

Palladium(II) *tert*-Butyl Peroxide Carboxylates. New Reagents for the Selective Oxidation of Terminal Olefins to Methyl Ketones. On the Role of Peroxymetalation in Selective Oxidative Processes

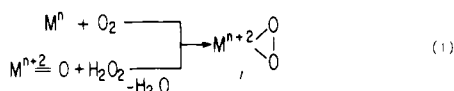
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Abstract: A new family of palladium(II) *tert*-butyl peroxidic complexes of general formula $[\text{RCO}_2\text{PdOO-}t\text{-Bu}]_4$ was synthesized and characterized by physicochemical methods and X-ray crystallography. The crystal structure of $[\text{CCl}_3\text{CO}_2\text{PdOO-}t\text{-Bu}]_4$ was determined. The molecule crystallizes with four formula units in the monoclinic space group $C2/c$ with $a = 17.867$ (7) Å, $b = 14.371$ (4) Å, $c = 21.126$ (3) Å, and $\beta = 112.63$ (2)°. The final indices based on the least-squares refinements with 2154 observations having $I > 3\sigma(I)$ are $R_1 = 0.055$ and $R_2 = 0.077$. The tetrameric molecule has crystallographic C_2 symmetry and approximately D_{2d} symmetry. The four palladium atoms are coplanar and are located approximately at the corners of a square. Four trichloroacetato bridging anions are alternatively above and below this square. The terminal oxygen atoms of the four *tert*-butyl peroxidic anions are located in the plane of the four palladium atoms and bridge these atoms two by two. The average Pd...Pd separation is 2.91 Å. The mean value of the peroxidic O-O bond distance is 1.49 Å. These complexes are highly efficient reagents for the selective stoichiometric oxidation of terminal olefins to methyl ketones at ambient temperature, and catalysts for the ketonization of terminal olefins by *tert*-butyl hydroperoxide. The removal of one oxygen atom from the *tert*-butyl peroxidic group in $[\text{CF}_3\text{CO}_2\text{PdOO-}t\text{-Bu}]_4$ (PPT) by the terminal olefin first affords the palladium *tert*-butoxy complex and then the π -allylic complex by rapid substitution of the *tert*-butoxy group for the olefin. Several π -allylic complexes of general formula $[\text{CF}_3\text{CO}_2\text{Pd}(\pi\text{-allyl})]_2$ were synthesized in this way from the reaction of PPT with both terminal and internal acyclic olefins. The consideration of the general features of the ketonization of terminal olefins by PPT has led us to suggest a mechanism involving a five-membered pseudocyclic peroxymetalation of the coordinated olefin. This mechanism strongly resembles that proposed for the epoxidation of olefins by molybdenum peroxo complexes and ketonization of terminal olefins by rhodium peroxo complexes involving a cyclic five-membered peroxymetalation of the olefin. This mechanism may afford a plausible explanation for the molybdenum-catalyzed epoxidation of olefins by alkyl hydroperoxides.

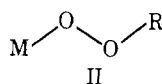
Introduction

Transition-metal peroxides are generally considered as the key intermediates in the selective oxidative processes involving molecular oxygen,² hydrogen peroxide, or alkyl hydroperoxides as the oxygen source.³ Peroxo complexes (type I) can be obtained either from the interaction of dioxygen with low-valent two-electron donor metal complexes or from the reaction of hydrogen peroxide with high-valent metal-oxo complexes (eq 1).⁴



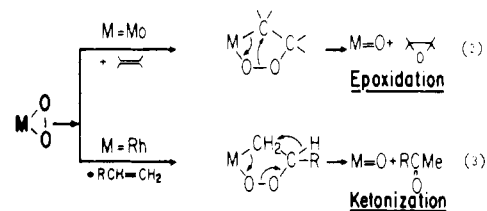
We have previously shown that oxygen can transfer from some peroxo complexes to olefins, selectively producing epoxides ($M = \text{Mo}$, eq 2)⁵ or methyl ketones ($M = \text{Rh}$, eq 3)⁶ through cyclic peroxymetalation of the olefin (Scheme I).

Contrary to peroxo complexes, there are still few reported examples of well-characterized alkyl peroxidic transition metal complexes (type II). To our knowledge, there exists only one X-ray structure determination of type II complexes ($M =$



pyridine cobaloxime, $R = \text{cumyl}$),⁷ while alkylperoxyiridium(III) complexes with the formula $\text{IrXL}_2(\text{CO})(\text{OO-}t\text{-Bu})_2$ ($X = \text{Cl, Br}$; $L = \text{PPh}_3, \text{AsPh}_3$) have also been isolated.⁸ This paper describes the synthesis and characterization of new palladium(II) *tert*-butyl peroxide carboxylates with the general formula $[\text{RCO}_2\text{PdOO-}t\text{-Bu}]_4$ and their properties as selective

Scheme I. Cyclic Peroxymetalation



oxidative reagents for the transformation of terminal olefins to methyl ketones.

Results and Discussion

I. Synthesis and Characterization of the Peroxidic Complexes. Palladium(II) acetate dissolves at room temperature in 80% *tert*-butyl hydroperoxide giving orange solutions from which fine yellow-orange particles are deposited after continuous stirring for about 2 h. Orange complexes were also obtained as precipitates in yields varying from 65 to 85% from the reaction of palladium(II) trichloroacetate or trifluoroacetate with excess *tert*-butyl hydroperoxide. An elemental analysis of these complexes indicated the general formula $\text{RCO}_2\text{PdOO-}t\text{-Bu}$ [$R = \text{Me}$ (**1a**), CCl_3 (**1b**), CF_3 (**1c**), C_5F_{11} (**1d**)] corresponding to the substitution of one carboxylate anion on the palladium by a *tert*-butyl peroxidic group according to reaction 4.



These complexes are stable in the solid state and can be stored for months in a refrigerator with no apparent decom-

Table I. Palladium(II) *tert*-Butyl Peroxide Carboxylates, $[\text{RCO}_2\text{PdOO-}t\text{-Bu}]_4$

complex	R	infrared absorptions, cm^{-1} ^a			NMR, ^b $\delta(t\text{-Bu})$, ppm	mol wt ^c	N Pd ^d
		$\nu(\text{O-O})$	$\nu(\text{C=O})$ asym	$\nu(\text{C=O})$ sym			
1a	CH ₃	855	1540 s	1420	1.38	1000	4
1b	CCl ₃	855	1615 s	1365 s	1.45	1400	4
1c [PPT]	CF ₃	860	1630 s	1450 w	1.36	1200	4
1d	C ₅ F ₁₁	870	1630 s	1420 w	1.33	2000	4

^a KBr disk. ^b Solvent CDCl₃. ^c Tonometric determination in CHCl₃, mol wt ± 50 . ^d Presumed number of palladium atoms per molecule.

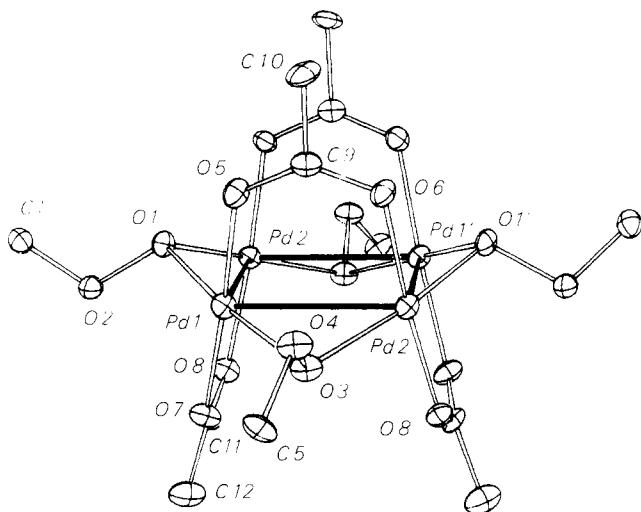


Figure 1. A drawing of a molecule of $[\text{CCl}_3\text{CO}_2\text{PdOO-}t\text{-Bu}]_4$. The chlorine atoms and the methyl groups have been omitted for clarity. Vibrational ellipsoids are drawn at the 50% probability level.

position. Upon heating, they melt with decomposition at 130–150 °C but do not explode and are not shock sensitive. They are soluble in most organic solvents, e.g., CH₂Cl₂, benzene, and THF, and are insoluble in light paraffins (except **1d**). They can be recrystallized from methylene chloride (**1b**) or diethyl ether (**1c**). Strongly basic solvent such as DMF and HMPA should be avoided because they profoundly alter the nature of the complexes (vide infra). Immediate evolution of iodine was observed when they react with acidic potassium iodide solutions, confirming the peroxidic nature of these complexes.

The infrared spectra of these complexes (Table I) exhibited a moderately intense absorption at 860–870 cm^{-1} attributable to the characteristic $\nu(\text{O-O})$ peroxidic stretching vibrations. The other infrared absorptions were assigned to the carboxylato group (1350–1600 cm^{-1}) and the *tert*-butyl peroxidic group at 1180 ($\nu(\text{C-C})$) and 2980 cm^{-1} ($\nu(\text{C-H})$). In addition, there was no evidence in the infrared region 3300–3600 cm^{-1} of any OH group belonging to a possibly coordinated *t*-BuOOH molecule. In the infrared spectra of the fluoro complexes **1c** and **1d**, the symmetric $\nu(\text{C=O})$ absorption of the carboxylato group at 1420–1450 cm^{-1} was very low compared with that of complexes **1a** and **1b** and with that of conventional metalcarboxylates,⁹ while the asymmetric $\nu(\text{C=O})$ absorption appears as an intense narrow band at 1630 cm^{-1} . This therefore indicates that the two C–O bonds in the fluorocarboxylato groups are not equivalent.

NMR spectra of the complexes (Table I) exhibited a singlet at δ 1.33–1.45 ppm (reference Me₄Si) attributable to the *tert*-butyl group of the peroxidic complexes. This corresponds to a slight deshielding effect by the metal of ca. 0.1–0.2 ppm in comparison with the free *t*-BuOOH (1.25 ppm). Molecular weight measurements indicated that the complexes **1a–d** are probably tetrameric in solution.

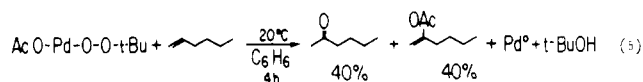
II. X-ray Structure of $[\text{CCl}_3\text{CO}_2\text{PdOO-}t\text{-Bu}]_4$. Suitable

single crystals of this compound were obtained by slow evaporation of dichloromethane solutions at 4 °C. These crystals belong to the monoclinic system, space group $C2/c$ (vide infra). The unit cell parameters were refined at room temperature using Mo K α radiation with the standard method of Busing and Levy on a Picker diffractometer: $a = 17.867$ (7) Å, $b = 24.371$ (4) Å, $c = 21.126$ (3) Å, $\beta = 112.03$ (2)°, $Z = 4$, $d_{\text{calcd}} = 1.90$ g cm^{-3} . Details of the data collection, structure determination, and refinement are given in the Experimental Section. The final positional and thermal parameters of the atoms appear in Table II. A listing of the observed and calculated structure amplitudes for those data used in the refinements is available.¹⁰

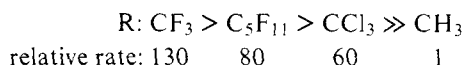
The structure consists of tetrameric molecules $[\text{CCl}_3\text{CO}_2\text{PdOO-}t\text{-Bu}]_4$, presenting crystallographic C_2 symmetry; the twofold symmetry axis is normal to the plane of the four palladium atoms (Figure 1). Table III lists the most important bond lengths and Table IV gives the bond angles. Four trichloroacetato anions are arranged alternatively above and below the plane of a slightly distorted square formed by four palladium atoms. The terminal oxygen atoms of four *tert*-butyl peroxidic anions lie approximately in the plane of the four palladiums and bridge these atoms two by two. Consequently, each palladium has a distorted trans square coordination formed by two terminal oxygen atoms of two *t*-Bu peroxidic anions (mean Pd–O = 1.994 (3) Å) and two oxygen atoms of the CCl₃CO₂[−] groups (mean Pd–O = 2.039 (5) Å). The terminal oxygen atoms of the *t*-Bu peroxidic anions present the expected pyramidal stereochemistry. In each group the Pd–O–Pd bond angle is close to 94° and the mean value of the two Pd–O–O angles is 110.5°. The peroxidic O–O bond distance of 1.49 Å is very close to that present in free hydroperoxides¹¹ and similar to that present in the cumyl peroxide (pyridine) cobaloxime.⁷ The four palladium atoms are coplanar; the two crystallographically independent Pd...Pd separations of 2.912 (1) and 2.923 (1) Å indicate that there is no direct interaction between these atoms. The symmetry of the tetrameric molecule $[\text{CCl}_3\text{CO}_2\text{PdOO-}t\text{-Bu}]_4$ is close to D_{2d} .

In the solid state palladium(II) acetate is a trimeric molecule in which the metal atoms are in a triangle with bridging acetate group.¹² The Pd...Pd distances in this trimer range from 3.10 to 3.20 Å. In contrast, the platinum acetate is a tetramer in which eight bridging acetate groups are arranged around a square cluster of platinum atoms (mean Pt...Pt distance = 2.495 Å) such that four acetate groups are in the plane of the cluster and four are alternatively above and below it.¹³ Thus, $[\text{CCl}_3\text{CO}_2\text{PdOO-}t\text{-Bu}]_4$ bears some resemblance with platinum acetate, the bridging acetate groups located in the plane of the cluster being replaced by the *tert*-butyl peroxidic anions.

III. Oxidation of Olefins by the Peroxidic $[\text{RCO}_2\text{PdOO-}t\text{-Bu}]_4$ Complexes. Addition of 1-hexene to solution of the acetate peroxidic complex **1a** (1-hexene: Pd = 50) in anhydrous benzene at 20 °C produced a mixture of 2-hexanone (40% yield based on Pd) and 2-acetoxy-1-hexene (40%) after 4-h reaction time (eq 5). This reaction occurred with the precipitation of metallic palladium.



We anticipated that formation of the methyl ketone and the vinylic ester would result from the nucleophilic attack of the *tert*-butyl peroxidic group and the acetato group, respectively, on the coordinated olefin (*vide infra*). Accordingly, on the metal we replaced the nucleophilic acetato group by the strong electron acceptor trifluoroacetato group, in order to prevent the parallel vinylic ester formation. The reaction of palladium *tert*-butyl peroxide trifluoroacetate (**1c**, PPT) with 1-hexene under the same conditions resulted in the formation of only 2-hexanone with a 98% yield (based on Pd) in less than 10 min reaction time. Similarly, the peroxidic complexes **1b** and **1d** only afforded 2-hexanone from 1-hexene in quantitative yields. The reactivity of the peroxidic complexes **1a-d** toward 1-hexene, estimated from 2-hexanone formation at 1-h reaction time (temperature 20 °C, solvent benzene, olefin: Pd = 1) followed the order



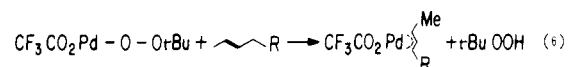
Hence, the reaction is *strongly accelerated* when the electron-attracting character of the carboxylato group bound on palladium *increases*, i.e. when the electron acceptor character of palladium toward olefins increases.

Except in the case of the acetato complex **1a**, and when the reaction medium is rigorously anhydrous, *no precipitation of metallic palladium* occurred during the reaction of complexes **1b-d** with 1-hexene. Furthermore, oxidation was not inhibited by the presence of strong dehydrating agents such as 2,2-dimethoxypropane, therefore excluding the possibility of a Wacker-type hydroxypalladation mechanism.⁶ In fact, when small amounts of water were present in the reaction medium, yields higher than 100% (based on Pd) were obtained and precipitation of metallic palladium occurred under these conditions. The best solvents for carrying out the oxidation of terminal olefins by PPT were anhydrous chlorinated solvents (e.g., methylene chloride, 1,2-dichloroethane, chlorobenzene), aromatic hydrocarbons (e.g., benzene, toluene), or nitro compounds (e.g., nitrobenzene). Oxidation was strongly inhibited in alcoholic solutions (e.g., 2-propanol, *tert*-butyl alcohol) or in basic solvents (e.g., DMF, HMPA). When small amounts of σ -donor ligands (e.g., pyridine, HMPA, 2,2-bipyridine, PPh₃), or strong complexing olefins (e.g., 1,5 cyclooctadiene) were added at the beginning of the reaction of PPT with 1-hexene (1-hexene:PPT = 50, ligand:PPT = 2), the oxidation did not occur. The addition of pyridine, 2,2-bipyridine, or PPh₃ to PPT in diethyl ether caused the precipitation of yellow complexes. An elemental analysis of these complexes gave unidentified formula, but both infrared and NMR measurements indicated the disappearance of the *tert*-butyl peroxidic group on palladium. Hence, not only does a competition for coordination sites between olefin and ligands exist, but the presence of strong complexing ligands causes a profound alteration of the complexes by destroying their peroxidic nature.

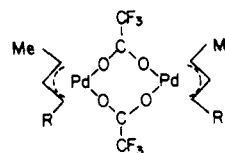
The reactivity of various olefins toward PPT at 20 °C in anhydrous benzene (olefin:PPT = 50) is shown in Table V. Terminal olefins are more rapidly oxidized to the corresponding methyl ketones which are the only oxygenated product detected from this reaction. Neither terminal aldehydes nor internal ketones were observed as byproducts. Note that the reactivity of terminal olefins toward PPT corresponds more closely to their reactivity with rhodium catalysts⁶ than with PdCl₂-CuCl₂ in the Wacker processes.¹⁴

Internal olefins were oxidized by PPT either very slowly or not at all. Instead a π -allylic complex is formed, resulting di-

rectly from the substitution of the *tert*-butyl peroxidic group on palladium by the olefin, as shown in reaction 6.



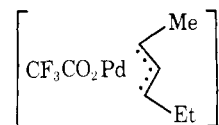
Various 2,4- π -allylic complexes of palladium were synthesized in this way using *cis*-2-pentene (**5b**, R = Me), *cis*-2-hexene (**5c**, R = Et), and *cis*-2-octene (**5d**, R = *n*-C₄H₉) as olefins (see Table VI). These complexes were easily obtained as pale yellow precipitates from solutions of PPT in these internal olefins. They were characterized by elemental analysis, infrared, and NMR spectrometry. The NMR spectra of the protons in the π -allylic moiety in these complexes are depicted in Table VI and are similar to those of known di- μ -acetato-bis(π -allyl)dipalladium complexes.^{15,16} Since mass spectrometry indicated a dimeric structure (see Experimental Section), we assume that the palladium trifluoroacetato 2,4- π -allylic complex possesses the known following structure.



In the oxidation of 1-hexene by PPT in dry benzene at 20 °C and under nitrogen, both the 2-hexanone yield and the nature of the resulting palladium complex depend on the olefin: Pd ratio. Plots of 2-hexanone formation vs. time for various 1-hexene:PPT ratios are shown in Figure 2.

(1) At 1-hexene:PPT = 1, the 1-hexene consumption and the 2-hexanone formation were followed by GLC using chlorobenzene as internal standard. For each equivalent of 1-hexene consumed, only 0.5 equiv of 2-hexanone was obtained, and the final yield in ketone (based on Pd) reached about 50% after 2-h reaction time for the complete conversion of 1-hexene; *tert*-butyl alcohol was also identified as a reaction product in about 50% yield.

A better approach to the features of this stoichiometric oxidation was revealed using NMR monitoring during the reaction, as shown in Figure 3. The NMR spectrum of PPT alone in CDCl₃ exhibited only a *tert*-butyl singlet at 1.36 ppm. After addition of a stoichiometric amount of 1-hexene, this signal at 1.36 ppm decreased and a new signal at 1.25 ppm gradually appeared during the reaction. The formation of 2-hexanone was revealed by a signal at 2.2 ppm (CH₃CO). At the same time, two signals at 5.9 (1 H) and 4.3 ppm (2 H) appeared, together with a small doublet at 3.9 ppm. These two signals were respectively assigned to the syn proton and the two anti protons of a 2,4-methylethyl disubstituted π -allyl group bound on palladium. These signals are deshielded about 0.6 ppm in comparison with those of the isolated



complex (**5c**₁) obtained directly from the reaction of PPT with *cis*-2-hexene (Table VI). Such a deshielding effect of 0.6 ppm of the syn and the two anti protons of the π -allylic group was also observed by Davidson between the NMR spectra of the dimeric form (**5c**₂) and the trimeric form (**5c**₃) of the equivalent acetato π -allylic complexes.¹⁶ This therefore suggests that, after having oxidized 1-hexene, PPT is transformed into a 2,4- π -allylic complex (**5c**₄) containing more than two palladium atoms per molecule (probably three or four). The doublet at 3.9 ppm was assigned to the syn H_d and the anti H_c protons

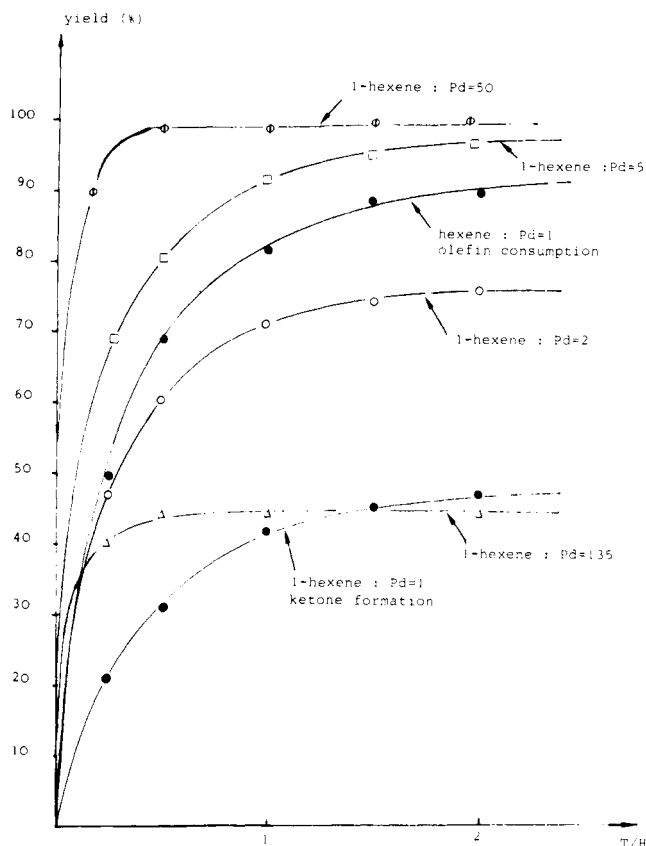


Figure 2. Oxidation of 1-hexene by PPT, temperature 20 °C, solvent benzene. All the curves (except one for 1-hexene: Pd = 1) represent the 2-hexanone formation vs. time.

Table V. Reactivity of Olefins toward PPT^a

olefin	product ^b	yield, ^d %	reaction time
1-hexene	2-hexanone	≥98	<10 min
1-octene	2-octanone	≥98	<10 min
styrene	acetophenone	≥98	50 min
1,7-octadiene	1-octen-7-one	70	1 h
<i>cis</i> -2-octene	5d ^c		
<i>cis</i> -2-hexene	5c ^c		

^a PPT (0.1 mmol); olefin: PPT = 50; solvent, anhydrous benzene; temperature, 20 °C. ^b Identified by GLC-MS coupling. ^c Isolated as pale yellow complexes from the solution (see Table VI). ^d GLC determination using *m*-xylene as internal standard. Yields are based on palladium.

of the 1,3 π -allylic complex **5e** which is obtained in amounts about tenfold less with respect to the 2,4- π -allylic complex **5c**₄. The NMR spectrum at the end of the reaction (Figure 3) indicates that 1-hexene has been entirely consumed, as shown by the disappearance of the vinylic protons at 5.2 ppm. For 1 mol of 1-hexene consumed, 0.5 mol of 2-hexanone and 0.5 mol of π -allylic complex (**5c**₄ + **5e**) were obtained, while 0.5 mol of PPT remains unreacted, in accord with the previous GLC analysis. The presence of 0.5 mol of unreacted PPT was further confirmed by the obtention of about 0.25 mol of supplementary 2-hexanone when an additional 1 mol of 1-hexene was added at the end of the stoichiometric oxidation. This then may be summarized by reactions 7 and 8. The first step consists of the

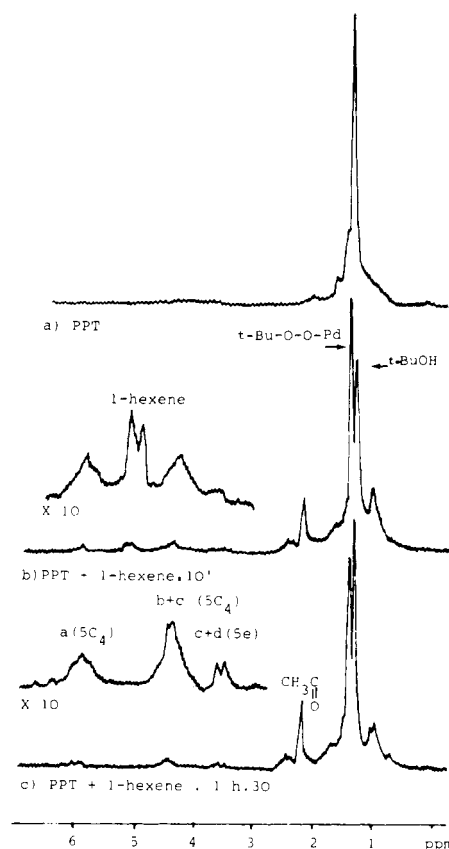
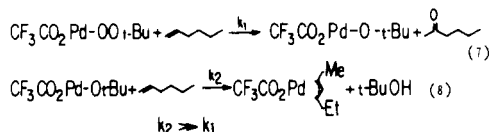
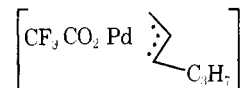


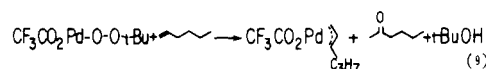
Figure 3. NMR monitoring of the oxidation of 1-hexene by PPT, temperature 20 °C, solvent CDCl₃, 1-hexene:PPT = 1.

removal of one oxygen atom on PPT by the olefin, producing the methyl ketone and the alkoxy complex. In the second step (eq 8), the alkoxy group on palladium is very rapidly substituted for the remaining olefin ($k_2 \gg k_1$), giving rise to the formation of the 2,4- π -allylic palladium complex (indicating an isomerization of the olefin on palladium) and *tert*-butyl alcohol.

(2) At 1-hexene: Pd = 2, the reaction was faster and ca. 75% of 2-hexanone was produced (Figure 2). Increasing the olefin: Pd ratio to 5 and then 50 increased the yield in 2-hexanone to a quantitative value ($\geq 95\%$), while the reaction rate became very fast. The final complex which resulted from the reaction of PPT with 1-hexene at a 1-hexene: Pd ratio of 50 was isolated by evaporation of the reaction mixture and recrystallization from CHCl₃. Elemental and NMR analysis, respectively, revealed the formula



(**5e**) and the 1,3- π -allylic structure, with $H_a = 5.4$, $H_b = 2.9$, $H_c = H_d = 3.9$ ppm (see Table VI). This can be therefore represented by reaction 9.

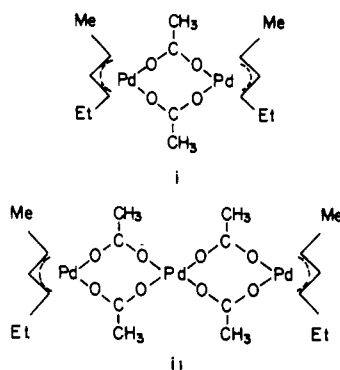


(3) At 1-hexene: Pd > 100, i.e., when PPT is dissolved in pure olefin, the yield in 2-hexanone is only ca. 45%, and the 1,3- π -allylic complex **5e** was isolated as the final product from the reaction mixture. This therefore suggests that under such conditions, owing to the high concentration of olefin, the *tert*-butyl peroxidic group in PPT is directly substituted for the olefin, in a way similar to that shown in reaction 6 for the

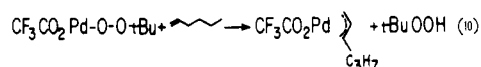
Table VI. NMR Shifts of π -Allyl Group in $[\text{RCO}_2\text{Pd}(\pi\text{-allyl})_2]$

π -allyl group	compd	R	a	b	c	d	e
	5a	CF ₃	5.4	3.0 (2 H)		4.2 (2 H)	
	5b	CF ₃	5.3	3.8 (2 H)			
	5c₁	CF ₃	5.3	3.8 (2 H)			
	5c₂	CH ₃ ^b	5.12	3.5 (2 H)			
	5c₃	CH ₃ ^c	5.72	4.18 (2 H)			
PPT + 1 hexene	5c₄	CF ₃ ^d	5.9	4.3 (2 H)			
	5d	CF ₃	5.25	3.8 (2 H)			
	5e	CF ₃	5.4 (1 H)	2.9 (1 H)		3.9 (2 H)	

^a Varian CFT-20, solvent CDCl₃; values relative to SiMe₄. ^b NMR spectrum of i taken from ref 12. ^c NMR spectrum of ii taken from ref 12. ^d See Figure 3.



reaction of PPT with internal olefins (eq 10).



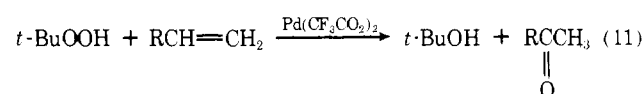
All these reactions 6–10 indicate that anion exchange occurs between the *tert*-butyl peroxidic group, the *tert*-butoxy group, and the olefins on palladium, while the internal ones substitute more readily the *tert*-butyl peroxidic group probably because of the formation of more stable π -allylic complexes. We therefore propose, for the oxidation of terminal olefins to methyl ketones by PPT, the mechanism depicted in Scheme II.

The first step probably consists of the complexation of the terminal olefin to palladium in PPT (1), affording the peroxidic π -olefinic complex 2. This agrees with the strong inhibiting effect observed when ligands competing with the olefin for vacant coordination sites are introduced into the reaction medium. This also agrees with the accelerating effect of the electron-attracting carboxylato groups on palladium on the oxidation rate, by increasing the electron attractor effect of the metal toward olefins.

The nucleophilic attack of the *tert*-butyl peroxidic group on the electrophilic coordinated olefin constitutes the *peroxy-palladation* step of this mechanism (2 \rightarrow 3) which, occurring in the coordination sphere of the metal, is necessarily *cis* with respect to the olefin.¹⁷ The peroxy-palladation of the olefin leaves a vacant coordination site which can be filled by intramolecular electron donation from the δ oxygen atom of the

peroxidic group to the metal. A pseudocyclic five-membered peroxometallic adduct results from this electron donation, which strongly resembles the closed peroxometallic adducts obtained from peroxy complexes in reactions 2 and 3 (Scheme I). Decomposition of 3 occurs with the rupture of the O–O bond, followed by a β -hydride migration, producing methyl ketone and the palladium *tert*-butoxy complex 4. This decomposition is similar to that of the closed rhodium peroxometallic cycle in reaction 3. In the absence of excess *tert*-butyl hydroperoxide, the *tert*-butoxy group in 4 is rapidly substituted for a new mole of olefin, producing the π -allylic complex 5 and *tert*-butyl alcohol. Such a π -allylic complex may also directly result from the substitution of the *tert*-butyl peroxidic group by the olefin when this is used in very large excesses (eq 10).

The initial PPT (1) can be regenerated from 4 when an excess of *t*-BuOOH is introduced into the reaction medium. In this case, the O-*t*-Bu group is directly substituted for the more nucleophilic OO-*t*-Bu group, and liberation of *tert*-butyl alcohol occurs. The formation of the methyl ketone can then occur on a catalytic scale, as shown in reaction 11.¹⁸

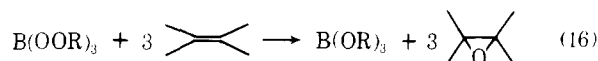


In order to confirm the validity of such a mechanism in its peroxy-palladation step (2 \rightarrow 3), we prepared the known *tert*-butyl peroxy mercurial 6 from the reaction of *t*-BuOOH with

(3) This mechanism explains the autoretardation effect by the alcoholic coproduct which competes with the hydroperoxide by forming metal-alkoxide bonds.

(4) This mechanism is similar to the mechanism we proposed for the epoxidation of olefins by peroxomolybdenum complexes, as shown in eq 2, with the only difference being that the five-membered peroxometallic intermediate (III) is pseudocyclic instead of being closed, and the resulting complex is Mo(VI) alkoxide instead of the Mo(VI) oxocomplex obtained from eq 2.

(5) The coordinating bond which is formed between the nucleophilic olefin and the electrophilic metal in complex II is a pure Lewis acid-Lewis base bond since Mo(VI) has no d electrons available for back-bonding to the olefin. It would therefore be expected that compounds having alkyl peroxidic groups bonded to a Lewis acid center should be active for the epoxidation of olefins. This is indeed verified in the case of boron, which is also active as a catalyst for the epoxidation of olefins by hydroperoxides,²⁶ and boron alkylperoxides B(OOR)₃ have been shown to stoichiometrically epoxidize double bonds (eq 16).²⁷ In this case, a mechanism similar to



that shown in Scheme III, involving pseudocyclic peroxyboration of the olefin, could be suggested.

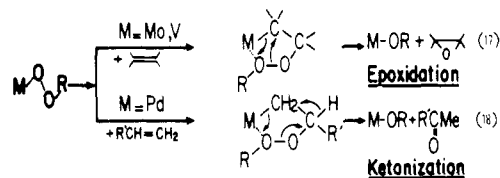
Conclusion

A common mechanism for oxygen transfer from transition-metal peroxides to olefins can be brought out from this study. This involves peroxymetalation of the olefin, which can be either cyclic if the starting complex is in a peroxo form (Scheme I) or pseudocyclic if the starting complex is in an alkyl peroxidic form (Scheme IV). The nature of the products resulting from the decomposition of the peroxometallic cycle depends on the electrophilicity of the metal. Strong d⁰ electrophilic metals such as Mo(VI) and V(V) direct the electron transfer toward the alkyl carbon atom, producing epoxide, while less electrophilic group 8 metals such as Pd or Rh direct the electron transfer toward the β-carbon atom, from which β-hydride migration produces methyl ketone.

The peroxymetalation process depicted in Schemes I and IV agrees with the general π-σ rearrangement procedure occurring in most transition-metal-catalyzed transformations of olefins.²⁸ Passing from the stoichiometric reactions depicted in Scheme I and IV to the catalytic oxidation of olefins involving O₂, H₂O₂, or ROOH as the oxygen source requires the regeneration of the initial peroxidic species from the reduced oxo or alkoxide final complex. The regeneration of peroxo from oxo complexes in Scheme I can be achieved either directly from the reaction with H₂O₂ (M = Mo, eq 1) or indirectly through hydrolysis to hydroxo species, Wacker-type hydroxymetalation of the olefin, and reaction with dioxygen (M = Rh).⁶ The regeneration of alkyl peroxidic complexes from reduced alkoxide complexes in Scheme IV is achieved directly through the addition of excess hydroperoxide, thus liberating the resulting alcohol (M = Pd or Mo).

The interpretation of the selective oxidation of olefins based on the peroxymetalation concept places these reactions inside the scope of conventional metal-catalyzed transformations of olefins. It fundamentally differs from the interpretation of selective epoxidation of olefins by organic peracids based on the nucleophilic attack of the olefin on the terminal peroxidic oxygen (Bartlett's mechanism).²⁹ Since recent calculations have shown that neither of the peroxidic atoms in peracids is electrophilic,³⁰ further insight is needed for reconciling the mechanisms of selective oxidation of olefins by organic and inorganic peroxidic reagents.

Scheme IV. Pseudocyclic Peroxymetalation



Experimental Section

Materials. Reagent grade palladium acetate (Alpha Inorganics), 80% *tert*-butyl hydroperoxide (Merck), trifluoro- and trichloroacetic acid (Merck), and perfluorohexanoic acid (P.C.U.K.) were used without further purification. Olefins (Aldrich reagent grade) were passed through a column containing active alumina to remove peroxidic impurities, distilled over sodium, and stored under nitrogen.

Apparatus. Infrared spectra were recorded by a Perkin-Elmer Model 457 and NMR spectra by a Varian CFT 20 (solvent CDCl₃). Mass spectra were obtained by a mass spectrometer AEI Model MS 12. Identification of products was achieved by GLC-MS coupling and comparison with the mass spectra of authentic samples. The molecular weight of the peroxidic complexes was measured by a tonometer, Hewlett-Packard VPO 301 (solvent CHCl₃).

Preparation of the Peroxidic Complexes [RCO₂PdOO-*t*-Bu]₄.
Palladium(II) *tert*-Butyl Peroxide Acetate (1a). Pd(OAc)₂ (1 g) was dissolved in 8 mL of 80% *tert*-butyl hydroperoxide by stirring at room temperature, giving a dark-orange solution. The solution was left overnight. Fine yellow-orange crystals were deposited from the reaction mixture. They were filtered, washed repeatedly with *n*-pentane, and dried in vacuo, yield 70%. Anal. Calcd for CH₃CO₂PdOO-*t*-Bu: C, 28.3; H, 4.72; O, 25.2; Pd, 41.7. Found: C, 28.16; H, 4.81; O, 25.31; Pd, 41.38.

Palladium(II) *tert*-Butyl Peroxide Trifluoroacetate (PPT). Although this complex can be prepared directly from palladium trifluoroacetate and *tert*-butyl hydroperoxide, we preferred to use a one-pot synthesis which gave pure PPT. Pd(OAc)₂ (1 g) was dissolved in 2 mL of trifluoroacetic acid, and 10 mL of *tert*-butyl hydroperoxide was added to the brown slurry. The mixture became a homogeneous, dark orange solution when stirred. After being stirred for 6 h at room temperature, fine orange crystals were deposited from the reaction mixture. They were filtered, washed repeatedly with *n*-pentane, and dried in vacuo, yield 85%. Anal. Calcd for CF₃CO₂PdOO-*t*-Bu: C, 23.3; H, 2.92; F, 18.5; Pd, 34.4. Found: C, 23.4; H, 3.0; F, 18.2; Pd, 33.8. This complex is soluble in CH₂Cl₂, benzene, and diethyl ether, and is insoluble in *n*-paraffins. See Table I for pertinent IR, NMR, and molecular weight data.

Palladium(II) *tert*-Butyl Peroxide Trichloroacetate (1c). This compound was prepared by a procedure similar to that employed for PPT, using palladium acetate (1 g), trichloroacetic acid (2 g), and *t*-BuOOH (10 mL). The peroxidic complex precipitated as fine yellow-orange crystals from the reaction mixture, yield 80%. Anal. Calcd for CCl₃CO₂PdOO-*t*-Bu: C, 20.1; H, 2.5; Pd, 29.6. Found: C, 20.5; H, 2.4; Pd, 29.2. This complex is soluble in methylene chloride, from which it can be recrystallized, and benzene and slightly soluble in *n*-pentane.

Palladium(II) *tert*-Butyl Peroxide Perfluorohexanoate (1d). This compound was prepared by the same procedure using palladium acetate (0.5 g), perfluorohexanoic acid (2 g), and *t*-BuOOH (8 mL). The peroxidic complex crystallized from the reaction mixture after removal of half of the solvent under reduced pressure, yield 60%. Anal. Calcd for C₅F₁₁CO₂PdOO-*t*-Bu: C, 23.6; H, 1.77. Found: C, 23.4; H, 1.8. This complex is soluble in *n*-pentane and most organic solvents.

Preparation of the π-Allylic Complexes. Di-μ-trifluoroacetato-(*syn*-1-methyl-3-ethyl-π-allyl)dipalladium (5c₁). PPT (0.1 g) was dissolved in 1 mL of *cis*-2-hexene at room temperature. Heat evolution occurred and a pale yellow complex precipitated from the reaction mixture. The compound was filtered and washed repeatedly with *n*-pentane, yield 70%. Anal. Calcd for [CF₃CO₂Pd-π-C₆H₁₁]₂: C, 31.7; H, 3.64; F, 18.8. Found: C, 31.6; H, 3.45; F, 18.1. Mass spectrum: *m/e* 606 (C₁₆H₂₂F₆O₄Pd₂ with Pd₂ = 214 most abundant isotopic figure), 491, 296, 82 (C₆H₁₀), 69 (CF₃), 67.

The analogous complexes **5b** and **5d** were prepared similarly from

the reaction of PPT with *cis*-2-pentene and *cis*-2-octene, respectively. Anal. Calcd for $[\text{CF}_3\text{CO}_2\text{Pd}-\pi\text{-C}_5\text{H}_9]_2$ (**5b**): C, 29.16; H, 3.12; F, 19.8. Found: C, 29.1; H, 3.05; F, 19.4. Calcd for $[\text{CF}_3\text{CO}_2\text{Pd}-\pi\text{-C}_8\text{H}_{15}]_2$ (**5d**): C, 36.3; H, 4.54; F, 17.27. Found: C, 36.2, H, 4.45; F, 17.1.

Di- μ -trifluoroacetato-(*syn*-1-*n*-propyl- π -allyl)dipalladium (5e). PPT (0.1 g) was dissolved in a mixture of 1-hexene (2 mL) and benzene (3 mL) under anhydrous conditions. The solution was stirred for 1 h under oxygen and then evaporated under vacuum. The residue was washed with *n*-pentane and filtered. Recrystallization from CHCl_3 -*n*-pentane yielded the product as pale yellow crystals (yield 70%). The compound was less stable than the previous 2,4- π -allylic complexes and darkened upon exposure to air. It should therefore be stored under dry argon. Anal. Calcd for $[\text{CF}_3\text{CO}_2\text{Pd}-\pi\text{-C}_6\text{H}_{11}]_2$: C, 31.7; H, 3.64; F, 18.8. Found: C, 31.5; H, 3.5; F, 18.5.

Oxidation Procedures and Product Analysis. The olefins were oxidized in a small double-jacketed glass flask connected to a vacuum-argon line. The oxidation was carried out in rigorously anhydrous apparatus and reaction conditions. In a typical procedure, the peroxidic complex (0.2–0.5 mmol) was dissolved in benzene containing an internal standard (*m*-xylene), and the solution was equilibrated for 15 min before the reaction was started. The olefin was introduced at the initial stage of the reaction, and the evolution of the oxidation was followed by GLC analysis of aliquot samples (3-m long column of diethylene glycol succinate 20% on Chromosorb). The oxygenated products were mostly identified by GLC-MS coupling and comparison of the mass spectra with those of authentic samples.

X-ray Data Collection and Processing. A parallelepipedic crystal of $[\text{CCl}_3\text{CO}_2\text{PdOO-}i\text{-Bu}]_4$ with dimensions $0.12 \times 0.15 \times 0.23$ mm was sealed in a Lindemann glass capillary and mounted on a rotation-free goniometer head.³¹ All quantitative data were obtained using a Picker FACS/1 four-circle diffractometer controlled by a PDP 8/A computer using graphite-monochromated $\text{Mo K}\alpha$ radiation. Intensity data were collected using the $\theta/2\theta$ flying step-scan technique with a scan rate of 2° min^{-1} , 2θ scan width of $2.4 + (\text{Mo K}\alpha_{1,2} \text{ splitting})^\circ$, and step-time intervals of 2 s.³² An attenuator was inserted on the diffracted beam when the scan count exceeded 7000 Hz. The intensities of three reflections were monitored throughout the data collection period at intervals of 2 h; their values decayed by 25% during the data collection period. About 6000 independent reflections were measured within $5^\circ < 2\theta < 55^\circ$, using a prescan method. All reflections with $\sigma^2(I)/I > 15$ during prescan were not measured.

The raw step-scan data were converted to intensities with their standard deviation using the Lehman-Larson algorithm³³ on a Univac 1110 computer. These intensities were then corrected for Lorentz and polarization factors and a linear decay factor; absorption corrections were applied using a numeric integration method.³⁴ The data set was then transferred to a PDP11/60 computer and the structure was solved using the Enraf-Nonius structure determination package.³⁵ Statistical tests on the distribution of normalized structure factors showed that the space group is $C2/c$ and not Cc . MULTAN³⁶ failed to give a solution which corresponded to the Patterson function. The structure was solved using the heavy-atom method and refined by full-matrix least squares using 2154 independent reflections having $I > 3\sigma(I)$ and anisotropic thermal parameters for all nonhydrogen atoms.

Final indices are $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_2 = ((\sum w |F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2} = 0.055$ and 0.077 , respectively, with $w = 1 / (\sigma_{\text{count}}^2 + (pI)^2)$, $p = 0.06$. The unit weight observation is 1.793.

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Supplementary Material Available: X-ray structural data of $[\text{CCl}_3\text{CO}_2\text{PdOO-}i\text{-Bu}]_4$, positional and thermal parameters (Table II), bond lengths (Table III), bond angles (Table IV) and listing of

structure factor amplitude (13 pages). Ordering information is given on any current masthead page.

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