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CYCLOADDITION OF GROUP VIII METAL—DIOXYGEN COMPLEXES TO ELECTROPHILIC OLEFINS

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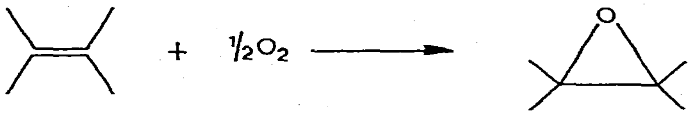
Summary

The dioxygen complexes $(Ph_3P)_2MO_2$ (M = Pd, Pt) readily add to electrophilic olefins, such as 1,1-dicyano-olefins, at room temperature, to give cyclic peroxy-adducts in high yield. The adducts undergo thermal decomposition in solution to carbonyl compounds, the reaction proceeding via carbon—carbon bond cleavage.

Introduction

The direct oxidation of olefins with molecular oxygen to give epoxides or carbonyl compounds (reactions 1 and 2) is a thermodynamically favourable reaction. That these transformations do not occur is due to the absence of low-energy pathways for the reactions (molecular mechanisms are both spin and symmetry forbidden).



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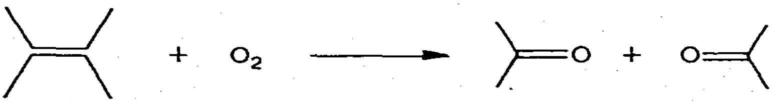

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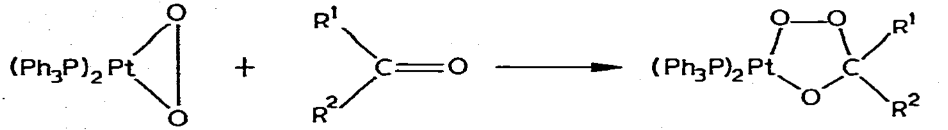
Olefins are indeed oxidized by molecular oxygen under relatively mild conditions, but this occurs via a free-radical chain-reaction involving attack at the reactive, allylic C—H bonds of the olefin. These reactions have limited utility because they give complex mixtures of oxidation products [1]. In order to be selective, any direct oxidation must involve an ionic (non-radical) process, the rate of which is high enough to compete effectively with the ubiquitous free-radical autoxidation.

In recent years much interest has been devoted to the homogeneous activation of molecular oxygen by metal complexes, and a wide variety of stable dioxygen complexes, mainly of Group VIII metals in low oxidation states, have been synthesized (for reviews see ref. 2). The reactions of these metal—dioxygen complexes with olefins have been extensively studied [3-9], in the expectation that they might provide a basis for direct, non-radical oxidation processes. However, the oxidation of olefins in the presence of low-valent, Group VIII metal complexes has been shown [8,9] to involve the generation and consumption of organic peroxide intermediates via radical chain-reactions.

Simple olefins are readily susceptible to attack by electrophiles but are unreactive towards nucleophiles. In order to react readily with the double bond of simple olefins, therefore, a peroxidic species should contain an electrophilic oxygen centre. The chemical reactivity of the oxygen moiety in metal—dioxygen complexes, however, resembles that of nucleophilic peroxide anions rather than that of electrophilic peracids [10]. The observed [11,12] facile cyclo-addition of the platinum—dioxygen complex $(Ph_3P)_2PtO_2$ to the carbonyl group of aldehydes and ketones (reaction 3) is in accord with this nucleophilic character of coordinated dioxygen.



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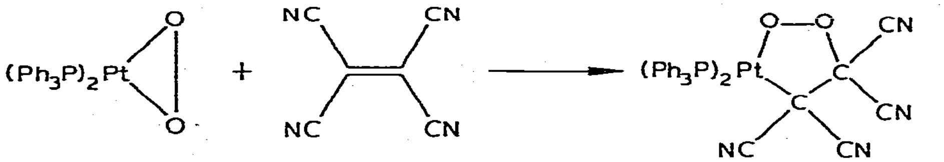
Ugo has recently reported [13] an analogous cycloaddition with the strongly electrophilic olefin tetracyanoethylene.



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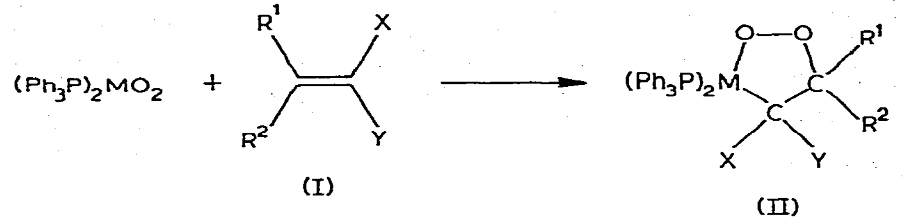
In order to gain more information about the reactivity of metal—dioxygen complexes we have examined the scope of the reaction of Group VIII metal—dioxygen complexes with electrophilic olefins. We have also investigated the chemistry of the cyclic peroxy-adducts formed in this reaction.

Results

Adduct formation between metal—dioxygen complexes and olefins: olefin reactivity

Simple olefins, such as 1-octene, styrene and cyclohexene, or strongly nucleophilic olefins, such as 2,3-dimethyl-2-butene and dioxene, failed to react with $(Ph_3P)_2MO_2$ (M = Pd or Pt) in solution at 60°C. On the other hand, electrophilic olefins, such as the 1,1-dicyano-olefins Ia-Ie, reacted instantaneously with $(Ph_3P)_2MO_2$ at room temperature to give the cyclic peroxy-adducts II in essentially quantitative yield (see also Experimental).



(5)

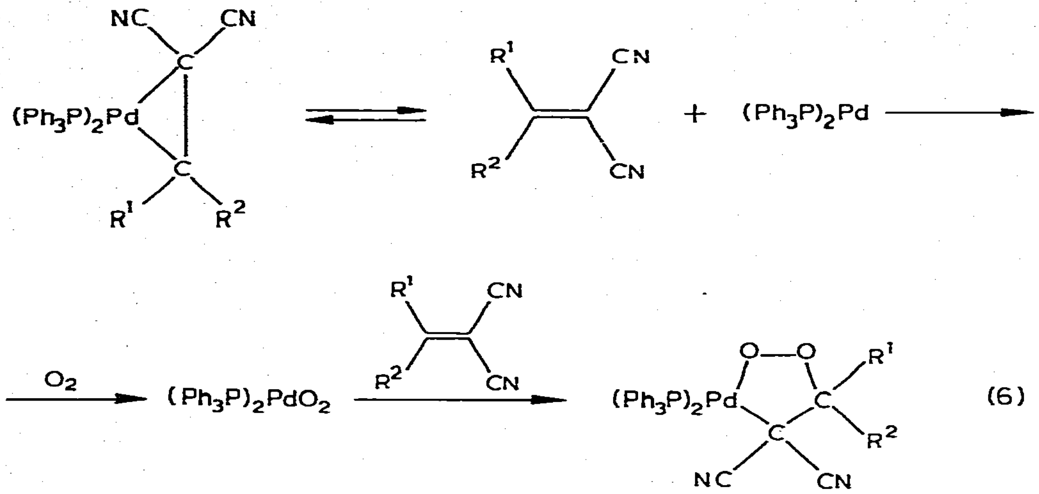
M = Pd or Pt
(a) $R^1 = R^2 = X = Y = CN$
(b) $X = Y = CN, R^1 = R^2 = CH_3$
(c) $X = Y = CN, R^1 = H, R^2 = C_6H_5$
(d) $X = Y = CN, R^1 = H, R^2 = p\text{-}CH_3OC_6H_4$
(e) $X = Y = CN, R^1 = H, R^2 = p\text{-}NO_2C_6H_4$
(f) $X = CN, Y = NO_2, R^1 = H, R^2 = C_6H_5$
(g) $X = CN, Y = NO_2, R^1 = H, R^2 = p\text{-}CH_3C_6H_4$
(h) $X = CN, Y = NO_2, R^1 = H, R^2 = p\text{-}CH_3OC_6H_4$
(i) $X = H, Y = NO_2, R^1 = R^2 = CH_3$
(j) $X = Y = CF_2Cl, R^1 = R^2 = H$
(k) $X = Y = COCH_3, R^1 = H, R^2 = C_6H_5$
(l) $X = Y = CO_2Et, R^1 = R^2 = CH_3$
(m) $X = CN, Y = CO_2Et, R^1 = R^2 = CH_3$

The adducts were prepared by adding the olefin to a solution of $(Ph_3P)_2MO_2$ in methylene chloride or chloroform at room temperature. They were isolated from the solution (by precipitation with pentane) as crystalline, yellow (M = Pd) or off-white (M = Pt) solids that were relatively stable at room temperature (vide infra).

In order to be capable of adduct formation with $(Ph_3P)_2MO_2$ the olefin should, in general, be substituted with two strongly electron-withdrawing groups at one of the olefin carbons. Thus, whereas the 1,1-dicyano-olefins Ib-e reacted instantaneously at room temperature, monocyano-olefins (crotononitrile, acrylonitrile) or 1,2-dicyano-olefins (maleonitrile, fumaronitrile) gave no reaction after 5 days.

The 1-cyano-1-nitro-olefins If-Ih also reacted instantaneously with $(Ph_3P)_2MO_2$ at room temperature. The platinum adducts were stable, but the palladium adducts underwent rapid decomposition in solution. The latter could, however, be prepared and studied at −25°C. The nitro group has such a powerful activating effect that even 1-nitro-2-methylpropene (Ii), which is activated by only one electron-withdrawing group, formed adducts with $(Ph_3P)_2MO_2$ at room temperature. The olefin Ij, although substituted with two powerful electron-withdrawing CF_2Cl groups, formed no adduct with $(Ph_3P)_2MO_2$ at room temperature. Similarly, the unsaturated diketone Ik and diester Il gave no reaction with $(Ph_3P)_2MO_2$. The nitrile ester Im slowly formed an adduct with $(Ph_3P)_2PtO_2$ ($t_{1/2}$ = ca. 1.5 h at room temperature). A slow reaction was also observed with $(Ph_3P)_2PdO_2$ to give acetone, presumably formed via the adduct (vide infra).

The adducts IIc-IIh (M = Pd) were also prepared by bubbling oxygen into a solution of the olefin complex, $(Ph_3P)_2Pd(\text{olefin})$ (obtained by reaction of $(Ph_3P)_4Pd$ with the olefin), at room temperature. Complexes containing olefins that did not form an adduct with $(Ph_3P)_2PdO_2$ (e.g. maleonitrile) simply released the free olefin under these conditions. This suggests that the reaction proceeds via dissociation of the olefin complex (which is known to occur in solution) followed by further reaction between the olefin and the dioxygen complex, e.g.



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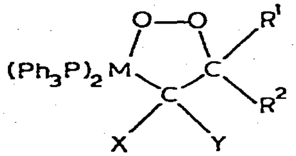
The platinum complexes, $(Ph_3P)_2Pt$(olefin), did not react with oxygen, which is in agreement with their greater stability towards dissociation compared to the palladium complexes.

Other olefins examined that gave no reaction with $(Ph_3P)_2MO_2$ were: 1,1-dichloropropene, methylmethacrylate, 1,2-dibenzoylethene and divinylsulphone.

Other Group VIII metal—dioxygen complexes were cursorily examined. No reaction was observed between Ib and the Rh^I complex $(Ph_3P)_2(t\text{-}BuNC)RhCl(O_2)$ [15] at room temperature, but adduct formation was observed at 60°C. Similarly, the Ir^I complex $(Ph_3P)_2Ir(CO)Cl(O_2)$ [16] did not react with Ib at room temperature. At 60°C the formation of acetone was observed, indicating the transient formation of a thermally unstable adduct (vide infra).

Evidence for the structure of the adducts: NMR spectra

The adducts II have been characterized by NMR, IR (see Experimental) and by their subsequent reactions (vide infra). The structures of the adducts were established as II rather than as the alternative structures III or IV on the



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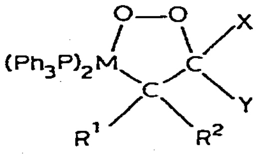

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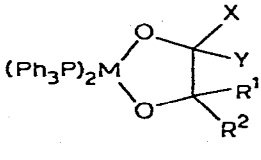
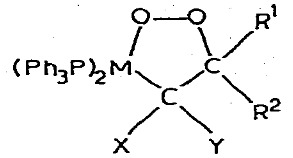


(IV)

basis of their NMR spectra. The ^1H NMR spectral data are given in Table 1. The chemical shifts for the *gem*-dimethyl group in IIb were virtually the same for M = Pd and M = Pt, which would be expected for structures II or IV, but not

TABLE 1

^{1}H NMR DATA[a] FOR THE ADDUCTS



Structure				Chemical shifts[b] (ppm)	
X	Y	R^1	R^2	M = Pd	M = Pt
CN	CN	CH_3	CH_3	CH_3 1.62 (2.31)	CH_3 1.65
CN	CO_2Et	CH_3	CH_3		CH_3 1.65, 1.47 (2.42, 2.33)
CN	CN	H	C_6H_5	H 5.23 (7.82)	H 5.02, $^3J(^{195}Pt-H) = 19$ Hz
CN	CN	H	$p-CH_3OC_6H_4$	H 5.19 (7.67) OCH_3 3.73 (3.92)	H 4.99, $^3J(^{195}Pt-H) = 19$ Hz OCH_3 3.70
CN	CN	H	$p-NO_2C_6H_4$	H 5.27 (7.91)	H 5.07, $^3J(^{195}Pt-H) = 20$ Hz
CN	NO_2[c]	H	C_6H_5	H 5.72 (8.68)	H 5.42, $^3J(^{195}Pt-H) = 30$ Hz
CN	NO_2[c]	H	$p-CH_3C_6H_4$	H 5.68 (8.64) CH_3 2.22 (2.50)	H 5.37, $^3J(^{195}Pt-H) = 30$ Hz CH_3 2.21
CN	NO_2[c]	H	$p-CH_3OC_6H_4$	H 5.68 (8.62) OCH_3 3.70 (3.95)	H 5.36, $^3J(^{195}Pt-H) = 31$ Hz OCH_3 3.66
H	NO_2[d]	CH_3	CH_3	H 4.55 (6.97), d.d., $^3J(^{31}P-H) = 7$ and 4 Hz CH_3 1.62, 1.27 (2.28, 1.97)	H 4.52, tr, $^3J(^{31}P-H) = 4.5$ Hz CH_3 1.55, 1.32

[a] Measured at ca. 30°C in $CDCl_3$ (0.2 *M*) containing tetramethylsilane as internal standard. [b] δ values are ± 0.02 ppm; *J* values are ± 0.3 Hz; the values in parentheses are the chemical shifts for the free olefin in $CDCl_3$ solution. [c] The NMR spectra of the palladium adducts were recorded at —25°C in $CDCl_3$ (0.1 *M*). [d] The NMR spectrum of the palladium adduct was recorded at 0°C in $CDCl_3$ (0.2 *M*).

for III. Also in support of II or IV but not III is the fact that the protons of the *gem*-dimethyl group exhibited no ^{195}Pt satellite signals [17]. The proton of the C—H group in IIc-IIh, on the other hand, did exhibit ^{195}Pt satellite signals, as would be expected for structure II.

The ^{13}C NMR spectra of IIb exhibited a singlet (22.3 ppm) due to the *gem*-dimethyl group and a doublet [119 ppm; $J(^{31}P—C) = 10$ Hz] due to the *gem*-dicyano group; signals from the other two quaternary carbon atoms were not visible. The carbon atoms of the *gem*-dicyano group exhibited ^{195}Pt satellite signals [$J(^{195}Pt—C) = 70$ Hz], whereas the carbon atoms of the *gem*-dimethyl group did not; this can be the case only for structure II. The results of protolysis experiments on the adducts (vide infra) also militate against structure IV.

Thermal decomposition of the cyclic adducts

We have studied the thermal decomposition of the cyclic adducts II in solution by following the progress of the reaction by NMR.

The thermal stability of the adducts is markedly dependent on the nature of the metal, M. The platinum adducts could be kept for several days in solution at room temperature without appreciable decomposition; they underwent facile decomposition only at temperatures of 100°C or higher. The corresponding pal-

TABLE 2

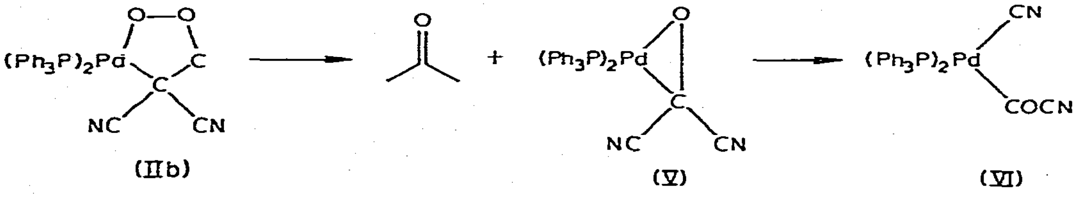
HALF-LIVES FOR THE DECOMPOSITION OF THE PALLADIUM ADDUCTS (II)[a]

Adduct	Temperature (°C)	$t_{1/2}$ (min)	$k \times 10^4$ (s^{-1})
IIb	23.5	30	3.9
	30.5	12	9.3
	40	5	23
	48	2.5	47
IIc	41	7	16
IId	39.5	4	30
IIe	38	1	105
IIh	0	2	58

[a] 0.2 *M* solution in $CDCl_3$.

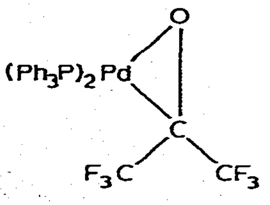
ladium adducts, on the other hand, decomposed readily in solution at room temperature (see Table 2). Nyman et al. [12] similarly found that the cyclic adducts formed from $(Ph_3P)_2PdO_2$ and ketones thermally decomposed much faster than the corresponding adducts with $(Ph_3P)_2PtO_2$. Because of their more facile decomposition we studied the palladium adducts in more detail. The reactions were first-order in adduct over at least two half-lives. The half-lives for the decomposition of several palladium adducts (in $CDCl_3$) are given in Table 2. The activation energy for the decomposition of IIb (M = Pd) was 82.5 ± 3 kJ mol^{-1}. The rate of decomposition of the adducts was influenced significantly by the nature of the substituents (see Table 2), the cyano-nitro-adducts IIf-IIh being much less thermally stable than the dicyano-adducts IIb-IIe.

In all the examples studied, thermal decomposition of II produced the carbonyl compound R^1R^2CO in high yield (identified by NMR and GLC). For example, IIb produced acetone (> 95% yield) together with a palladium complex that exhibited IR bands (at 2160 and 2185 cm^{-1}) characteristic of cyano groups. Purely from stoichiometric considerations we expected that this complex would have structure V or VI.



(7)

Both V and VI are formally derived by the oxidative addition of $(Ph_3P)_2Pd$ to carbonyl cyanide, $CO(CN)_2$. The former is analogous to the product of the reaction between $(Ph_3P)_4Pd$ and hexafluoroacetone [18] (VII):

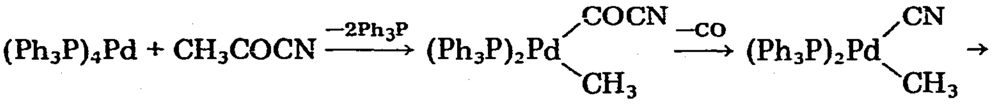


(VII)

However, attempts to synthesize V or VI by reaction of $(Ph_3P)_4Pd$ with $CO(CN)_2$ in benzene or methylene chloride at room temperature led exclusively to the formation of *cis*-$(Ph_3P)_2Pd(CN)_2$*, presumably via the sequence:

$$(Ph_3P)_4Pd + CO(CN)_2 \xrightarrow{-2Ph_3P} cis\text{-}(Ph_3P)_2Pd(CN)COCN \xrightarrow{-CO} cis\text{-}(Ph_3P)_2Pd(CN)_2 \quad (8)$$

Similarly, reaction of $(Ph_3P)_4Pd$ with pyruvonitrile at room temperature produced acetonitrile in quantitative yield:



$$(Ph_3P)_4Pd + CH_3COCN \xrightarrow{-2Ph_3P} (Ph_3P)_2Pd\begin{matrix}\nearrow COCN\\ \searrow CH_3\end{matrix} \xrightarrow{-CO} (Ph_3P)_2Pd\begin{matrix}\nearrow CN\\ \searrow CH_3\end{matrix} \rightarrow \quad (9)$$

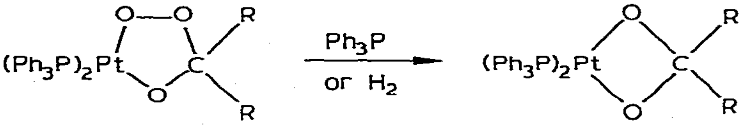
$$\rightarrow (Ph_3P)_2Pd + CH_3CN$$

The above result does not rule out the possibility that the unknown palladium complex is *trans*-$(Ph_3P)_2Pd(CN)COCN$ as the *trans* isomer would be expected to be less prone to decarbonylation.

In the reaction of $(Ph_3P)_2PdO_2$ with an excess of Ib in an atmosphere of oxygen, only one mole of olefin was converted to acetone per mole of $(Ph_3P)_2$-PdO_2. The oxidative cleavage of the olefin by $(Ph_3P)_2PdO_2$ is, thus stoichiometric and not catalytic.

Attempted reduction of the cyclic peroxy-adducts

Nyman et al. [12] found that the cyclic peroxy-adduct VIIIa could be reduced to the corresponding four-membered ring compound IXa with triphenylphosphine. The corresponding adduct with acetone VIIIb did not react with triphenylphosphine, but was reduced by hydrogen.

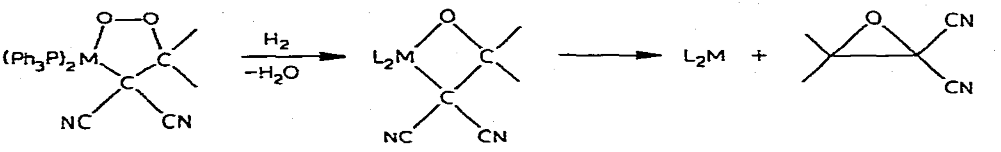


(10)

(VIII) (IX)

(a) $R = CF_3$
(b) $R = CH_3$

We have therefore attempted to reduce the cyclic peroxy-adducts II with molecular hydrogen. We envisaged the production of epoxides via the four-membered ring adduct.



(11)

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* Identical with *cis*-$(Ph_3P)_2Pd(CN)_2$ obtained from reaction of $(Ph_3P)_4Pd$ with $(CN)_2$.

The adduct IIb (M = Pt) was not reduced by molecular hydrogen in 3 days at room temperature in methylene chloride. The adduct was similarly unaffected by treatment with excess triphenylphosphine in $CDCl_3$ for 24 h at 60°C. Reduction did take place on treatment with dimethylphenylphosphine or methyldiphenylphosphine in $CDCl_3$, as was demonstrated by the formation of the corresponding phosphine oxides (determined by NMR and GLC analysis). The reactions were, however, complicated by exchange of the phosphine ligands, and for complete reduction a large excess of phosphine was required. We have not been able to isolate any pure products from these reactions.

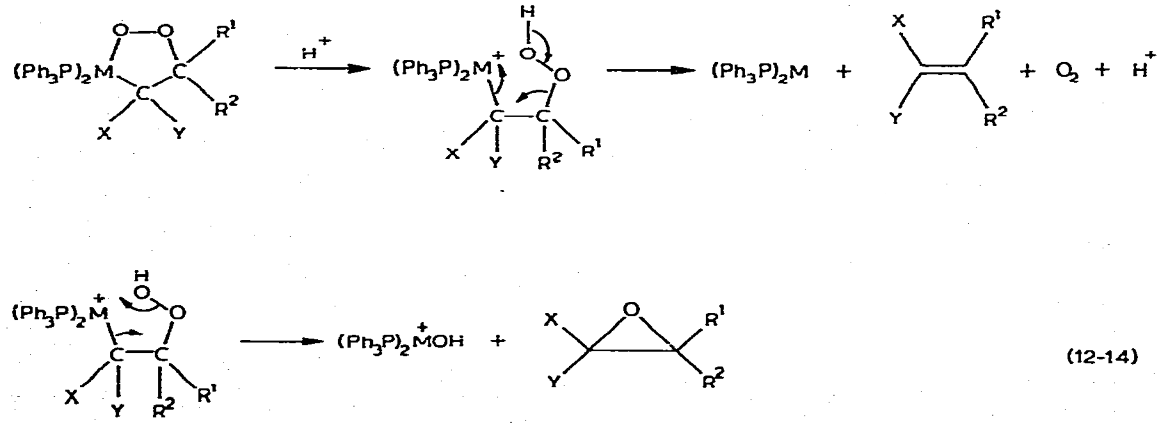
Cleavage with trifluoroacetic acid

We studied the cleavage of a few adducts with trifluoroacetic acid in order to provide additional support for the proposed structure II. Reactions were followed by NMR, and products determined by NMR and GLC analysis.

Addition of a stoichiometric amount of trifluoroacetic acid to a solution of the platinum adduct IIh (M = Pt) in $CDCl_3$ at 28°C resulted in the immediate formation of an intermediate [$\delta(H) = 5.43$ ppm; $J(^{195}Pt—H) = 28$ Hz], which gradually decomposed ($t_{1/2}$ = ca. 30 min) to give the original olefin Ih. The adduct IIb (M = Pt) under the same conditions yielded a 1/1 mixture of the olefin Ib and the corresponding epoxide. When IIb (M = Pt) was treated with trifluoroacetic acid in the presence of excess triphenylphosphine the olefin Ib was the sole product. This suggests that the epoxide formation proceeds via a peroxide intermediate, and can be circumvented by reducing the peroxide with triphenylphosphine. A crossed reaction of IIh (M = Pt) with trifluoroacetic acid in the presence of Ib produced no epoxide from the latter, demonstrating that the epoxide is not formed in a subsequent step by, for example, reaction of the olefin with hydrogen peroxide.

Treatment of the palladium adduct IIb (M = Pd) with trifluoroacetic acid resulted in the instantaneous formation of a mixture of the olefin and the epoxide (molar ratio 1/2).

The above results are not consistent with a structure IV for the adducts, which would be expected to yield the corresponding 1,2-diols upon reaction with acid. We tentatively suggest that the scheme shown below adequately explains the above results.



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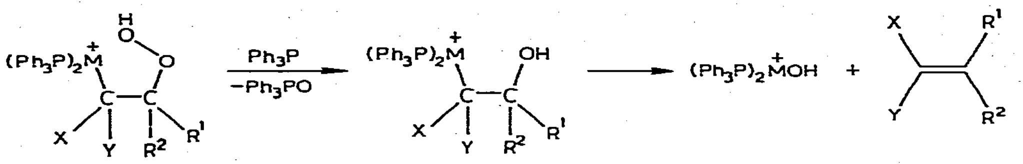


Discussion

Nucleophilic addition of metal—dioxygen complexes to electrophilic olefins

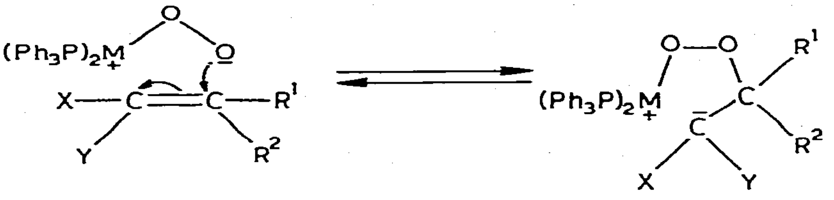
An increase in the reactivity of molecular oxygen upon coordination with transition metals is expected for the following reasons:

(1) Coordinated dioxygen is generally diamagnetic, and reactions with diamagnetic substrates are, therefore, spin allowed.

(2) The metal can hold the dioxygen and the substrate in adjacent coordination sites, thus lowering the activation energy for the reaction.

Facile formation of dioxygen complexes is characteristic of Group VIII metals in low oxidation states (e.g. Pd^0, Pt^0, Ir^I, Rh^I). In these complexes, transfer of charge from the filled metal *d*-orbitals to the empty π^* antibonding orbitals of oxygen renders the latter more nucleophilic in character; that is, enhances its reactivity towards electrophiles. Consequently, they undergo facile addition with electrophilic olefins to give cyclic peroxy-adducts, but are unreactive towards non-functionalized olefins.

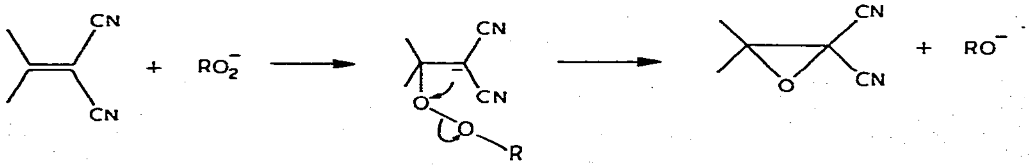
The reactivities of the various olefins towards $(Ph_3P)_2MO_2$ (vide supra) demonstrate that the requirements for facile reaction are that the olefin be substituted with powerful electron-withdrawing groups that are capable of stabilizing a negative charge by resonance. These results are consistent with a mechanism involving stepwise, nucleophilic addition of $(Ph_3P)_2MO_2$ to the olefin.



(15)

(X)

This is analogous to the initial step in the nucleophilic additions of alkylperoxy anions [19] and carbonyl oxides [20] (formed by dissociation of ozonides) to electrophilic olefins, which lead to the formation of epoxides.



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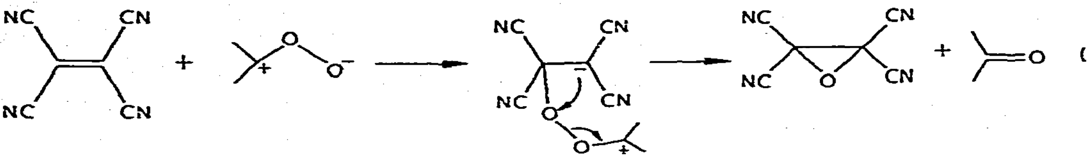

(17)

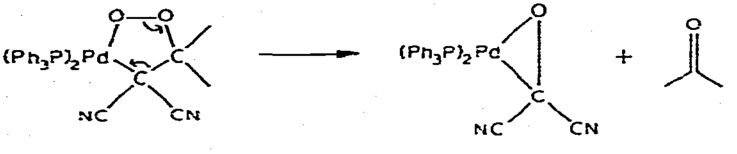
That epoxide formation from X does not occur may be attributed to the lack of a driving force for the elimination of $(Ph_3P)_2M{=}O$, in contrast to the favourable elimination of RO^- or R_2CO.

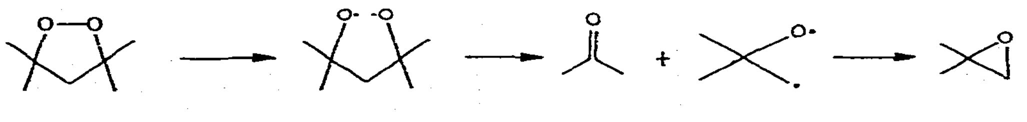
The lack of reaction between $(Ph_3P)_2MO_2$ and the unsaturated diketone Ik and diester Il, and the very slow reaction with the nitrile ester Im is rather surprising. Ester groups are generally almost as strongly activating as cyano groups in nucleophilic additions to olefins, and keto groups are even better [21]. A possible explanation is that steric hindrance by the large Ph_3P groups causes ring closure of X to II to be difficult when the olefin is substituted with CO_2Et or $COCH_3$ groups, but facile when it is substituted with the much smaller cyano groups.

The much lower reactivity of the Rh(I) and Ir(I) complexes in these reactions is consistent with their lower nucleophilicity compared to the Pt^0 and Pd^0 complexes. However, steric factors may also play an important role in determining the reactivity of various metal—dioxygen complexes towards olefins.

Carbon—carbon bond cleavage in the thermal decomposition of the cyclic peroxy-adducts

In all the examples studied, thermal decomposition of the cyclic peroxy-adducts II led to selective cleavage of the double bond of the original olefin. The overall reaction constitutes a transition metal-promoted cleavage of an olefin with molecular oxygen. The reaction appears to be general for Group VIII metals since it was promoted by Ir^I and Rh^I complexes as well as by Pd^0 and Pt^0 complexes. The reaction is, however, a stoichiometric one; only 1 mole of olefin is converted per mole of metal complex. This is because in the cleavage of the cyclic peroxy-adduct the original Pd^0 or Pt^0 complex is not regenerated (vide supra). Several possible mechanisms may be envisaged for the thermal decomposition of II. The reaction may be concerted (reaction 18) or may involve initial homolysis of the O—O bond as in the analogous [22] 1,2-dioxolanes (reaction 19). Alternatively, the reaction may proceed via initial heterolysis (or homolysis) of the Pt—O bond, leading to the formation of an unstable dioxetane intermediate (reaction 20). Dioxetanes are known [23] to rapidly decompose to carbonyl compounds in the presence of trace amount of metals. On the basis


(18)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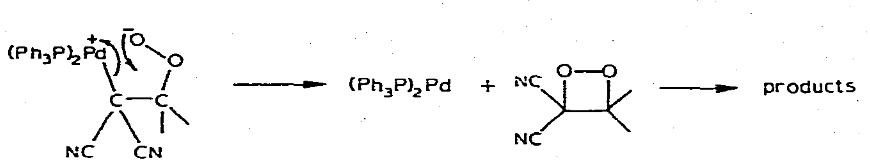

(20)

of the available evidence it is not possible to distinguish with any certainty between these different mechanisms.

Experimental

Materials

The olefins 1,1-dicyano-2-methylpropene (Ib) [24], maleonitrile [25], β,β-dicyanostyrenes (Ic-Ie) [26], β-cyano-β-nitrostyrenes (If-Ih) [27], 1-nitro-2-methylpropene (Ii) [28], 1,1-bis(difluorochloromethyl)ethene (Ij) [29], β,β-diacetylstyrene (Ik) [30], 1,1-bis(ethoxycarbonyl)-2-methylpropene (Ij) [31], and 1-cyano-1-ethoxycarbonyl-2-methylpropene (Im) [32] were synthesized by published procedures. Carbonyl cyanide was prepared from tetracyanoethylene oxide [33]. The epoxide of Ib was prepared by the method of Payne [19]. The complexes $(Ph_3P)_4Pt$ [34], $(Ph_3P)_4Pd$ [35], $(Ph_3P)_2PtO_2 \cdot C_6H_6$ [36], $(Ph_3P)_2PdO_2$ [37], $(Ph_3P)_2Ir(CO)Cl(O_2)$ [16], $(Ph_3P)_2(t\text{-}BuNC)RhCl(O_2)$ [15] and *trans*-$(Ph_3P)_2Pd(CN)_2$ [38] were also prepared by reported methods.

Physical measurements

Infrared spectra were recorded on a Perkin—Elmer 457 instrument. NMR spectra were recorded on a Varian A60 or a Bruker WH90 instrument using an internal tetramethylsilane (TMS) standard.

General method of preparation of the adducts (II)

Solutions of the adducts for NMR experiments were prepared by adding the olefin (0.1 mmol) to a solution of $(Ph_3P)_2MO_2$ (0.1 mmol) in deuterochloroform (0.5 ml). In all cases where reaction occurred a clear solution was immediately obtained, which varied in colour from pale yellow to orange. NMR analysis of the solutions indicated that the adducts were formed in essentially quantitative yield.

The addition of pentane or ether to the solutions resulted in the precipitation of the adducts as yellow (M = Pd) or off-white (M = Pt) solids in high yield (> 75%). They could be recrystallized from methylene chloride/pentane mixtures. Their IR spectra (KBr discs) exhibited no bands due to olefinic double bonds or to the O—O bond of $(Ph_3P)_2MO_2$ (825 and 877 cm^{-1} for M = Pt and Pd, respectively). The adducts IIb-IIh exhibited a single, sharp band in the region 2200-2220 cm^{-1} due to the cyano group (10-30 cm^{-1} lower than in the parent olefin).

The adducts were soluble in chloroform, methylene chloride, benzene and acetone. They were insoluble in ether, methanol and pentane. Some of the adducts (e.g. IIi-IIh) were soluble in acetonitrile, whilst others (e.g. IIb) were insoluble. Although their NMR and IR spectra indicated that they were pure, we were unable to obtain satisfactory or consistent elemental analyses for the adducts, which can probably be attributed to their limited stability. Where no reaction occurred immediately (as shown by NMR) the reaction mixtures were allowed to stand for several days at room temperature and were periodically examined (by NMR) to determine if the reaction had occurred. Reactions with $(Ph_3P)_2PdO_2$ could be carried out only at room temperature because this complex is thermally unstable (it decomposes slowly in solution at room temperature to palladium metal and triphenylphosphine oxide [29]). $(Ph_3P)_2PtO_2$, on the other hand, is thermally quite stable (it decomposes readily only above 120°C) [39], and when reactions of this complex with the unreactive olefins tetramethylethylene, crotononitrile, methyl methacrylate and II were attempted at 60°C, no reaction took place.

Complex IIb (M = Pd)

1,1-Dicyano-2-methylpropene (0.111 g, 1.05 mmol) was added to a solution of $(Ph_3P)_2PdO_2$ (0.662 g, 1.0 mmol) in methylene chloride (10 ml) at 0°C. After 1 min the solution was poured into ether (100 ml). The product separated as golden yellow crystals which were filtered off, washed with ether and dried in vacuo; yield 0.643 g (84%), m.p. (CH_2Cl_2/pentane) 118-123°C (dec.).

Complex IIb (M = Pt)

1,1-Dicyano-2-methylpropene (0.291 g, 2.75 mmol) was added to a solution of $(Ph_3P)_2PtO_2 \cdot C_6H_6$ (1.606 g, 1.94 mmol) in methylene chloride (50 ml) at room temperature. After 5 min the solution was poured into pentane (500 ml). The product separated as white crystals which were filtered off, washed with ether and dried in vacuo; yield 1.484 g (89%), m.p. (CH_2Cl_2/pentane) 180-181°C.

Complex IId (M = Pt)

β,β-Dicyano-*p*-methoxystyrene (0.405 g, 2.2 mmol) was added to a solution of $(Ph_3P)_2PtO_2 \cdot C_6H_6$ (1.658 g, 2.0 mmol) in methylene chloride (50 ml). After 5 min the solution was poured into pentane (500 ml) and the product (off-white crystals) filtered off, washed with ether and dried in vacuo; yield 1.847 g (99%), m.p. 144-148°C.

Complex IIh (M = Pt)

β-Cyano-β-nitro-*p*-methoxystyrene (0.306 g, 1.5 mmol) was added to a solution of $(Ph_3P)_2PtO_2 \cdot C_6H_6$ (0.829 g, 1.0 mmol) in methylene chloride (25 ml). After 2 min the pale yellow solution was poured into pentane (150 ml) to give an off-white solid which was filtered off, washed with 4 X 50 ml ether and dried in vacuo; yield 0.738 g (77%), m.p. (CH_2Cl_2/pentane) 149-151°C (dec.).

Complex IIa (M = Pt)

Freshly sublimed tetracyanoethylene (0.055 g, 0.43 mmol) in methylene chloride (10 ml) was added to $(Ph_3P)_2PtO_2 \cdot C_6H_6$ (0.330 g, 0.4 mmol) in methylene chloride (10 ml). The solution was allowed to stand for 10 min. Removal of the methylene chloride and trituration of the residue with ether produced an off-white solid; yield 0.280 g (80%), m.p. (CH_2Cl_2/Et_2O) 182-183°C.

Complex IIa (M = Pd)

$(Ph_3P)_2PdO_2$ (0.662 g, 1.0 mmol) was added to a solution of freshly sublimed tetracyanoethylene (0.128 g, 1.0 mmol) in ethanol (25 ml). The solution was stirred for 10 min. The product separated as pale yellow crystals and was filtered off, washed with ether and dried in vacuo; yield 0.587 g (74%), m.p. 131-132°C.

Reaction of $(Ph_3P)_4Pd$ with $CO(CN)_2$

A solution of $(Ph_3P)_4Pd$ (0.577 g, 0.5 mmol) and $CO(CN)_2$ (0.040 g, 0.5 mmol) in benzene (10 ml) under argon was allowed to stand for 5 days at room temperature. The product separated as white crystals and was filtered off, washed with benzene and dried; yield 0.36 g (93%), m.p. 230-231°C, ν(CN) 2135 cm^{-1}. The product was identical (mixed m.p., IR) with *cis*-$(Ph_3P)_2Pd(CN)_2$ prepared by reaction of $(Ph_3P)_4Pd$ with $(CN)_2$ (vide infra). The reaction was also carried out in methylene chloride and produced *cis*-$(Ph_3P)_2Pd(CN)_2$ in 81% yield. In one instance the reaction mixture (in CH_2Cl_2) was worked up immediately by adding pentane to precipitate the product. The infrared spectrum of the product indicated that it was a mixture of *cis*-$(Ph_3P)_2Pd(CN)_2$ and, presumably, the adduct *cis*-$(Ph_3P)_2Pd(CN)COCN$. The infrared spectrum [ν(CN) 2160, 2190 cm^{-1}, ν(CO) 1640 cm^{-1}] of the latter was very similar to that of the unidentified palladium complex formed in the decomposition of IIb (M = Pd).

Reaction of $(Ph_3P)_4Pd$ with $(CN)_2$ [40]

Cyanogen (prepared by reaction of KCN with $CuSO_4$ at 50°C) was bubbled through a solution of $(Ph_3P)_4Pd$ (0.577 g, 0.5 mmol) in benzene (15 ml), with stirring, under an atmosphere of argon, for 15 min. *cis*-$(Ph_3P)_2Pd(CN)_2$ separated as a white solid; yield 0.167 g (49%), m.p. (CH_2Cl_2/pentane) 230-231°C, ν(CN) 2135 cm^{-1}. The product was isomerized to the *trans*-isomer [m.p. 330-333°C, ν(CN) 2135 cm^{-1}], which was identical (mixed m.p., IR) with *trans*-$(Ph_3P)_2Pd(CN)_2$ prepared from *trans*-$(Ph_3P)_2PdCl_2$ and KCN [38], by heating under reflux in chloroform for 5 h. The infrared spectra of the *cis*- and *trans*-isomers were very similar, but differed in the aromatic region in that the *trans*-isomer had extra bands at 765 and 746 cm^{-1}. No isomerization was observed when the *cis*-isomer was heated under reflux in benzene/methanol (1/1) for 5 h, the *cis*-isomer being recovered unchanged.

Thermal decomposition of IIb (M = Pd)

A solution of the adduct (1.65 g, 2.0 mmol) in CH_2Cl_2 (25 ml) was heated under reflux for 3 h. The formation of acetone was demonstrated by GLC and NMR analysis. The solution was evaporated to dryness to leave a brown solid; yield 1.30 g, ν(CN) 2160, 2185 cm^{-1}, broad absorption at 1620 cm^{-1}. The product was soluble in methylene chloride, benzene and methanol, and insoluble in ether and pentane.

That the product is *trans*-$(Ph_3P)_2Pd(CN)COCN$ is suggested by the fact that when the reaction mixture from $(Ph_3P)_4Pd$ plus $CO(CN)_2$ was worked up immediately by adding pentane to precipitate the product, a mixture was obtained which consisted of *cis*-$(Ph_3P)_2Pd(CN)_2$ together with another complex (presumably *cis*-$(Ph_3P)_2Pd(CN)COCN$) whose infrared spectrum was very similar to that of the above unknown thermal decomposition product (2160, 2190, 1640 cm^{-1}, cf. 2160, 2185 and 1620 (br) cm^{-1}). Treatment of the unknown thermal decomposition product with potassium cyanide in refluxing methanol for 3 days gave *trans*-$(Ph_3P)_2Pd(CN)_2$ (m.p. and mixed m.p. 330-333°C). The complex was unaffected by treatment with excess triphenylphosphine or with dry hydrogen chloride in methylene chloride. The latter result would not be expected for a complex with structure V, which should be readily cleaved by hydrogen chloride.

Assuming that the complex was VI, we attempted to isomerize it to the *cis*-isomer, which would then be expected to decarbonylate to *cis*-$(Ph_3P)_2Pd(CN)_2$. The complex was recovered unchanged after photolysis (243.7 nm; in methylene chloride) for 24 h. Heating the complex under reflux in chloroform for 48 h also had no effect.

Attempted reduction of IIb (M = Pt)

Hydrogen was bubbled slowly through a stirred solution of IIb (M = Pt; 0.1 mmol) in methylene chloride (10 ml) for 3 days at room temperature. Removal of the solvent left unchanged IIb. A solution of IIb (0.1 mmol) and triphenylphosphine (0.2 mmol) in chloroform (0.5 ml) was heated under reflux for 15 h. Complex IIb was again recovered unchanged. When excess dimethylphenylphosphine was added to a solution of IIb in $CDCl_3$ an immediate reaction took place and the formation of dimethylphenylphosphine oxide was observed by NMR. No pure platinum complex could be isolated from the reaction mixture. GLC analysis of the solution showed that neither 1,1-dicyano-2-methylpropene (IIb) nor the corresponding epoxide was present. Reduction of IIb, albeit slower, was also observed when methyldiphenylphosphine was used. Here again no products could be identified.

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