$  (19). Addition of a stoichiometric amount of  $MeSO_3H$  to an anhydrous solution of  $(Ph_3P)_2PdO_2$  in  $CH_2Cl_2$ -1-octene solution in anaerobic condition, results in an immediate change in color from green to bright red, and progressive formation of 2-octanone (50 % based on Pd) and  $Ph_3PO$  (36 %), while no precipitation of metallic palladium occurs. The quantity of 2-octanone produced was found proportional to the quantity of added  $MeSO_3H$  until a ratio  $H^+ : Pd = 1$ . Addition of  $HBF_4$  instead of  $MeSO_3H$  results in lower yields in 2-octanone (ca 20 %), but in this case, the final complex has been identified as  $[(Ph_3P)_2Pd(OH)_2Pd(Ph_3P)_2]^+BF_4^-$  (20). A labeling study using  $(Ph_3P)_2Pd^{16}O_2$ ,  $MeSO_3H$ , 1-octene, and an excess of  $H_2^{18}O$  indicated the exclusive incorporation of unlabeled oxygen into the resulting 2-octanone, showing that the oxygen source in this reaction is molecular oxygen, and not water as in the Wacker Process. Only terminal olefins were selectively oxidized to the corresponding methyl ketone. Internal cyclic and acyclic olefins were found unreactive.



Treatment of  $(Ph_3P)_2PdO_2$  with a strong coordinating acid such as  $CF_3CO_2H$  results in a quite complete inhibition of the reaction, which is probably due to the occupation of the vacant site by the trifluoroacetate group in 33 (eq 22). Equation 23 illustrates a plausible interpretation of the oxidative properties of 32 in the presence of strong non-coordinating acids. Protonation of 32 results in the opening of the peroxy group liberating a vacant site adjacent to the hydroperoxidic group in 34. The complexation of terminal olefin in 35 is followed by a pseudocyclic hydroperoxypalladation giving the intermediate 36 which decomposes to produce the methyl ketone and the hydroxo complex which ends in the form of a di- $\mu$ -hydroxo complex 37. A further evidence for the involvement of palladium hydroperoxidic species as reactive intermediate has been obtained from the transmetalation reaction of mercury in  $CF_3CO_2HgCH_2CHPh-OH$  by palladium in  $Li_2PdCl_4$ , producing the unstable pseudocyclic palladium peroxidic adduct which decomposes to give acetophenone in 85 % yield (THF, 20°C, 4h) (18). 2-Octanone has also been produced, albeit in lower yields (ca 20 %), from the reaction of 32 with 1-octene in the presence of an alkylating agent such as  $FSO_3Me$ ,  $CF_3SO_3Me$  or  $Ph_3C^+BF_4^-$ . Also in this case, a change in color from green to bright red was observed, but in every case, the medium was heterogeneous. A mechanism similar to that of eq 23 could be suggested, with the formation of reactive alkylperoxidic species.

### III. PLATINUM CATALYSTS

Platinum dioxygen complexes such as  $L_2PtO_2$  ( $L =$  phosphine) are known to catalyze the oxidation of phosphines (2), or to cause oxidative cleavage of electrophilic olefins (21). However, like the palladium analogues, they are quite reluctant to react with unactivated olefins. Platinum hydroperoxidic species have been postulated as intermediates in the acid hydrolysis of Pt peroxy complexes (19).  $L_2Pt(CF_3)OOH$  complexes ( $L =$  bidentate diphosphine) have been recently synthesized but were also found inactive toward olefins (22). We have used the procedure previously described for  $PdO_2$  complexes, in order to induce a reactivity toward olefins of the platinum analogues. However, no oxygenated products were detected from the reaction of  $(Ph_3P)_2PtO_2$  with both terminal (1-octene) or internal (norbornene, cyclohexene) olefins in the presence of  $MeSO_3H$  or  $Ph_3C^+BF_4^-$  (eq 25). This absence of reactivity was

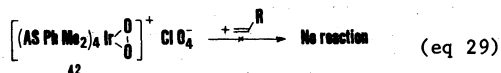




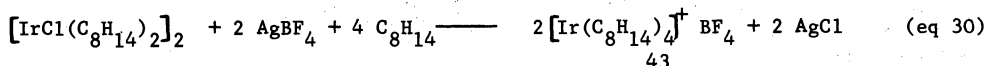
Thus, in contrast to palladium, platinum forms less-well defined alkyl peroxidic complexes with tBuOOH, which are far less reactive toward olefins. This reactivity however exists, and is strongly dependent upon the electrophilic character of the metal favoring the complexation of the olefin. Another difficulty in the case of platinum catalysed oxidation of olefins comes from the fact that platinum (II) is more easily oxidized to Pt (IV), in contrast to palladium.

#### IV. IRIIDIUM CATALYSTS

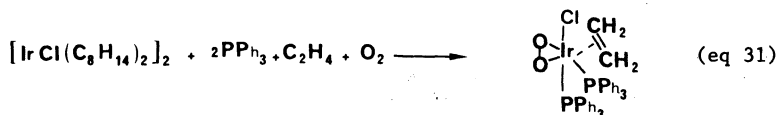
In contrast to rhodium cationic dioxygen complexes (8), iridium analogues such as  $[(\text{AsPhMe}_2)_4\text{IrO}_2]\text{ClO}_4$  (24) do not undergo an oxygen transfer reaction to terminal olefins such as 1-octene (eq 29). No reaction occurs even in the presence of a stoichiometric amount of a strong acid, such as  $\text{MeSO}_3\text{H}$  or  $\text{HBF}_4$ .



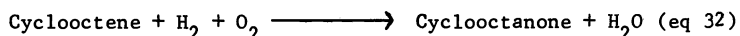
Iridium dioxygen complexes being inactive with respect to terminal olefins, we have studied the reactivity of iridium (I)  $\pi$ -olefinic complexes toward molecular oxygen. Our attempts to synthesize the complex  $[\text{IrCl}(1,7\text{-octadiene})_2]_2$  failed, so we started from the known  $[\text{IrCl}(\text{cyclooctene})_2]_2$  compound, and we prepared *in situ* the iridium cationic complex  $[\text{Ir}(\text{C}_8\text{H}_{14})_4]^+\text{BF}_4^-$  from the reaction of the di- $\mu$ -chloro complex with  $\text{AgBF}_4$  in  $\text{CH}_2\text{Cl}_2$  in the presence of an excess of cyclooctene (eq 30)



The orange solution of 43 in  $\text{CH}_2\text{Cl}_2$  absorbed one mole of dioxygen per mole of iridium, and the solution became green. However, no formation of cyclooctanone was detected by GLC analysis (eq 33) (12). All attempts to isolate this green complex, probably having olefin and  $\text{O}_2$  coordinated on the same metal, failed even in the presence of ligands such as phosphines or 2,2'-bipyridine. It is noteworthy that a stable iridium complex having both ethylene and dioxygen coordinated to the same metal has been synthesized, without any oxygen transfer reaction occurring in this case (eq 31) (25)



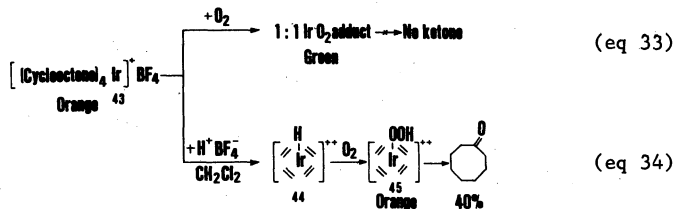
Hence, it appears that coordination of olefin and dioxygen on the same metal center is a necessary but not sufficient condition for achieving an oxygen transfer reaction. A suitable position for both substrate and reagent is also required in the coordination sphere of the metal. James and coworkers have recently shown that cyclooctene can be catalytically oxidized to cyclooctanone and water by a mixture of  $\text{H}_2 + \text{O}_2$  in the presence of  $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$  (eq 32) (26)



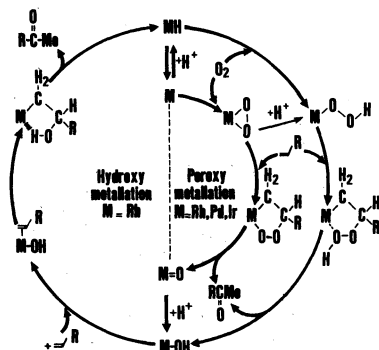
Ir-OOH species, obtained from the reaction of  $\text{O}_2$  with iridium hydride, have been assumed to be the reactive intermediates in this reaction. As we did for rhodium and palladium, we have tried to generate reactive iridium hydroperoxidic species by carrying out the oxidation by  $\text{O}_2$  of the cationic complex 43 in the presence of one equivalent of  $\text{HBF}_4$  and excess cyclooctene (12). The orange solution of 43 in  $\text{CH}_2\text{Cl}_2$  absorbed one mole of dioxygen per mole of iridium in 4h at  $20^\circ\text{C}$  without change in color, but glc analysis indicated the formation of cyclooctanone in ca 40% based on iridium. A plausible mechanism for this reaction shown in eq 34 involves the protonation of the cationic complex 43 by  $\text{HBF}_4$ , followed by  $\text{O}_2$  addition giving the hydroperoxidic species 45. Ketone formation would result from the intramolecular hydroxymetalation of a coordinated cyclooctene molecule. It should be pointed out that ketone yields obtained with iridium are much lower than those previously observed with rhodium. However, less than one oxygen atom can be transferred to the olefin. This indicates that a consecutive hydroxymetalation of olefin on iridium does not occur, thus preventing a catalytic formation of ketone.

#### CONCLUSION

We have shown in this study that molecular oxygen can be activated by group 8 metal complexes, and transferred to unactivated olefins, provided that reactive peroxidic species are



produced. Oxygen transfer from transition metal peroxides requires the complexation of the olefin on a suitable position with respect to the peroxidic moiety on the coordination sphere of the metal. It likely occurs according to a cyclic peroxymetalation procedure (from a peroxy metal complex), or according to a pseudocyclic peroxymetalation procedure (from alkyl or hydroperoxidic metal complexes). Amongst those metals, rhodium alone can use both oxygen atoms for the oxidation of two moles of olefins. Palladium and iridium complexes only transfer the peroxidic oxygen atom. These results are summarized in Scheme IV.



Scheme IV

Platinum peroxidic complexes are reluctant to react with olefins, except when the metal is strongly electrophilic e.g. in  $[(\text{CF}_3\text{CO}_2)_2\text{Pt}(\text{OOtBu})(\text{tBuOH})_2]$ . The interpretation of the oxidative properties of group VIII transition metal complexes based on the behavior of their peroxidic derivatives, allows a rationalization of catalytic oxidation of olefins whatever the oxygen source is  $\text{O}_2$ ,  $\text{ROOH}$  or  $\text{H}_2\text{O}_2$ . The peroxymetalation concept places these reactions inside the scope of conventional metal-catalyzed transformation of olefins.

**Acknowledgments** - I thank sincerely my coworkers named in references, who have contributed to the work carried out in these laboratories. These comprise Mrs F. Igersheim ( $\text{O}_2$  Activation), Mr R. Charpentier ( $\text{Pd-OOtBu}$ ), Mr M. Roussel and Mr J. Guibourd ( $\text{Pd-H}_2\text{O}_2$ ), Dr J.M. Bregeault ( $\text{Pt-H}_2\text{O}_2$ ) and the Laboratory of Professor R. Weiss (X-ray crystal structure)

## REFERENCES

- (a) R.D.Jones, D.A. Summerville and F. Basolo, *Chem.Rev.*, **79**, 139, (1979)  
 (b) L.Vaska, *Acc.Chem.Res.*, **9**, 175 (1976)  
 (c) J.S. Valentine, *Chem.Rev.*, **73**, 235 (1973)  
 (d) V.Y.Choy and C.J. O'Connor, *Coord.Chem.Rev.*, **9**, 145 (1972)  
 (e) G. Henrici-Olivé and S. Olivé, *Angew.Chem.Int. Ed.Engl.*, **13**, 29 (1974)
- (a) G. Wilke, H. Sholt and P. Heimbach, *Angew.Chem.Int. Ed.Engl.*, **6**, 92 (1967)  
 (b) A. Sen and J. Halpern, *J.Am.Chem.Soc.*, **99**, 8337 (1977) and references therein
- S. Otsuka, A. Nakamura and Y. Tatsuno, *J.Am.Chem.Soc.*, **91**, 6994 (1969)
- A. Fusi, R. Ugo, A. Pasini and S. Cenini, *J.Organo.metall.Chem.*, **26**, 417 (1971)
- H. Mimoun, *J.Mol.Cat.*, **7**, 1 (1980)
- (a) C. Dudley and G. Read, *Tetrahedron Lett.*, **52**, 5273 (1972)  
 (b) C. Dudley, G. Read and P.J.C. Walker, *J.Chem.Soc.Dalton.Trans.*, 883 (1977)

7. H. Mimoun, M.M. Perez-Machirant and I. Serée de Roch, J. Am. Chem. Soc. **100**, 5437 (1978)
8. F. Igersheim and H. Mimoun, J. Chem. Soc. Chem. Commun., 559 (1978). Nouv. J. Chim., **4**, 161 (1980)
9. R. Tang, F. Mares, N. Neary and D.E. Smith, J. Chem. Soc. Chem. Commun., 274 (1979)
10. H. Mimoun, I. Sere de Roch and L. Sajus, Tetrahedron **26**, 37 (1970)
11. V.I. Sokolov, Izvest. Akad. auk. USSR, 1089 (1972)
12. F. Igersheim. Ph.D. Thesis (1981)
13. H.L. Roberts and W.R. Symes. J. Chem. Soc. A, 1450 (1968)
14. H. Mimoun, R. Charpentier, A. Mitschler, J. Fisher and R. Weiss. J. Am. Chem. Soc., **102**, 1047 (1980)
15. B.M. Trost and P.J. Metzner, J. Am. Chem. Soc., **102**, 3572 (1980)
16. H. Mimoun, R. Charpentier and M. Roussel. GER.OFFEN **2**, 949, 847 (to IFP), 1980
17. M. Roussel and H. Mimoun. J. Org. Chem. **45**, 5387 (1980). Tsuji and coworkers have independently found that  $\alpha, \beta$  unsaturated esters and ketones are oxidized to  $\beta$ -keto esters and 1,3-diketones by t-Bu OOH or H<sub>2</sub>O<sub>2</sub> using Na<sub>2</sub>PdCl<sub>4</sub> as catalyst. J. Tsuji, H. Nagashima, and K. Hori, Chem Lett., 257 (1980)
18. F. Igersheim and H. Mimoun, Nouv. J. Chim **4**, 711 (1980).
19. S. Muto, H. Ogata and Y. Kamiya, Chem Lett, 809 (1975). S. Bhaduri, L. Casella, R. Ugo, R. Raithby C. Zuccaro and M.B Hursthouse, J. Chem. Soc. Dalton, Trans., 1624 (1979)
20. G.W. Bushwell, K.R. Dixon, D.G. Hunter and J.J. Mc Farland, Can. J. Chem., **50**, 3694 (1972)
21. R.A. Sheldon and J.A Van Doorn, J. Organometal. Chem., **94**, 115 (1975)
22. R.A. Michelin, R. Ros and G. Strukul, Inorg. Chim. Acta **37**, L 491 (1979)
23. J.M. Bregeault and H. Mimoun. Nouv. J. Chimie (in the press)
24. L.M. Haines, Inorg. Chem., **10**, 1685 (1971)
25. H. Van Gaal, H.G.A.M. Cuppers, A. Van der Ent, J. Chem. Soc. Chem. Commun., 1594 (1970)
26. B.R. James, Adv. Chem. Ser., **191**, 253 (1980)