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Transition Metal Percarboxylates, Alkylperoxides, and Hydroperoxides

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Data on methods for preparing transition metal percarboxylates, alkylperoxides, and hydroperoxides are systematically reviewed. The factors determining their stability and the most typical routes for their reactions are discussed. The ability of these compounds to act as efficient carriers of oxygen atoms to substrates of various kinds is emphasised using numerous examples.
The bibliography includes 179 references.

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I. INTRODUCTION

The development of the chemistry of peroxide complexes of transition metals (TMPC's), such as complexes of the types $L_nM\langle^{O}_{O}|$, L_nMOOML_n, L_nMOOR (where M is a transition metal, L an organic or other ligand, and R = H, alkyl or a substituted alkyl, or R'CO), is of great importance for solving theoretical and practical problems in the catalytic oxidation of substrates of various kinds. The large amount of data so far accumulated give good reason to suppose that peroxide complexes with this structure, which are intermediates in biological oxygenation processes[1,2] and the catalytic oxidation of alkenes, alkanes, alcohols, amines, phosphines, sulphides, etc. by molecular oxygen and hydroperoxides,[3-11] are responsible for the transfer of oxygen to the oxidisable substrate, which may take place stereospecifically or stereoselectively.

The natural interest of research workers in reactions involving peroxide complexes leads to the publication in the domestic and foreign literature of an ever increasing amount of pertinent data which needs classifying. Progress in the chemistry of transition metal mono- [metal] and di-[metal]-peroxo-complexes $L_nM\langle^{O}_{O}|$ and L_nMOOML_n is comparatively fully reported in a number of reviews.[12-16] The role of the peroxides L_nMOOR (TMPC) in the mechanism of catalytic epoxidation and ketonisation of alkenes is discussed in detail in other reviews.[3-10]

There is an absence of articles of a general nature in which various aspects of the chemistry of TMPC's, such as methods of preparation, physicochemical properties, and stoichiometric and catalytic oxidation involving them, might be discussed.

The aim of the present review is to fill an existing gap in the classification of data on the chemistry of transition metal percarboxylates and alkyl- and hydro-peroxides.

II. METHODS OF PREPARATION

1. Transition Metal Alkylperoxides

Transition metal alkylperoxides are the most widespread of the TMPC's presently known.

The first peroxides of this type to be prepared were titanium compounds with the general composition $R_{4-n}Ti(OOR)_n$, which are formed by the reaction of titanium halides or alkoxides with t-butyl hydroperoxide:[17]

$$TiCl_4 + n\,Bu^tOOH \xrightarrow[NH_3\cdot py]{0\div 20^\circ C} (Bu^tOO)_nTiCl_{4-n} + n\,HCl, \quad (1)$$

$$Ti(OPr^i)_4 + n\,Bu^tOOH \xrightarrow[py]{0\div 20^\circ C} (Bu^tOO)_nTi(OPr^i)_{4-n} + n\,Pr^iOH. \quad (2)$$

This method[17] for preparing TMPC's, the basis of which is substitution of one of the ligands attached to the metal (usually a halide, hydroxide, or alkoxide):

$$L_nMX + ROOH \rightarrow L_nMOOR + HX \quad (3)$$

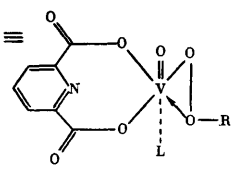
has also been used to prepare alkylperoxides of titanium (X = acac, OEt; $R = Bu^t$),[7,18-20] vanadium (X = OEt, OPr^i, OBu^t, $R = Bu^t$),[21-26] and palladium and platinum (X = an anion of a carboxylic or sulphonic acid; R = alkyl, aryl, or arylalkyl;[27-30] or X = OH; $R = Bu^t$ [31,32]).

If X in the complex L_nMX in Eqn.(3) is a halogen or a carboxylate anion, in place of ROOH the alkali metal salts can be used. The alkylperoxides of palladium, platinum,zirconium, and rhodium have been obtained in this way.[30,33-35]

The preparations[3] of the alkylperoxides of the vanadium dipicolinates (dipic)V(O)(OOR)L [L = H_2O or HMPT (hexametapol); R = Bu^t, cumyl],[36,37] which are described by Eqns.(4) and (5):

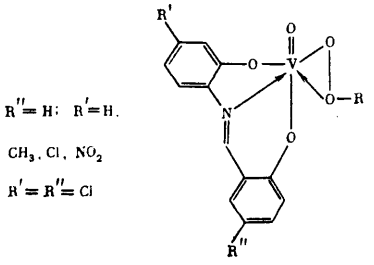
$$V_2O_5 + \text{dipic}\,H_2 + ROOH \xrightarrow{H_2O} \text{(dipic)}\,V(O)(OOR)\cdot H_2O \quad (4)$$

$$V(O)(OPr^i)_3 + HMPT + \text{dipic}\,H_2 + ROOH \rightarrow \text{(dipic)}V(O)(OOR).HMPT + 3Pr^iOH \quad (5)$$

(dipic)V(O)(OOR)·L ≡ 

are variations on Eqn.(3).

Alkylperoxides of oxo-[*N*-(2-oxidophenyl)salicylideneiminato]-vanadium have been obtained in a similar way:[38]

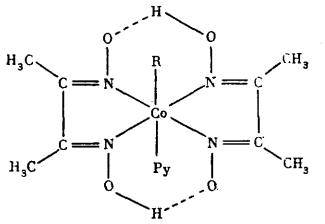


Reactions (4) and (5) have been shown to proceed via the complexes (dipic)V(O)OH.H_2O and (dipic)V(O)(OPr^i).HMPT respectively, which react with ROOH to form the desired products.

The replacement of the ligands attached to the metal by the alkylperoxide moiety can be initiated by ultraviolet light, as in the reaction of alkylpyridinecobaltoximes R[Co]py with R'OOH:[39]

$$R\text{-}[Co]\text{-}py + 2R'OOH \xrightarrow[C_6H_6/N_2]{h\nu} py[Co]OOR' + R'OOR, \quad (6)$$

where R = cumyl or t-butyl, and R' = $C(CH_3)_3$, $C(CH_3)_2C_6H_5$, $CH(CH_3)C_6H_5$, C_6H_{11}, or $CH(CH_3)C_6H_4CH_3$, and [Co] represents a Co^{II} oxime or $(Dmg)_2Co$.



This last process[39] takes place via a stage in which there is photodissociation of the metal–carbon bond and the (py)Co^{II} complex formed then reacts with ROOH.

Another general method for the preparation of transition metal alkylperoxides is based on the attachment of ROOH or the peroxide moiety OOR to transition metal complexes (TMC's), which may take place with or without a change in the oxidation state of the metal:

$$L_nM + ROOH \longrightarrow L_nM^{+}\bar{O}OR \quad (7a)$$

$$L_nM + ROOH \longrightarrow L_nM^{2+}(\bar{O}OR)(H^-) \quad (7b)$$

$$L_nM + RO_2^{\cdot} \rightarrow L_nM^{+}\bar{O}OR \quad (8)$$

$$L_nM{=}O + ROOH \rightarrow L_nM\begin{matrix}OOR\\OH\end{matrix} \quad (9)$$

Reaction(7)† has been carried out in the following cases:

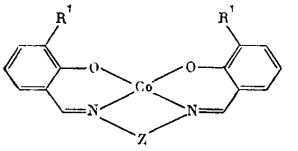
(1) For $(Arene)_2Cr$ complexes and molybdenum and tungsten cyclopentadienyl complexes Cp_2MX_2 (X = Cl, Br, I), giving the peroxides $Ar_2Cr^{+}(OOR.ROOH)^{-}$ (R = Bu^t, cumyl)[40] and $Cp_2MX_2^{+}(OOR.ROOH)^{-}$ (R = t-butyl, cumyl, t-pentyl, or α-phenylethyl)[41–43] respectively:

$$L_nM + 3ROOH \underset{-S}{\overset{SH}{\rightleftarrows}} L_nM^{+}(OOR{\cdot}ROOH)^{-} + ROH + H_2O \quad (10)$$

(2) For cobalt pyridine-acetylacetonates[44] and cobalt(II) complexes with Schiff bases, in reactions with t-butyl and cumyl hydroperoxides, to form cobalt(III) peroxides:[44–47]

$$2[Co^{II}] + 3ROOH \xrightarrow[CH_2Cl_2]{20^\circ C} 2ROO\text{—}[Co^{III}] + ROH + H_2O \quad (11)$$

where [Co^{II}] are the complexes

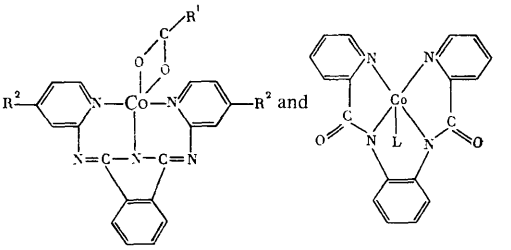


R^1=H; Z=MeN$\begin{matrix}(CH_2)_3\\(CH_2)_3\end{matrix}$ (Co (NMe salpr)), $(CH_2)_2$ (Co (salen)), OC_6H_4 (Co (salphen)),

HN$\begin{matrix}(CH_2)_3\\(CH_2)_3\end{matrix}$ (Co (salpr));

R^1=OMe, Z=$(CH_2)_2$ (Co (MeO salen))

and also other Co^{II} complexes: the 1,3-bis-(2-pyridylimino)isoindole and *N,N'*-bis-(2'-pyridinecarboxamido)-1,2-benzene complexes



Co(R^2BPI^{1-},OCOR^1) Co(BPB)(4-Mepy)

(3) For the iridium complexes $IrX(CO)L_2$ (L = PPh_3, PPh_2Me, or $AsPh_3$), which react with t-butyl and cumyl hydroperoxides to give either mono- (X = I) or bis-alkylperoxides (X = Cl, Br):[48–50]

$$IrI(CO)L_2 + ROOH \rightarrow Ir(H)I(OOR)(CO)L_2 \quad (12)$$

$$IrX(CO)L_2 + 2ROOH \rightarrow \begin{matrix}L\\OC\end{matrix}\!\!\begin{matrix}OOR\\|\\Ir\\|\\X\end{matrix}\!\!\begin{matrix}OOR\\L\end{matrix} \quad (13)$$

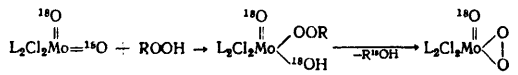
The complex Ir(H)I(OOR)(CO)L_2 is unstable and is converted to the more stable peroxide Ir(CO)(OOR)I_2L_2 by successive elimination of HI and addition of I_2.

Reaction (8) has been studied in detail as one of the effective methods of inhibiting radical-chain processes involving ROOH or O_2.[51–67] The reaction occurs for TMC's in various groups of the Periodic Table.

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† Reaction (7a) includes oxidation of the initial metal complex to the hydroxide $L_nM^{+}OH^{-}$, the reaction of which with ROOH [Eqn.(3)] also gives the desired product.

An example of Eqn.(9) is the formation of alkylperoxide complexes from the labelled oxo-complex of molybdenum $L_2Cl_2Mo(^{18}O)_2$:[9]



(14)

The possible preparation of alkylperoxide complexes by the reaction of TMC's with ROOH is also discussed in a number of papers on the specific synthesis of these compounds—derivatives of titanium,[68] zirconium,[69] vanadium,[21-26] chromium,[40], and molybdenum,[41] in numerous papers on the hydroperoxide catalytic oxidation of substrates of various kinds (alkenes, alkanes, alcohols, ethers, amines, etc.) on vanadium,[70-76] chromium,[77,78] molybdenum and tungsten,[9,10,70-75] manganese,[79] rhodium,[3-10,80-86] iridium, palladium, and platinum,[3-10] and titanium[20,87] compounds, and in studies of the mechanism of the catalysed decomposition of alkyl hydroperoxides.[88,89]

Methods for preparing alkylperoxide complexes are not restricted to reactions of TMC's with ROOH. A considerable number of these compounds are obtained by auto-oxidation of TMC's. If the latter contain a metal–alkyl bond or one emerges during their oxidation, alkylperoxide complexes are usually formed by the insertion of an oxygen molecule into this bond:

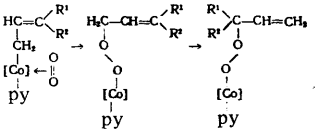
$$L_nM-R+O_2\rightarrow L_nMOOR \qquad (15)$$

Reaction (15) has been studied in greatest detail for the alkylcobaloximes R–[Co]–L.[90-103] Depending on the energy of the Co–R bond, which is determined by the nature of R and the ligand in the axial position, the insertion of oxygen may occur under ambient conditions, on photochemical irradiation, or at high temperatures in a chloroform, acetone, or methanol solution:

$$py-[Co]-R+O_2\xrightarrow{h\nu}py-[Co]-OOR \qquad (16)$$

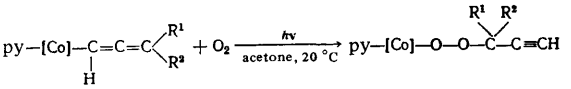
where [Co] represents the cobaloxime.

When R is a substituted allyl group, isomerisation of this group can occur simultaneously with the insertion of oxygen by a concerted mechanism:[97]



(17)

When R is a substituted allenyl or prop-2-ynyl group, in both cases the product contains a prop-2-ynyl radical:



(18)

The mechanism of the insertion of oxygen into the Co–R bond has not been unambiguously established. For the thermal insertion [py(Dmg)$_2$Co–R complexes] three possible mechanisms are proposed: a radical,[96] cryptoradical,[97] and molecular[97] mechanism. Data on the thermal stability of alkylcobaloximes and the kinetics of their oxidation[94,97] agree to a large extent with the cryptoradical mechanism:

$$RCoL\overset{\Delta}{\rightleftharpoons}\{R^{\cdot}\cdots\dot{C}oL\} \qquad (19)$$

$$\{R^{\cdot}\cdots{}^{\cdot}CoL\}+O_2\rightarrow ROOCoL \qquad (20)$$

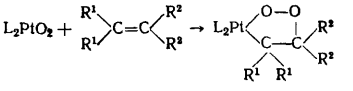
According to data in Ref.102 the mechanism of the photochemical insertion of oxygen into the Co–C bond can be described by reactions (19) and (20), the only difference being that the formation of the radical pair is initiated by light, although the role of light in the mechanism of photochemical oxidation of alkylcobaloximes has not been unambigously established.[97,101,104]

The production of tungsten benzylperoxide R_3WOOR from hexabenzylditungsten (–74 °C) not only touches on the metal–carbon bond but also on the metal–metal bond.[69,105]

The formation of platinum peroxides by Eqns.(21) and (22) [106-108] provides an illustration of a method for producing alkylperoxide complexes by the oxidation of an M–R bond formed *in situ*.

$$LPtMe_2+RI+O_2\rightarrow LPtMe_2(I)OOR \qquad (21)$$

(L = 1,10-phenanthroline or bipyridyl: R = Pr^i or But^t);



(22)

[R^1 = Me, R^2 = CN; R^1 = R^2 = CN; L = PPh_3, P(cyclo-C_6H_{11})$_3$].

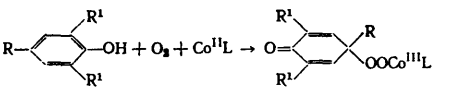
Reaction (21) may also have a radical non-chain mechanism, including a reaction of the platinum complex with RO_2 radicals.[107]

The formation of a C–Pt bond in the reaction of the oxygen complex $(PPh_3)_2Pt.O_2$ with $XCPh_3$ (X = Cl, Br) according to Eqn.(23) is unlikely on steric grounds:[108]

$$(PPh_3)_2Pt\cdot O_2+XCPh_3\xrightarrow{-40-\,-78^\circ C}(PPh_3)_2Pt(X)OOCPh_3 \qquad (23)$$

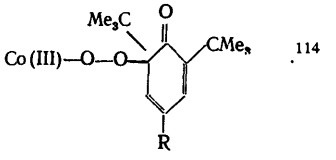
Indirect evidence for the formation of alkylperoxide complexes in accordance with Eqn.(15) has been obtained in studies of the processes of auto-oxidation of other TMC's with σ-bonded organic ligands, viz. $Cp_2Zr(R)Cl$,[34] tetrabenzylzirconium and tetrabenzylhafnium, dialkylzirconocene and dialkylhafnocene,[69,105] the zirconium complex $(tritox)_2ZrMe(OCMe_2CH=CH_2)$ (tritox = Bu^t_3CO),[109] and hexakis(trimethylsilylmethyl)dimolybdenum.[69]

The formation of peroxide compounds of the LCoOOR type on auto-oxidation of cobalt salfuryl [sic?; Schiff base ligands based on salicylaldehyde and amines (Ed.of Translation)] complexes, and also pyridinecobaloxime, which do not contain a direct cobalt–carbon bond and do not form one in the intermediate stages of the reaction, is described by Eqn.(24).[45,110,118]



(24)

where L = $(DmgH)_2$py, salpr, NMe(salpr), and other substituted salfuryl ligands and R^1 = CMe_3. Where R is an aryl group the cobalt-peroxide bond is formed in position 2 of the phenyl ring:

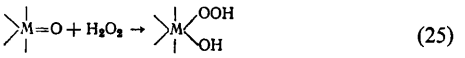


A distinctive feature of this process [Eqn.(24)] is that the formation of the peroxide CoOOR takes place at the stage where there is a reaction of the phenoxyl radical and the complex $Co^{II}L$, which are formed as intermediates, with the oxygen molecule.[115,118]

2. Transition Metal Hydroperoxides

Transition metal hydroperoxides L_nMOOH are not so numerous as alkylperoxide complexes. Their methods of preparation are in general similar to those described above for L_nMOOR, i.e. based on the reaction of a TMC with either H_2O_2 or molecular oxygen.

The preparation of permolybdic and pertungstic acids by the addition of H_2O_2 to the metal oxides is well known:[119]

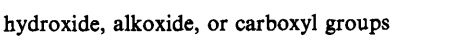


(25)

A similar reaction occurs in the preparation of vanadium hydroperoxides from the complexes $L_nV=O$, where L is picoline.[120] The fact that the vanadyl group is able to react with H_2O_2 but is unaffected by ROOH [see Eqns.(4) and (5) and also Refs.21–26] can be attributed to the higher acidity of hydrogen peroxide compared to an alkylhydroperoxide, which is necessary for the protonation of the vanadyl group and subsequent formation of vanadium hydroxide.

The reaction of H_2O_2 with π-complexes of chromium $(Arene)_2Cr$ and of molybdenum and tungsten Cp_2MX_2 leads to the formation of the hydroperoxides $(Arene)_2Cr^+(OOH.H_2O_2)^-$ [43] and $Cp_2MX_2^+.(OOH.H_2O_2)^-$ [42] respectively. The stoichiometry of the reaction corresponds to Eqn.(10).

The possible reaction of Fe^{II} with H_2O_2 to form the peroxide $Fe^{II}OOH$ has been discussed:[121]

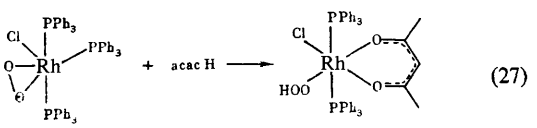


(26)

The substitution of hydroxide, alkoxide, or carboxyl groups attached to the metal by the OOH moiety of hydrogen peroxide in accordance with Eqn.(3) is proposed for the preparation of the vanadium peroxides $V(O)(OR)_2OOH$ and $V(O)(OR)(OOH)_2$ from $VO(acac)_2$,[120] the iron peroxides $[FeL(OH)OOH]^{3-}$ from $[FeL(OH)]^{2-}$ and $[FeL(OH)_2]^{3-}$ (L = ethylenediaminetetra-acetate),[122] and the platinum peroxides $L_2Pt(R)OOH$ from the complexes $L_2Pt(R)OH$, where L = PPh_3, PPh_2Me, $PPhMe_2$, or $P(PhCH_2)_3$ and R = Me, Ph, $PhCH_2$, or CF_3.[32]

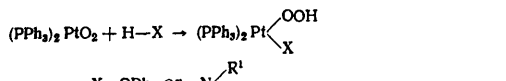
Labile hydroperoxide complexes of platinum $[L_2Pt(OOH)(solv)]^+$ and iridium $Ir(OOH)(Cl_2)(C_8H_{12})$ can be obtained by inserting an oxygen molecule into the M–H bond in the corresponding hydrides $[L_2Pt(H)(solv)]^+$ (L = PPh_3, $PPhMe_2$, or PEt_3; solv = an alkene)[33] or $Ir(H)(Cl)_2(C_8H_{12})$.[123]

Reactions of stable oxygen complexes with compounds that are hydrogen-atom donors are also used to obtain the hydroperoxides L_nMOOH. A rhodium hydroperoxide is produced by the reaction of the dioxygen complex $(PPh_3)_3Rh(Cl)O_2$ with acetylacetone in benzene or dimethoxyethane:[124,125]



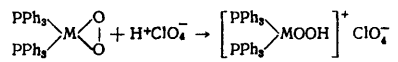
(27)

The reaction of this same dioxygen complex with cyclopentadiene in dimethoxyethane gives the hydroperoxide $(PPh_3)(\eta^5\text{-}C_5H_5)(Cl).RhOOh$. Platinum hydroperoxides are formed by the reaction of $(PPh_3)_2PtO_2$ with imides and phenols:[126]



(28)

Pt, Pd, and Rh hydroperoxides can also be obtained by the reaction of the oxygen complexes $(PPh_3)_2MO_2$ with proton donors:[51,127,131]



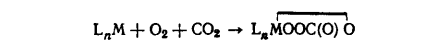
(29)

Consideration has also been given to the possible production of transition metal hydroperoxides as intermediates in the oxidation of the CH bond by a chromium peroxo-complex CrO_5L [L = py, bipy, or phen (1,10-phenanthroline)],[132] the oxidation of water in the presence of manganese complexes,[133] the oxidation with oxygen of a mixture of *p*-nitrophenylhydrazone with the complex Co^{II}(MeO.salen)(py),[116] and also in the oxidation of organic and inorganic substrates by oxygen and H_2O_2 catalysed by Rh, Pd, and Ir complexes.[3–10]

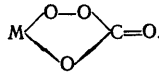
3. Percarboxylate Complexes

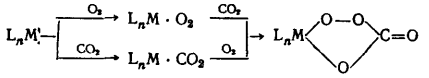
Percarboxylate complexes have been reported for Group VIII metals only.

The oxidation of complexes of these metals with molecular oxygen in a CO_2 medium gives percarboxylate complexes in accordance with overall equation:[128,134–136]



(30)

I.r. and ^1H n.m.r. spectroscopic results[135] and X-ray structure analysis[79] show that the peroxocarbonate ligand is bidentate, forming a five-membered  ring with the metal. Reaction (30) may occur by the insertion of either CO_2 into an  three-membered ring, as is known for compounds of Rh, Ir,[79,135] and Pt,[108,128,134] or an oxygen molecule into a metal–carbon dioxide bond, as is typical of nickel complexes:[137]

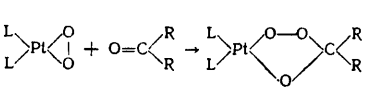


(31)

The reaction of the oxygen complexes $(PPh_3)_2PtO_2$ [138] or $Mn(II)O_2$, where Mn(II) represents a porphyrin complex of manganese,[139] with ClCOPh leads to formation of the perbenzoates $(PPh_3)_2PtCl(OOCOPh)$ or Mn(III)OOCOPh respectively. All the indications are that the process takes place via a stage in which an M–COPh metal–carbon bond is formed.

Perbenzoate complexes of rhodium and iridium can be obtained by the reaction of the complexes $M(CO)(MeCN)(PPh_3)_2ClO_4$ with an excess of the sodium salt of *m*-chloroperbenzoic acid in dichloromethane at 0 °C.[140]

There is a certain similarity between the perbenzoates and the perketyl complexes of platinum which are obtained by the addition of aldehydes and ketones to L_2PtO_2, using a excess of the aldehyde or ketone with respect to the oxygen complex:[106,108,127,128,137]



(33)

L=PPh_3, P(C_6H_{11})$_3$; R=CH_3, Ph

To conclude our report on methods for preparing transition metal peroxide complexes a mention must be made of the similarity in structure between the TMPC's discussed above and the oxygenated

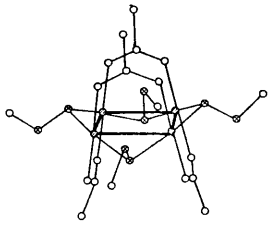
forms of metalloenzymes, e.g. Fe_fOOR, where Fe_f is an iron-containing fragment and R = H, alkyl, or R'CO.

These peroxides are regarded as important intermediates in the oxidation, by molecular oxygen, of myoglobin and haemoglobin in solutions of phenols, amines, and hydrazines[140–142] and of cytochrome P-450 in carboxylic acid solutions,[136,137] the oxidation of horse-radish peroxidase by hydroperoxides ROOH,[146,147] and the catalytic oxidation of substrates of various kinds on metalloenzymes and model systems.[11,148–152]

III. PROPERTIES

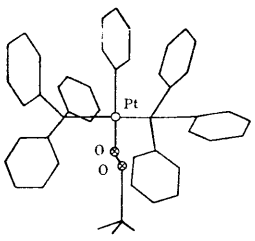
Most of the TMPC's that have been isolated, which number almost 200, are crystalline solids but a few are liquids.

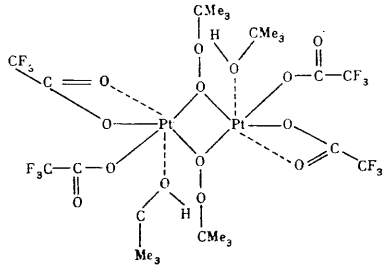
They have a considerably higher solubility in polar solvents than in non-polar solvents owing to a significant amount of ionic character in the bond between the metal and the peroxide moiety. When isolated from solutions TMPC's occur as monomers, dimers, tetramers, and also as associates with hydroperoxides and the corresponding alcohols. The structures of some TMPC's are given below:



$[(CCl_3CO_2)Pd(OOBu^t)]_4$

o – Pd, ⊗ – O in a peroxide group (Ref.28)




CMe3
H
CMe3
O
O
O

Furthermore, the solvents may react chemically with the TMPC's by various routes which arise from both the polar covalent or ionic character of the M—OOR bond and the labile nature of the O—O bond.

In view of what has been discussed above we shall consider the reactions of TMPC's in solution, which can be provisionally divided into three types: (1) reactions with preservation of the MOOR moiety; (2) protolysis or hydrolysis of the peroxide group; and (3) cleavage of the peroxide group.

Reactions of the first type include protolysis of the ligands attached to the metal[158] or their replacement,[94,158] both of which occur with cobalt alkyl peroxides:

$$\underset{(R = CHMe_2,\ L = H_2O)}{ROOCo(DmgH)_2L} + H^+ \rightleftharpoons [ROOCo(Dmg_2H_2)L]^+ \quad (34)$$

$$LCoOOR + H_2O \rightleftharpoons H_2O \cdot CoOOR, \quad (35)$$

(L = pyridine, piperidine, or 2-methylpyrazine; R = Me, Et, Pr^i, Ph).

Reactions analogous to (34) and (35) can be regarded as intermediate stages in the protolysis and hydrolysis of peroxide groups, which occur for peroxide complexes of various metals:[45,50,94,158]

$$L_nMOOR \xrightarrow[(a)]{H^+X^-} L_nMX + ROOH \quad (36)$$

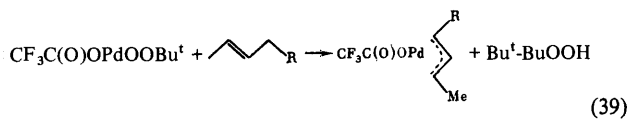
$$L_nMOOR \xrightarrow[(b)]{H_2O} L_nMOH + ROOH, \quad (37)$$

where H^+X^- is a carboxylic or mineral acid.

Reaction (36) [108,154] usually proceeds at a rapid rate, indicating that the M—OOR bond is appreciably ionic. If HX is a mineral acid the process can be explosive and accompanied by decomposition of the ROOH product.[154] The polar character of the M—OOR bond accounts for the instability of cobalt alkylperoxide complexes in chlorine-containing solvents such as chloroform and dichloromethane[45] and of platinum TMPC's in alkyl bromides;[108] this may be due to a reaction of these TMPC's with the C—halogen bond in the solvent:

$$(salen)CoOOBu^t + R\text{-}Cl \rightarrow (salen)CoCl + ROOBu^t \quad (38)$$

If the M—OOR bond is weakly polar, as in peroxide complexes of Pd,[28] the OOR group can be exchanged with an alkene (all the better if the double bond is internal rather than terminal):



(39)

An oxidation-reduction process can occur in a TMPC:

$$L_nM^+OOR^- \rightarrow L_nM^0 + RO_2^{\cdot} \quad (40)$$

This reaction is known as one of the methods for generating $RO_2^{\cdot}$ radicals[139,159] in a transition metal complex—hydroperoxide system.

Reactions of TMPC's which are accompanied by decomposition of the peroxide group are the most numerous. In accordance with the effect of M, L, and R on the stability of the peroxide complexes L_nMOOR, as discussed above, the most probable route for the decomposition of these compounds is rupture of the O—O bond[9,26,104,157] which may occur by either a homolytic or a heterolytic mechanism, and may be unimolecular or bimolecular.

The spontaneous homolysis of the O—O bond leads to formation of a radical pair [Eqn.(41)], the fate of which depends on the nature of the metal-complex radical (i.e. the oxidation state of the metal and its ligand environment), the nature of the solvent, etc.:[17,19,26,49,118,160]

$$L_nMOOR \rightarrow L_nMO^{\cdot} + {}^{\cdot}OR \quad (41)$$

The kinetic and activation parameters of reaction (41) have been determined for $(EtO)_3TiOOCMe_3$.[160] The activation energy of the process is low, 50.2 and 79.5 kJ mol^{-1} in CCl_4 and ethylbenzene respectively. A similar value for the activation energy (54.4 kJ mol^{-1}) was found for the homolysis of the peroxide bond in the cobalt complex $Co^{III}(BPI)(OAc)(OOBu^t)$.[118]

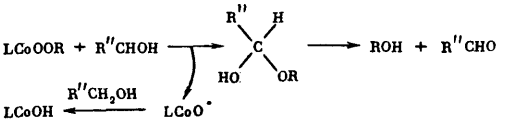
Heterolytic rupture of the O—O bond was proposed in Refs.2 and 9 and confirmed for percarboxylate complexes of iron:[145]

$$L_nM^{+n}OOR^- \rightarrow (L_nMO)^{+n} + RO^- \quad (42)$$

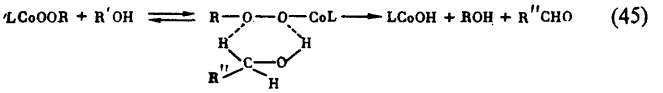
Rupture of the O—O bond can occur by the reaction of the peroxide moiety of a TMPC with a C—H bond in the solvent, especially if the latter has a mobile hydrogen atom:

$$L_nMOOR \xrightarrow[-R^{\cdot}]{R'\text{-}H} L_nMOH + RO^{\cdot} \quad (43)$$

It has been shown, in the case of the cobalt peroxides LCoOOR (L = salpr, R = *p*-quinol), that TMPC's can be reduced by alcohols (other than tertiary) to the corresponding hydroxides (at 10° to 20 °C).[112] The alcohols are converted to the corresponding aldehydes. The rate of the reaction increases with increasing acidity of the hydroxy groups and mobility of the α-hydrogen atoms in the ROH. Two possible mechanisms are proposed for this reaction [Eqns.(44) and (45)], both of which involve rupture of the O—O bond:



(44)



(45)

The concerted mechanism for the transfer of hydrogen atoms to the peroxide bonds seems more preferable, since it corresponds more to the effect of the nature of the R'OH on the rate of the reaction and to the polar character of the Co—OOR bond, which favours the formation of hydrogen bonds.

Under mild conditions (0 °C, methanol or diglyme as solvent) pyCoOOR (R = benzyl, propyl, or cyclohexyl) are reduced by the $NaBH_4$/NaOH system again with cleavage of the O—O bond:[92,97,99]

$$PyCoOOR \xrightarrow[NaOH]{NaBH_4} ROH + PyCoOH \quad (46)$$

Reductive rupture of the O—O bond in the platinum phenylethylperoxide $(Ph_3P)Pt(Br)OOCH(Me)Ph$ under the action of lithium hydroaluminate also takes place under very mild conditions (−78 °C, THF solvent).[108]

If the decomposition of the TMPC involves more than one molecule there may be not only destruction of the peroxide group but also a redistribution of the non-peroxide ligands between the metal atoms of the TMPC molecules taking part in the reaction; this occurs in reactions of the complex $IrCl(OOBu^t)(OCOCF_3)(CO).(PPh_3)_2$.[50]

Changes in a TMPC, which are accompanied by the loss of the peroxide oxygen, may also occur by intramolecular oxidation of a metal–carbon bond or a ligand attached to the metal of a donor-acceptor type, and also as the result of a bimolecular reaction with substrates of various kinds (S).

Reactions of the first type are known for peroxides of zirconium,[69] cobalt,[104] and palladium and rhodium:[33,35,125,155]

$$Cp_2Zr(R')OOR \rightarrow Cp_2Zr(OR')OR \quad (47)$$

$$(acac)Cl(PPh_3)_2RhOOH \rightarrow (acac)Cl(PPh_3)RhOH + Ph_3P{=}O \quad (48)$$

Reactions of the second type are more numerous and take place according to the following general scheme:

$$L_nMOOR + S \rightarrow L_nMOR + SO \quad (49)$$

These can be regarded as stages in the transfer of oxygen from ROOH to a substrate in the catalytic oxidation cycle of the latter and are therefore of particular interest in a practical, as well as a theoretical, respect. For this reason it is appropriate to consider TMPC reactions that are described by Eqn.(49) in more detail.

IV. PARTICIPATION IN REACTIONS WHERE THERE IS STOICHIOMETRIC OXIDATION OF ORGANIC AND INORGANIC SUBSTRATES

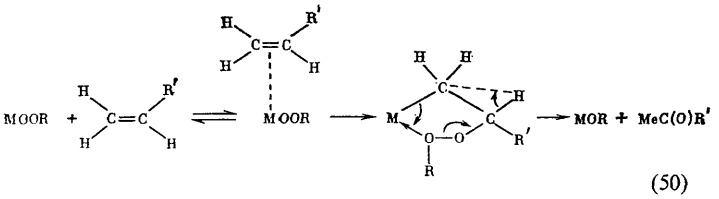
The ability of TMPC's to act as oxygen atom donors in their reactions with organic substrates (alkenes, aromatic hydrocarbons, cycloalkanols, and alkanes) and hetero-organic or inorganic substrates (PPh_3, CO, NO) has been conclusively demonstrated in numerous instances.[28–32,126,156] The ketonisation of alkenes has been investigated in greatest detail. In the temperature range 0° to 100 °C peroxide complexes of Pd and Pt oxidise terminal linear alkanes to ketones with high selectivity.[28–32,157] Iridium (III) alkylperoxides[110] and hydroperoxides[32] are also able to oxidise terminal alkenes. Since many peroxides have the composition $[L_nMOOR]_m$ it is suggested that the active form is the monomeric form produced by decomposition of the associates in solution.[29]

Cyclic and internal linear alkenes are not usually oxidised. Reactions of the latter with t-butylperoxides of Pd are accompanied by displacement of the corresponding hydroperoxide [Eqn.(38)]. At high concentrations of the terminal alkenes the ketone yield decreases owing to competitive exchange of the t-butylperoxy group by the alkene. In the opinion of the authors of Ref.9 the high sensitivity of the ketonisation reaction of alkenes to their structure is due to the predominant influence of steric factors on this reaction. However, the role of electronic factors is no less significant. This is confirmed, for example, by the considerable increase in the reactivity of the peroxide compounds $RCO_2PdOOBu^t$ and $(PPh_3)_2(R')Pt.(OOBu^t)$ towards alkenes when the electron-accepting properties of R [28] and R' [32] respectively are increased:

R	CH_3	CCl_3	C_6H_4	CF_3
Relative rate of ketonisation reaction	1	60	80	130
R'	Ph	<o-NCC_6H_4	<CF_3	—

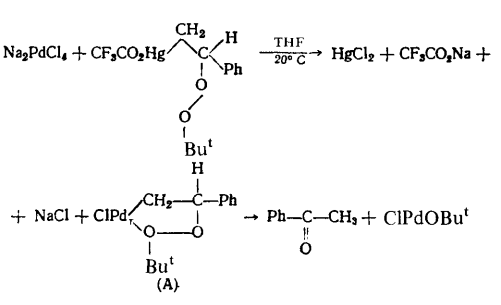
In general, the activity of Pd and Pt peroxides of the composition $L_2(R')MOOR$ as carriers of oxygen to the alkene depends on many factors including the size of the L groups (increasing the volume of L leads to a decrease in the activity of the TMPC) and their mutual orientation (*trans*-forms of alkylperoxides are more active than *cis*-forms), the electronic effects of R' and the nature of R (the hydroperoxides of Pd and Ir are considerably more active than the alkylperoxides of these metals but the reverse is true for Pt peroxides).[32] It is characteristic that, given a similarity in the rules governing the variation of the reactivity of the peroxides as a function of the nature of the ligands attached to the metal, Pd alkylperoxides and hydroperoxides are significantly more active as oxygen carriers than their Pt analogues.[28–32,156]

It is generally accepted[3–10] that the transfer of oxygen from the TMPC to the alkene during its ketonisation takes place by a peroxometallation mechanism, the main stages of which are coordination of the alkene by the metal, formation of a five-membered pseudocyclic intermediate, and its subsequent decomposition to the ketone and an alkoxo- or hydroxo-complex:



(50)

The coordination of the alkene stage is confirmed by the inhibiting effect on the rate of oxygen transfer caused by adding alcohols, strongly complexing solvents (dimethylformamide, hexamethylphosphoryl triamide), and alkenes (1,5-cyclo-octadiene),[28] and also the reduction in the ketone yield in the presence of these substances.[48] The formation of the five-membered pseuydocyclic complex was demonstrated by using the reaction of a stable peroxide compound of mercury with palladium salts.[28] The resultant unstable intermediate (A) decomposes to form a ketone:



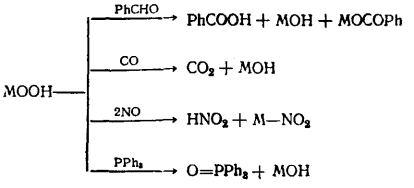
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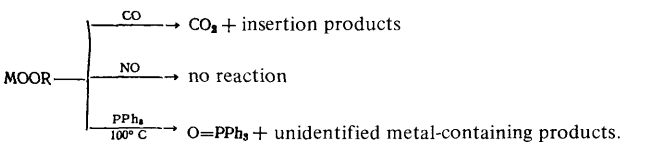
Proof of the formation of a peroxometal ring is also obtained by other preparations of such compounds, which in many cases are fairly stable[108,127,128,134,135,161] [see Eqns.(30), (31), and (33)].

Mechanisms for the decomposition of the ring containing the metal other than that considered in Eqn.(50) are also possible.[9]

Pd and Pt alkylperoxides and hydroperoxides are highly active in oxidising benzaldehyde and a number of inorganic compounds—CO, NO, and PPh_3 (Scheme 1).[31,126]

Scheme 1

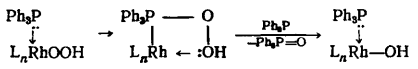




All the reactions except the last take place at 20 °C (THF solvent, nitrogen atmosphere). In these reactions, in contrast to the ketonisation of alkenes, the hydroperoxides of both platinum and palladium are more active than their alkylperoxides; this is indicated by the milder conditions under which the various compounds are oxidised by MOOH and also by the higher reaction rates.

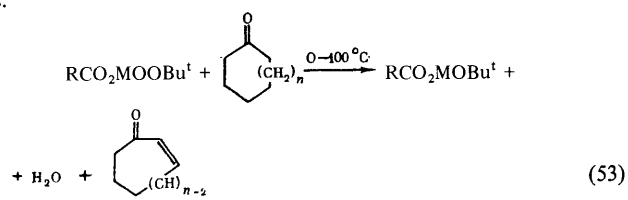
Triphenylphosphine is oxidised in accordance with reaction (49) by treatment with the cobalt alkylperoxide (Bu^tOO)Co(salen) (T = 20 °C),[45] the platinum percarboxylates $(PPh_3)_2PtX(OOCOPh)$, where X = Cl (T = −78 °C) [48] or Br,[103] the rhodium alkylperoxide (1,5-cyclo-octadiene)Rh($OOBu^t$) KBF_4,[33] and the rhodium hydroperoxide $(PPh_3)_2$(acac)(Cl)RhOOH (T = 20 °C).[125,155] The yield of triphenylphosphine oxide is almost quantitative.

The mechanism of the oxidation of triphenylphosphine by the rhodium hydroperoxide[155] (which can be extended to the other reactions in scheme 1 above) involves the formation of a four-membered pseudocyclic complex which undergoes a further reaction with liberation of the products mentioned:



(52)

As oxygen-atom donors the Pd and Pt peroxides $RCOOMOOBu^t$ (R = Me, CCl_3, CF_3) are capable of oxidative dehydrogenation of cycloalkanones (C_5-C_{12}) to the corresponding cycloalkyl-1-en-3-ones.[156]



(53)

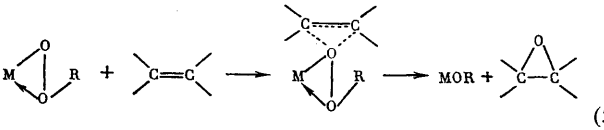
The ability of cobalt alkylperoxides to oxidise alkanes and cycloalkanes, cyclic and acyclic alkenes, and alkylbenzenes to the corresponding ketones, aldehydes, alcohols, epoxides, and peroxides has been noted.[118] In the opinion of the authors the ability of alkylperoxide complexes to oxidise the hydrocarbons listed above depends on their thermal stability. An increase in thermal stability reduces the oxidative properties of the complexes.

Alkylperoxides and hydroperoxides of transition metals (primarily molybdenum, vanadium, and tungsten) are highly selective oxidising agents for converting alkenes to the corresponding oxides. Evidence has been obtained for the participation of MOOR in the alkyl hydroperoxide epoxidation reactions of alkenes—both indirect evidence[70,162] and direct evidence in the case of $(PPh_3)_2ClPt.(OOCOPh)$ [48,49] and $Cp_2MX_2^+(OOR.ROOH)^-$ (X = Cl, Br; R = H, t-butyl, cumyl).[163,164] The ability of $Cp_2MX_2^+(OOR.ROOH)^-$ to cause epoxidation depends on the metal (W < Mo), the halide ligand (Cl < Br), R (cumyl < t-butyl), and on the alkene (oct-1-ene < cyclohexene). It is suggested that the active form of the metal alkylperoxide or hydroperoxide is the monomeric form $Cp_2MX.(OOR)^+X^-$, in which the alkylperoxide moiety is attached to the metal by a polar covalent bond:

$$[Cp_2MX_2]^+ OOR^- \rightleftarrows [Cp_2MX(OOR)]^+ X^- \qquad (54)$$

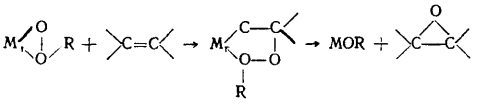
Metal alkylperoxides with a purely or nearly ionic bond between the metal and the peroxide moiety either have no ability to transfer an oxygen atom to alkenes (e.g. the alkali metal salts of organic hydroperoxides[165]) or have a very small ability to do so (e.g. platinum alkylperoxides in strongly electron-donating media[32]). These results indicate that the effectiveness of transition metal alkylperoxides as oxygen carriers depends on the degree of covalency of the M−OOR bond.[164] A similar conclusion was drawn in Ref.10.

The epoxidation of alkenes by the action of Mo, V, and W TMPC's may proceed by the following mechanisms: (1) by a direct reaction of the alkene molecule with the peroxide moiety:[7]



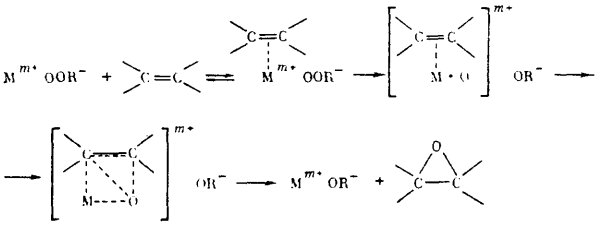
(55)

(2) by a peroxometallation mechanism[3-9,14,15] similar to that discussed above for the ketonisation of alkenes by Pd, Pt, and Ir TMPC's:



(56)

and (3) with the involvement of $(MO)^{m+}$ intermediates (m = 5 for V and 6 for Mo and W),[163] which can be formed from MOOR by heterolytic fission of the peroxide bond[29,145] and can be oxygen-atom donors in the triplet state:

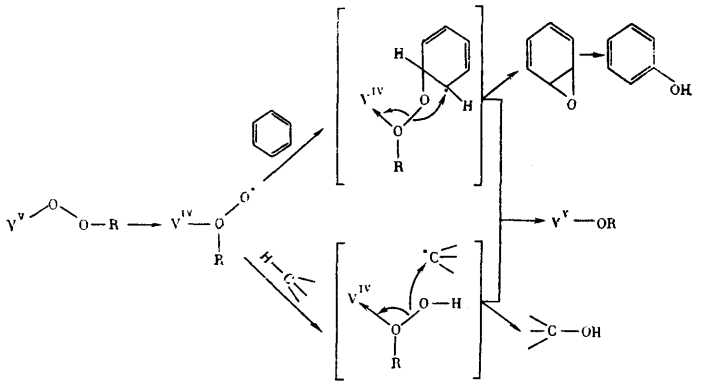


(57)

The vanadium alkylperoxides (dipic)V(O)(OOR)L (R = t-butyl, cumyl; L = H_2O, HMPT) oxidise not only alkenes but also aromatic and saturated hydrocarbons.[36] The selectivity of the processes is usually low. The reactions with alkenes (methylstyrene, butene, cyclohexene, 2-methylpentene) give epoxides (not more than 8% yield) and also the products of oxidative fission and allylic oxidation—aldehydes (10−22%), ketones (4−10%), and alcohols (8−30%).

In contrast to the dipicolinate complexes the compounds (R−OPhsal−R″)V(O)OOR form epoxides with alkenes with a high selectivity,[38] which, in the opinion of those authors, is due to weak coordination of the peroxide oxygen with vanadium; in the dipicolinate complexes the strong coordinate bond between the peroxide oxygen and the hetero-atom hinders coordination of the alkene and consequently inhibits the reaction. A more probable reason for the observed differences in the oxidising properties of the vanadium peroxides is the ability of the dipicolinate alkylperoxide complexes to change into oxygen carriers of a different kind, as is evident from the fact that they oxidise not only alkenes but also aromatic (benzene, toluene, ethylbenzene) and saturated (cyclohexane) hydrocarbons. The latter are oxidised to form hydroxylation products (9−40%), aldehydes (13−27%), and ketones (3−14%).

For the hydroxylation of hydrocarbons by this vanadium alkylperoxide the following mechanism, which is also possible for the oxidation of alkanes, is proposed:



The possible production of octanones by the oxidation of octane with $(Bu^tOO)V(O)(OBu^t)_2$ at room temperature has also been reported.[23,24]

V. PARTICIPATION IN THE CATALYTIC OXIDATION OF ORGANIC AND INORGANIC SUBSTRATES

The formation of TMPC's as intermediates in the catalytic oxidation of organic compounds has been suggested in work on the oxidation of pyrocatechol by oxygen on enzymes containing Fe^{2+}, of the dioxygenase type, and on their model systems,[1,148] and in the oxidation of aromatic compounds and aliphatic alcohols by hydrogen peroxides on an Fe^{III}–pyrocatechol complex.[1,150–152] Similar proposals were subsequently made in a number of papers concerned with the catalytic oxidation of organic[8,10,11,27,31,70–74,110,166–176] and inorganic substrates.[29,31]

Now that a large number of TMPC's have been prepared and their ability to transfer oxygen to organic and inorganic compounds demonstrated (see Section IV), there is no doubt as to the decisive role of these peroxides in the hydroperoxide oxidation of alkenes to the corresponding epoxides on Ti^N, V^V, Cr, and Mo^{VI} complexes[3–10, 69,162,173–178] and to ketones on Pd^{II}, Pt^{II}, Ir^{II}, and Rh^I complexes, [3–10,28,85,116] in the hydroxylation and ketonisation of alkanes on V^V,[23,24] Pd^{II},[1,25] and Co^{III} [46,118] complexes, and also in the oxidation by molecular oxygen of olefins to ketones on Rh^{III} [28] and Pd^{II} [178,179] complexes and phenols to quinones and quinols on Co^{II} complexes.[103,110] The same is true regarding the role of TMPC's in the hydroperoxide oxidation of compounds of phosphorus, sulphur, nitrogen, etc.[31] Generalised schemes have been published for some of the best studied of these catalytic processes.[3–5,10,28,110]

The formation of transition metal alkylperoxides and hydroperoxides as intermediates is energetically very advantageous in catalytic reactions involving molecular oxygen because breaking the O–O single bond in the peroxides requires an energy of 190–250 kJ mol^{-1} [172] whereas dissociation of the oxygen molecule requires 490, 397, or 368 kJ mol^{-1} respectively for the different states $O_2 \rightarrow 2O$ $O_2^* \rightarrow 2O$, and $O_2^- \rightarrow O + O^-$.[1]

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The formation of peroxide compounds with the composition L_nMOOR, where R = H, alkyl, or PhCO, is thus characteristic of the transition metals in almost all Groups of the Periodic Table and can therefore be regarded as one of their inherent fundamental properties; the stability of TMPC's which varies over a wide range, depends on the nature of the metal, the ligands attached to it, the nature of R, and, in solution, on the nature of the solvent, all of which together affect the degree of charge transfer from the metal to the peroxide moiety and hence the energy of the peroxide bond. The most typical routes for reactions of TMPC's are: (a) fission of the peroxide bond, which may be spontaneous (homolytic or heterolytic) or due to an interaction with substrates of various kinds, or (b) intra- or inter-molecular transfer of an oxygen atom to an oxidisable substrate; there are good reasons for supposing that the TMPC's which are intermediates in numerous catalytic processes for the oxidation of organic and inorganic compounds by peroxides are responsible for the transfer of oxygen to the oxidisable substrate.

Further study of methods of preparing TMPC's and their properties will make it possible to determine the nature of the actual carriers of oxygen to substrates of various kinds in the homogeneous, heterogeneous, and enzyme catalysis of the processes for oxidation of these substrates by molecular oxygen and by hydroperoxides and to develop methods for obtaining valuable oxygen-containing products and effective initiating systems for the polymerisation of unsaturated compounds.

REFERENCES

1. G.L.Eichorn (Editor), "Inorganic Biochemistry" (Translated into Russian), Mir, Moscow, 1978, Vol.2.
2. D.I.Metelitsa, Uspekhi Khim., 1982, **51**, 1818 [Russ.Chem. Rev., 1982(11)].
3. H.Mimoun, J.Mol.Catal., 1980, **7**, 1.
4. H.Mimoun, Angew.Chem., 1982, **94**, 750.
5. R.A.Sheldon, Aspects Homog.Catalysis, 1981, **4**, 3.
6. R.A.Sheldon, J.Mol.Catal., 1983, **20**, 1.
7. F.Di Furia and G.Modena, Pure and Appl.Chem., 1982, **54**, 1853.
8. F.Di Furia and G.Modena, Rev.Chem.Intermediates, 1985, **6**, 51.
9. P.Chaumette, H.Mimoun, Z.Saussine, et al., J.Organometal. Chem., 1983, **250**, 291.
10. K.B.Sharples, S.S.Woodard, and M.Finn, Pure and Appl. Chem., 1983, **55**, 1823.
11. N.S.Enikolopyan, K.A.Bogdanov, L.V.Karmilova, and K.A.Askarov, Uspekhi Khim., 1985, **54**(3), 369 [Russ.Chem. Rev., 1985(3)].
12. R.Boca, Coord.Chem.Rev., 1983, **50**, 1.
13. P.D.Smith, B.R.James, and D.H.Dolphin, Coord.Chem.Rev., 1981, **39**, 31.
14. G.Henrici-Olivé and S.Olivé, "Coordination and Catalysis" (Translated into Russian), Nauka, Moscow, 1980, p.358.
15. K.B.Yatsimirskii (Editor), "Uspekhi Khimii Koordinatsionnykh Soedinenii" (Progress in the Chemistry of Coordination Compounds), Naukova Dumka, Kiev, 1976.
16. A.V.Savitskii and V.I.Nelyubin, Uspekhi Khim., 1975, **44**(2), 214 [Russ.Chem.Rev., 1975(2)].
17. A.G.Davies and E.Buncel, B.P.827366; Ref.Zhur.Khim., 1962, 6L110.

18. Yu.N.Anisimov and S.S.Ivanchev, Zhur.Obshch.Khim., 1971, **41**, 2248.
19. V.I.Oleshchuk and Yu.N.Anisimov, "VIII Vsesoyuznaya Konferentsiya po Khimii Organicheskikh Peroksidov. Tezisy Dokladov" (Eighth All-Union Conference on the Chemistry of Organic Peroxides. Abstracts of Papers), ONPO "Plastpolimer", Leningrad, 1985, p.101.
20. O.Bortolini, C.Campello, and F.Di Furia, J.Mol.Catal., 1982, **14**, 63.
21. N.N.Batryshin, G.V.Koshkina, Kh.E.Kharlampidi, and N.M.Lebedeva, Neftekhimiya, 1982, **22**, 673.
22. N.N.Batyrshin, Kh.E.Kharlampidi, and A.A.Gaifulin, and N.M.Lebedeva, "IV Mezhdunarodnyi Simpozium po Gomogennomu Katalizu. Tezisy Dokladov" (Fourth International Symposium on Homogeneous Catalysis. Abstracts of Papers), LTI, Leningrad, 1984, Vol.2, p.167.
23. I.V.Spirina, V.N.Alyasov, V.N.Glushakova, et al., Zhur.Org. Khim., 1982, **18**, 1796.
24. I.V.Spirina, V.N.Alyasov, V.N.Glushakova, and N.A.Skorodumova, Oxid.Communs., 1984, **6**, 301.
25. F.Di Furia, G.Modena, R.Curci, et al., J.Mol.Catal., 1982, **14**, 219.
26. V.N.Alyasov, S.P.Korneva, L.I.Vyshinskaya, et al., Zhur. Obshch.Khim., 1984, **59**, 1837.
27. I.Ygersheim and H.Mimoun, Nouv.J.Chim., 1980, **4**, 711.
28. H.Mimoun, R.Charpentier, A.Mitschler, et al., J.Amer.Chem. Soc., 1980, **102**, 1047.
29. J.M.Bregeault and H.Mimoun, Nouv.J.Chim., 1981, **5**, 287.
30. H.Mimoun and R.Chaprentier, French P.claim 244 285; Ref. Zhur.Khim., 1982, 21H203.
31. G.Strukul, R.Ros, and R.A.Michelin, Inorg.Chem., 1982, **21**, 495.
32. G.Strukul, R.A.Michelin, J.A.Orbell, and Z.Randaccio, Inorg.Chem., 1983, **22**, 3707.
33. N.Oshima, Y.Namatani, H.Fuku, et al., J.Organometal.Chem., 1986, **303**, 21.
34. T.F.Blackburn, J.A.Labinder, and J.Schwartz, Tetrahedron Lett., 1975, **35**, 3041.
35. N.Oshima, Y.Hamatani, H.Fukui , et al., J.Organometal. Chem., 1986, **303**, 21.
36. H.Mimoun, P.Chaumette, M.Mignard, and Z.Saussine, Nouv.J.Chim., 1983, **7**, 467.
37. P.Chaumette, H.Mimoun, Z.Saussine, et al., J.Organometal. Chem., 1983, **250**, 291.
38. H.Mimoun, M.Mignard, P.Brechot, and Z.Saussine, J.Amer. Chem.Soc., 1986, **108**, 3711.
39. C.Giannotti, C.Fontaine, A.Chiaroni, et al., J.Organometal. Chem., 1976, **113**, 57.
40. Yu.A.Aleksandrov, V.M.Fomin, A.V.Lunin, and V.G.Tsvetkov, Zhur.Obshch.Khim., 1980, **48**, 936.
41. A.O.Kolmakov, V.M.Fomin, Yu.A.Aleksandrov, et al., Zhur. Obshch.Khim., 1980, **50**.
42. Yu.A.Aleksandrov, A.O.Kolmakov, and V.M.Fomin, Zhur. Obshch.Khim., 1983, **53**, 2389.
43. Yu.A.Aleksandrov, V.M.Fomin, and A.O.Kolmakov, article deposited at ONIITEKhIM (Cherkassy), 1985, No.131khp-85.
44. Yu.S.Zimin, E.P.Talzi, V.M.Nekipelov, and K.I.Zamaraev, React.Kinet.Catal.Lett., 1985, **29**, 219.
45. A.Nishinaga, H.Tomita, and H.Ohara, Chem.Lett., 1983, **11**, 1751.
46. Z.Saussine, E.Barazi, A.Robine, et al., J.Amer.Chem.Soc., 1985, **107**, 3534.
47. L.Saussine, A.Robine, and H.Himoun, French P. claim 2 559 154; Ref.Zhur.Khim., 1986, 19P220.
48. B.L.Booth, R.N.Haszeldine, and G.R.H.Neuss, J.Chem.Soc. Chem.Communs., 1972, 1077.
49. B.L.Booth, R.N.Haszeldine, and G.R.H.Neuss, J.Chem.Soc. Dalton Trans., 1982.
50. B.L.Booth, R.N.Haszeldine, and G.R.H.Neuss, J.Chem.Soc. Dalton Trans., 1982, 511.
51. R.Ugo, A.Fusi, G.H.Lauderighi, and L.Gasella, J.Mol.Catal., 1980, **7**, 51.
52. N.M.Emanuel', Uspekhi Khim., 1981, **50**(10), 1721 [Russ. Chem.Rev., 1981(10)].
53. R.W.Brandon and C.S.Elliott, Tetrahedron Lett., 1967, 4375.
54. M.C.R.Symons, J.Chem.Soc.A, 1970, 1889.
55. A.N.Zverev, V.G.Vinogradova, and Z.K.Maizus, Izv.Akad. Nauk SSSR, Ser.Khim., 1975.
56. N.M.Emanuel, Z.K.Maizus, and V.G.Vinogradova, React. Kinet.Catal.Lett., 1981, **17**, 77.
57. A.L.Aleksandrov and E.T.Denisov, Izv.Akad.Nauk SSSR, Ser. Khim., 1969, 1652.
58. L.A.Tavadyan, V.A.Mardoyan, and A.B.Nalbandyan, Dokl.Akad.Nauk SSSR, 1981, **259**.
59. L.A.Tavadyan, V.A.Mardoyan, and A.B.Nalbandyan, "IV Mezhdunarodnyi Simpozium po Gomogennomu Katalizu. Tezisy Dokladov" (Fourth International Symposium on Homogeneous Catalysis. Abstracts of Papers), LTI, Leningrad, 1984, Vol.2, p.273.
60. N.A.Zverev, V.G.Vinogradova, and Z.K.Maizus, Izv.Akad. Nauk SSSR, Ser.Khim., 1979.
61. V.G.Vinogradova, N.K.Kul'kova, Z.K.Maizus, and N.M.Emanuel', Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 2118.
62. I.I.Moiseev and G.A.Kovtun, "Khimicheskaya Svyaz' i Stroenie Molekul" (The Chemical Bond and the Structure of Molecules), Nauka, Moscow, 1984, p.249.
63. E.T.Denisov and N.M.Emanuuel', Uspekhi Khim., 1958, **27**, 365.
64. N.M.Emanuel, Z.K.Maizus, and V.G.Vinogradova, React. Kinet.Catal.Lett., 1977, **6**, 119.
65. A.B.Nazaletskii, V.G.Vinogradova, and Z.K.Maizus, Dokl. Akad.Nauk SSSR, 1980, **253**, 153.
66. E.Cadenas, A.Boveris, and B.Chance, Biochem.J., 1980, **187**, 131.
67. I.I.Moiseev and G.A.Kovtun, Koord.Khim., 1983, **9**, 1155,
68. H.Ledon and F.Varescon, Inorg.Chim., 1984, **23**, 2735.
69. P.B.Brindley and M.J.Scotton, J.Chem.Soc.Perkin Trans.II, 1981, 419.
70. A.O.Shong and K.B.Shorpless, J.Org.Chem., 1977, **42**, 1587.
71. E.D.Mihelich, Tetrahedron Lett., 1976, **49**, 4729.
72. K.B.Sharpless and T.R.Verhoeven, Aldrichimica Acta, 1979, **12**, 63.
73. R.B.Dehnel and G.H.Witham, J.Chem.Soc.Perkin Trans.I, 1979, 953.
74. F.Di Furia and G.Modena, Recl.trav.chim., 1979, **98**, 181.
75. E.D.Mihelich, K.Daniels, and D.Y.Eickhoff, J.Amer.Chem. Soc., 1981, **103.**
76. O.Bortolini, F.Di Furia, and G.Modena, J.Mol.Catal., 1983, **19**, 319.
77. Yu.A.Aleksandrov, V.M.Fomin, A.S.Lunin, et al., Zhur. Obshch.Khim., 1981, **51**, 1681.

78. G.F.Pustarnikova and V.M.Solyanikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 2191.
79. M.Constantini, A.Dromard, M.Jouffret, and J.Brossard, J.Mol. Catal., 1980, **7**.
80. S.Uemura and S.RPatil, Chem.Lett., 1982, 1743.
81. B.R.James and E.Ochiai, Can.J.Chem., 1971, **49**, 975.
82. B.R.James and E.Ochiai, Can.J.Chem., 1972, **50**, 520.
83. J.Martin, C.Martin, M.Faray, and J.-M.Bregeault, Nouv.J. Chim., 1984, **8**, 141.
84. K.Hirai, A.Nutton, and P.M.Maitlis, J.Mol.Catal., 1981, **10**, 203.
85. M.Bressan, F.Morandini, A.Morvillo, and P.Rigo, J.Organometal.Chem., 1985, **280**, 139.
86. M.Faray, J.-M.Bregeault, J.Martin, and C.Martin, J.Organometal.Chem., 1984, **276**, 23.
87. O.Bortolini, F.Di Furia, and G.Modena, J.Mol.Catal., 1985, **33**, 241.
88. Yu.S.Zimin, E.P.Talzi, V.M.Nekipelov, et al., React.Kinet. Catal.Lett., 1985, **29**, 225.
89. E.P.Talzi, Yu.S.Zimin, V.P.Babenko, and V.M.Nekipelov, Kinetika i Kataliz, 1986, **24**, 117.
90. C.Giannotti, A.Gaudemer, and C.Fontaine, Tetrahedron Lett., 1970, 3209.
91. K.N.V.Duong, C.Fontaine, C.Giannotti, and A.Gaudemer, Tetrahedron Lett., 1971, 1187.
92. C.Fontaine, K.N.V.Duong, C.Merienne, et al., J.Organometal. Chem., 1972, **38**.
93. C.Giannotti, C.Fontaine, and A.Gaudemer, J.Organometal. Chem., 1972, **39**, 381.
94. C.Giannotti, C.Fontaine, and B.Septe, J.Organometal.Chem., 1974, **71**, 107.
95. A.Chiaroni and G.Pascard-Billey, Bull.Soc.chim.France, 1973, 781.
96. C.Giannotti and B.Septe, J.Organometal.Chem., 1973, **52**, 36.
97. C.Merienne, C.Giannotti, and A.Gaudemer, J.Organometal. Chem., 1973, **54**, 281.
98. P.Maillard and C.Giannotti, Can.J.Chem., 1982, **60**, 1402.
99. F.R.Jensen and R.C.Kiskis, J.Organometal.Chem., 1973, **49**, 46.
100. F.R.Jensen and R.C.Kiskis, J.Amer.Chem.Soc., 1975, **97**, 5825.
101. C.Bied-Charreton and A.Gaudemer, J.Organometal.Chem., 1977, **124**, 57.
102. N.W.Alcock, B.T.Golding, and S.Mwesigye-Kibende, J.Chem. Soc.Dalton Trans., 1985, 1997.
103. A.Bedell and A.E.Martell, J.Amer.Chem.Soc., 1985, **107**, 7909.
104. B.D.Gupta and S.Roy, Inorg.Chim.Acta, 1985, **108**, 261.
105. P.B.Brindley and J.C.Hodgson, J.Organometal.Chem., 1974, **65**, 57.
106. G.Ferguson, M.Parves, P.K.Monagham, and R.J.Puddephatt, J.Chem.Soc.Chem.Communs., 1983, 267.
107. G.Ferguson, P.K.Monagham, M.Parves, and R.J.Puddephatt, Organometallics, 1985, **4**, 1669.
108. J.Tatsumo and S.Otsuka, J.Amer.Chem.Soc., 1981, **103**, 5833.
109. V.Luben and P.T.Wolczanski, J.Amer.Chem.Soc., 1985, **107**, 701.
110. M.Frostin-Rio, D.Pujol, C.Bied-Charreton, et al., J.Chem.Soc. Perkin Trans.I, 1984, 1971.
111. A.Nishinaga, S.Yamazaki, and T.Matsuura, Tetrahedron Lett., 1984, **25**, 5805.
112. A.Nishinaga and H.Tomita, Tetrahedron Lett., 1980, **21**, 1261.
113. A.Nishinaga and H.Tomita, Tetrahedron Lett., 1979, 2863.
114. A.Nishinaga, K.Nishizawa, H.Tomita, and T.Matsuura, J.Amer.Chem.Soc., 1977, **99**, 1287.
115. A.Nishinaga, H.Tomita, and T.Matsuura, Tetrahedron Lett., 1980, **21**, 3407.
116. A.Nishinaga, H.Tomita, M.Oda, and T.Matsuura, Tetrahedron Lett., 1982, **23**, 339.
117. A.Nishinaga, H.Tomita, K.Nishizawa, and T.Matsuura, J.Chem.Soc.Dalton Trans., 1981, 1504.
118. A.Nishinaga, J.Chem.Soc.Jap.Chem.and Ind.Chem., 1985, 378.
119. M.Prafus, J.C.Lecog, and J.P.Serimann, Fundam.Res. Homogeneous Catal.Proc. I Intern.Conf.Homogeneous Catal.Corpus Christi. Tex, 1978, Vol.3, Plenum Press,New York–London, 1979, p.327.
120. H.Mimoun, Z.Saussine, E.Daire, et al., J.Amer.Chem.Soc., 1983, **105**, 3101.
121. G.A.Hamilton, Adv.Enzymol., 1969, **33**, 55.
122. R.E.Hester and E.M.Nour, J.Raman Spectroscopy, 1981, **11**, 35.
123. M.T.Atlay, M.Preece, G.Strukul, and B.R.James, Can.J.Chem., 1983, **61**, 1332.
124. H.Suzuki, S.Matsuura, J.Moro-Oka, and T.Ikawa, Chem.Lett., 1982, 1011.
125. J.Moro-Oka and H.Suzuki, J.Synth.Org.Chem.Jap., 1983, **41**, 316.
126. S.Cenini, F.Porta, and M.Pizzotti, J.Organometal.Chem., 1985, **296**, 291.
127. A.S.Berenblyum, L.I.Lakhman, I.I.Moiseev, and E.D.Radchenko, Koord.Khim., 1976, **2**, 841.
128. P.J.Hayward, D.M.Blake, G.Wilkinson, and C.J.Nyman, J.Amer.Chem.Soc., 1970, **92**, 5873.
129. A.Sen and J.Halpern, J.Amer.Chem.Soc., 1977, **99**, 8337.
130. S.Muto, H.Ogato, and Y.Kamiya, Chem.Lett., 1975, 809.
131. E.B.Boyar, D.S.More, and S.D.Robinson, J.Chem.Soc.Dalton Trans., 1985, 617.
132. E.Daire, H.Mimoun, and Z.Saussine, Nouv.J.Chim., 1984, **8**, 271.
133. A.B.Solov'eva, V.I.Mel'nikova, K.K.Pivnitskii, et al., Izv.Akad. Nauk SSSR, 1983, 2327.
134. H.C.Clark, A.Goel, and C.S.Wong, J.Organometal.Chem., 1978, **152**, 45.
135. M.G.Mason and J.A.Ibers, J.Amer.Chem.Soc., **104**, 5153,
136. L.Dahlenburg and C.Prengel, Organometallics, 1984, **3**, 934.
137. M.Aresta and C.F.Nobile, J.Chem.Soc.Dalton Trans., 1977, 709.
138. R.Ugo, A.Fusi, G.H.Lauderighi, and L.Gasella, J.Mol.Catal., 1980, **7**, 51.
139. J.T.Groves, J.Watanabe, and T.McMurray, J.Amer.Chem.Soc., 1983, **105**, 4489.
140. W.I.Wallace and W.Caugheu, Biochem.Biophys.Res. Communs., 1975, **62**, 681.
141. H.P.Mirsa and I.Fridovich, Biochemistry, 1976, **15**, 681.
142. D.I.Metelitsa and E.M.Popova, Biokhimiya, 1980, **45**, 1379.
143. J.J.Mieyal and J.L.Blumer, J.Biol.Chem., 1976, **251**, 3442.
144. R.E.White and M.J.Coon, Ann.Rev.Biochem., 1980, **49**, 315.
145. S.G.Sligar, K.A.Kennedy, and D.C.Pearson, Proc.Natl.Acad. Sci.USA, 1980, **77**, 1240.
146. D.Kelin and T.Mann, Proc.Roy.Soc.B, 1937, **122**, 119.
147. B.Chance, Arch.Biochem.Biophys., 1949, **22**, 224.
148. G.A.Hamilton, Adv.Enzymol., 1969, **33**, 55.
149. A.E.Martell, Proc.III Int.Conf.Coord.Chem.Debrecen, Hungary, 1970, p.46.

150. G.A.Hamilton and I.P.Friedman, J.Amer.Chem.Soc., 1963, **85**, 1008.
151. G.A.Hamilton and I.P.Friedman, J.Amer.Chem.Soc., 1966, **88**, 5266.
152. G.A.Hamilton, I.W.Hanifin, and I.P.Friedman, J.Amer. Chem.Soc., 1966, **88**, 5269.
153. V.M.Fomin, A.V.Lunin, Yu.A.Aleksandrov, and T.N.Aizenshtadt, Neftekhimiya, 1981, **21**, 602.
154. A.O.Kolmakov, V.M.Fomin, and Yu.A.Aleksandrov, article deposited at ONIITEKhIM (Cherkassy), 1985, No.124khp-85.
155. H.Suzuki, S.Matsuura, J.Moro-Oka, and T.Ikawa, J.Organometal.Chem., 1985, **286**, 247.
156. J.Collin, D.Commerenc, and J.Chauvin, J.Mol.Catal., 1982, **14**, 113.
157. Yu.A.Aleksandrov, V.M.Fomin, and A.O.Kolmakov, "III Vsesoyuznaya Konferentsiya po Metalloorganicheskoi Khimii. Tezisy Dokladov" (Third All-Union Conference on Organometallic Chemistry. Abstract of Papers), Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa, 1985, p.78.
158. H.S.Espenson and J.T.Chen, J.Amer.Chem.Soc., 1981, **103**, 2036.
159. N.N.Batyrshin, Kh.E.Kharlampidi, A.A.Gaifulin, and N.M.Lebedeva, Neftekhimiya, 1985, **25**, 244.
160. Yu.N.Anisimov and V.T.Oleshchuk, "Fiziko-khimicheskie Svoistva i Sintez Vysokomolekulyarnykh Soedinenii" (Physicochemical Properties and Preparation of High-molecular-weight Compounds), Naukova Dumka, Kiev, 1976 , p.12.
161. H.J.J.Chen and J.K.Kochi, J.Chem.Soc.Chem.Communs, 1977, 204.
162. V.S.Gumerova, A.G.Liakumovich, B.I.Popov, et al., Neftekhimiya, 1973, **13**, 682.
163. V.V.Fomin, A.O.Kolmakov, and Yu.A.Aleksandrov, article deposited at ONIITEKhIM (Cherkassy), 1985, No.478khp-85.
164. Yu.A.Aleksandrov, V.M.Fomin, and A.O.Kolmakov, "IV Mezhdunarodnyi Simpozium po Gomogennomu Katalizu. Tezisy Dokladov" (Fourth International Symposium on Homogeneous Catalysis. Abstracts of Papers), LTI, Leningrad, 1984, Vol.1, p.40.
165. V.M.Shekunova, Thesis for the Degree of Candidate of Chemical Sciences, Lobachevskii Gorky State University, Gorky, 1984.
166. A.Fusi, R.Ugo, A.Pasini, and S.Senini, J.Organometal.Chem., 1971, **26**, 417.
167. E.D.Mihelich, K.Daniels, and D.J.Eickhoff, J.Amer.Chem.Soc., 1981, **103**, 7690.
168. E.D.Mihelich, Tetrahedron Lett., 1979, **49**, 4729.
169. T.Itoh, K.Yitsukawa, K.Kaneda, and N.Teranishi, J.Amer. Chem.Soc., 1979, **101**.
170. P.Muller and C.Bobiller, Tetrahedron Lett., 1981, **22**, 5157.
171. O.Bortolini, V.Conte, F.Di Furia, and G.Modena, J.Mol. Catal., 1983, **19**, 331.
172. O.Bortolini, F.Di Furia, G.Modena, and S.Roberta, J.Mol. Catal., 1984, **22**, 313.
173. O.Bortolini, F.Di Furia, and G.Modena, J.Mol.Catal., 1985, **33**, 241.
174. E.Glotter and M.Zviely, J.Chem.Soc.Perkin Trans.I, 1986, 227.
175. E.Glotter and M.Zviely, J.Chem.Soc.Perkin Trans.I, 1986, 327.
176. E.Y.Corey and E.P.Barrette, Tetrahedron Lett., 1985, **26**, 5855.
177. I.D.Williams, S.F.Pederson, K.B.Sharpless, and S.J.Lippard, J.Amer.Chem.Soc., 1984, **106**, 6430.
178. R.S.Drago, A.Zurich, and E.D.Nyberg, J.Amer.Chem.Soc., 1985, **107**, 2898.
179. J.Muzart, A.Riahi, and J.P.Pete, J.Organometal.Chem., 1985, **280**, 269.

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