Diphosphine−Palladium and −Platinum Complexes as Catalysts for the Baeyer−Villiger Oxidation of Ketones: Effect of the Diphosphine, Oxidation of Acyclic Ketones, and Mechanistic Studies

Roberta Gavagnin, Maurizio Cataldo, Francesco Pinna, and Giorgio Strukul*

Department of Chemistry, University of Venice, Dorsoduro 2137, 30123 Venice, Italy

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A variety of Pd and Pt complexes of the type $[(P-P)M(\mu\text{-OH})]_2^{2+}$ (M = Pd, Pt; P−P = a series of tetraphenyldiphosphines) were tested in the Baeyer−Villiger oxidation of ketones with hydrogen peroxide. The effect of the diphosphine−metal ring size on the catalytic activity indicates that the larger the ring, the better the catalyst and that, in general, Pt complexes are superior. The complex modified with P−P = dppb is the most active catalyst and allows for the first time the oxidation of a series of acyclic ketones. The corresponding migratory aptitude series is in full agreement with the one known for the stoichiometric organic reaction employing peracids as oxidants. A test of the reactivity of different peroxidic oxidants (H_2O_2, *t*-BuOOH, $KHSO_5$, carbamide peroxide) shows that hydrogen peroxide is the most effective. A kinetic study of the oxidation of 2-methylcyclohexanone with $[(dppb)Pt(\mu\text{-OH})]_2^{2+}$ as the catalyst shows typical half-order dependence on the catalyst concentration, suggesting that the hydroxy dimer opens up to form the catalytically active species. The reaction is first order in ketone and hydrogen peroxide and is independent of the acidity of the system. The reaction is suggested to proceed via a quasi-peroxymetallacyclic intermediate and bears strong similarities to the stoichiometric organic reaction.

Introduction

The Baeyer−Villiger oxidation of ketones with peroxy acids is a reaction of significant synthetic interest that finds a variety of possible applications, e.g., the synthesis of antibiotics and steroids, pheromones, monomers for polymerization, etc. The whole subject has been reviewed several times.[1] The versatility of this reaction in synthetic organic chemistry is evident from the most recent of these reviews,[1g] which includes more than 1000 references.

Attempts to apply transition-metal catalysts to this important organic transformation have met with only limited success.[2] Catalytic methods, compared to their stoichiometric counterparts, may offer advantages such as the simplification of the operation conditions, the use of cheaper reactants, or less waste product formation.

We recently reported the first unambiguous example of transition-metal catalysis applied to the Baeyer−Villiger oxidation. It was suggested that, to be effective, the catalyst must be able to increase the nucleophilicity of the oxidant (H_2O_2) for attack at the electrophilic ketone center. More recently, other examples using the same primary oxidant and based on Re(VII)[4] and Ti(IV)[5] have appeared, in addition to the so-called Mukaiyama system,[6] the latter making use of dioxygen as the primary oxidant in the presence of a sacrificial aldehyde. It was also possible to perform the reaction enantioselectively[7] with moderate to good ee's using complexes modified with chiral ligands. From a synthetic point of view, the use of chiral transition-metal catalysts appears to be the only promising alternative to catalysis by microorganisms for the achievement of esters with (moderately) high optical purity and therefore is of foremost importance.

However, the scope of these promising catalytic systems is too limited to constitute a valid practical alternative to the use of stoichiometric amounts of organic peroxy acids. For example, they have proved so far unable to promote the oxidation of acyclic ketones. Following a preliminary account,[8] we report herein the use of a class of diphosphine hydroxy complexes of Pd-

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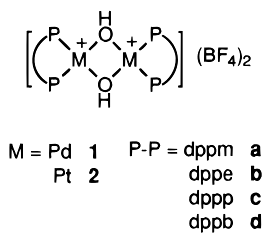
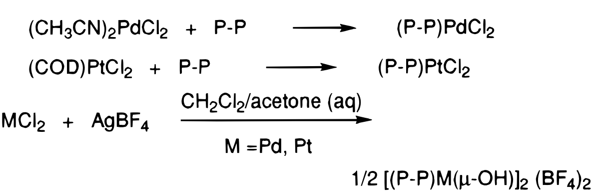
Chart 1[a]



[a] Legend: dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane.

Scheme 1



(II) and Pt(II) (Chart 1) as catalysts for the Baeyer–Villiger oxidation of ketones using hydrogen peroxide as the primary oxidant. As is indicated in Chart 1, the size of the diphosphine–metal ring was systematically changed in order to optimize the catalytic properties of the complexes. This has led to the discovery of a catalyst capable of promoting the oxidation of acyclic ketones. The essential mechanistic features of the reaction using this class of catalysts have been investigated through a kinetic analysis.

Results and Discussion

Synthesis and Characterization. The complexes shown in Chart 1 have been prepared by following the general procedure outlined some 25 years ago by Bushnell et al.[9] for $[(PPh_3)_2Pt(\mu\text{-}OH)]_2\,(BF_4)_2$. The procedure involves (Scheme 1) the introduction of the diphosphine into the coordination sphere of the metal using a suitable starting material (*trans*-$(MeCN)_2PdCl_2$ or (COD)-$PtCl_2$). Chloride abstraction from (P–P)MCl_2 (M = Pd, Pt) is then performed using 2 equiv of $AgBF_4$ in CH_2Cl_2/acetone solution. The chlorides are initially replaced by water, present as an impurity in reagent grade acetone, and upon addition of diethyl ether, the bridging hydroxy dimers precipitate out of solution.[10]

All Pt derivatives and most of the Pd derivatives have been reported previously (see Experimental Section). Only (dppb)$PdCl_2$ and $[(dppb)Pd(\mu\text{-}OH)]_2\,(BF_4)_2$ (**1d**) are new compounds, and they have been characterized by IR, NMR, and (only for **1d**) molar conductivity data. The IR spectrum of the complex (dppb)$PdCl_2$ shows typical Pd–Cl stretchings at 289 and 306 cm^{-1}, while the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 29.8 ppm (free dppb at δ −16.2 ppm). The IR spectrum of **1d** shows a medium-intensity O–H stretching band at 3593 cm^{-1}, and a strong broad band between 995 and 1100 cm^{-1} typical of BF_4^-, while the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 37.1 ppm. Additionally, the molar conductivity determined for a 10^{-3} M solution in MeOH gave 207 Ω^{-1} mol^{-1} cm^2, typical for a 2/1 electrolyte.[11]

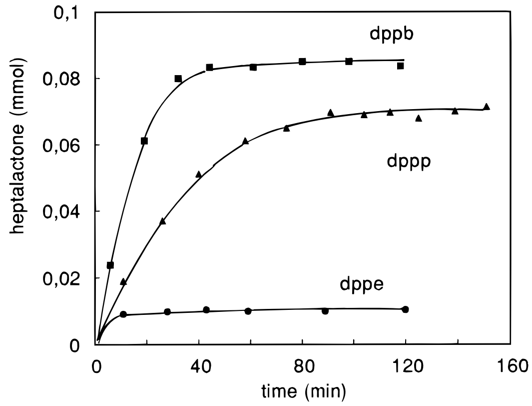


Figure 1. Effect of the diphosphine in $[(P\text{–}P)Pd(\mu\text{-}OH)]_2^{2+}$ complexes as catalysts for the Baeyer–Villiger oxidation of 2-methylcyclohexanone. Reaction conditions: Pd, 0.017 mmol; ketone, 1.7 mmol; H_2O_2, 1.7 mmol; DCE, 3.19 mL; *T*, 25 °C.

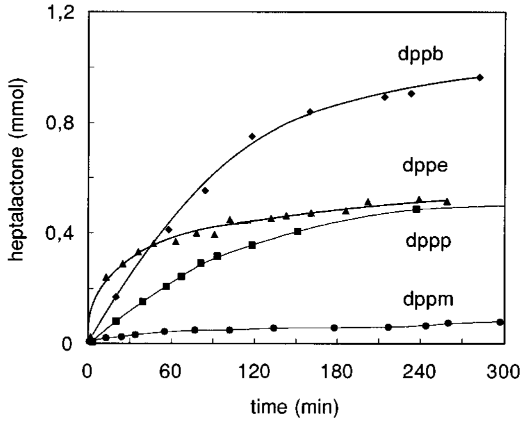


Figure 2. Effect of the diphosphine in $[(P\text{–}P)Pt(\mu\text{-}OH)]_2^{2+}$ complexes as catalysts for the Baeyer–Villiger oxidation of 2-methylcyclohexanone. Reaction conditions: Pt, 0.017 mmol; ketone, 1.7 mmol; H_2O_2, 1.7 mmol; DCE, 3.19 mL; *T*, 25 °C.

Effect of the Diphosphine. The effect of the diphosphine–metal ring size was tested by varying the length of the hydrocarbon chain linking together the phosphorus donors, as is indicated in Chart 1. The purpose of this was to examine the steric factors that may influence the reactivity of the complex, in analogy with previous results obtained with $[(P\text{–}P)Pt(CF_3)(CH_2Cl_2)]^+$ (P–P = a variety of diphosphines) in the epoxidation of 1-octene.[12] In this latter case, it was found that an increase in the bite angle of the diphosphine caused a decrease in the catalytic activity of up to 2 orders of magnitude, which correlated with the space available for coordination of the olefin.[12]

The test substrate chosen was 2-methylcyclohexanone, and the reaction conditions are reported in Figures 1 and 2, which summarize the results obtained. In all cases the selectivity of the reaction was >99%, as ϵ-heptalactone was the only reaction product observed. As shown, in the case of both Pd and Pt complexes there

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is a dependence on the nature of the diphosphine and the reactivity follows the order dppm < dppe < dppp < dppb. The catalytic activity is also dependent on the metal (Pd or Pt).

The Pd complexes are less active, as the amount of ϵ-heptalactone obtained is much lower, and the catalyst is able to perform just a few turnovers. The reaction solution, initially pale yellow, changed to orange within about 1 h and eventually darkened with concomitant precipitation of a brown solid, most likely Pd metal. Attempts to extend the catalyst lifetime using more coordinating solvents such as THF and EtOH were unsuccessful, in part because of solvent oxidation. In contrast, the Pt complexes were stable under the conditions used and turnovers as high as 55 were obtained.

The reactivity sequence found for the different diphosphines is opposite to that previously observed for the epoxidation reaction[12] and hence must be related to a different steric effect. It is possible that breakdown of the hydroxy bridge in the coordinatively saturated dimeric starting species to yield coordinatively unsaturated (P–P)Pt(OH) monomeric fragments is the preliminary step for catalytic activity. We tried to find some possible structural indications of this by analyzing crystallographic data found in the literature for some of the complexes used in this study. X-ray structural analyses of (μ-hydroxy)platinum complexes containing dppm,[13] dppp,[14] and dppb[13] have been published recently. Except for the expected increase in the P–Pt–P bite angle, which was observed also for the monomeric palladium diphosphine dichlorides,[15] no clear steric factor involving the hydroxy bridge could be found along the series. For example, while in the case of the dppm and dppb derivatives the two platinum coordination planes are coplanar,[13] in the case of the dppp derivative the two coordination planes form a dihedral angle of about 40°.[14]

Effect of the Oxidant. The reactivity of other peroxidic oxidants in the oxidation of 2-methylcyclohexanone was checked using the most active catalyst (**2d**). The oxidants chosen were hydrogen peroxide, potassium caroate ($KHSO_5$), *tert*-butyl hydroperoxide, and carbamide peroxide (CP), i.e., the adduct between urea and hydrogen peroxide. The reaction was tested at room temperature, under the usual reaction conditions, and the results are summarized in Figure 3. As can be seen, H_2O_2 is the most effective oxidant, while *t*-BuOOH is a very poor one. Even after several days the maximum conversion observed was less than 1%. Moderate oxidation properties are displayed by $KHSO_5$, while in the case of CP, despite a good initial activity, the maximum conversion never exceeded 10% (CP is sparingly soluble in DCE, the solvent chosen for the comparison test).

Oxidation of Acyclic Ketones. Given the good catalytic properties of **2d** in combination with H_2O_2 as the oxidant, we have tested the reactivity for the oxidation of a series of simple acyclic ketones (Chart 2). These are all methyl ketones in which the second group was chosen in order to determine a possible order of migratory aptitude, in analogy to what is known for the organic reaction.[1]

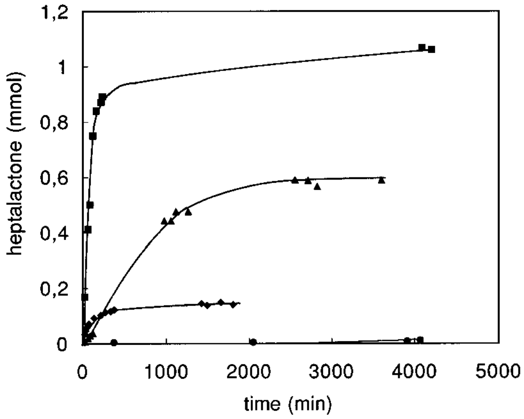


Figure 3. Effect of the oxidant in the Baeyer–Villiger oxidation of 2-methylcyclohexanone using $[(dppb)Pt(\mu\text{-}OH)]_2^{2+}$ as catalyst: (circles) *t*-BuOOH; (diamonds) CP; (triangles) $KHSO_5$; (squares) H_2O_2. Reaction conditions: Pt, 0.017 mmol; ketone, 1.7 mmol; oxidant, 1.7 mmol; DCE as solvent; *T*, 25 °C.

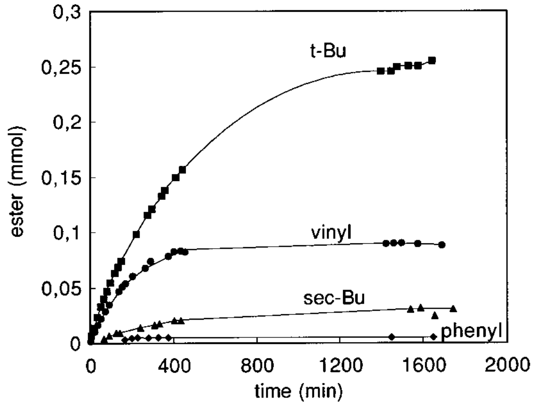
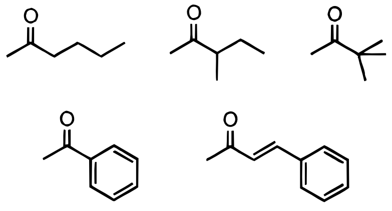


Figure 4. Oxidation of substituted methyl ketones (see Chart 2) catalyzed by $[(dppb)Pt(\mu\text{-}OH)]_2^{2+}$. Reaction conditions: Pt, 0.017 mmol; ketone, 1.7 mmol; H_2O_2, 1.7 mmol; DCE as solvent; *T*, 25 °C.

Chart 2



Reactions were performed at room temperature with the exception of the oxidation of acetophenone, which was observed only at 58 °C. A summary of the results is reported in Figure 4. No activity was observed in the case of 2-hexanone even after 24 h at 70 °C. In general, the order of migratory aptitude is

tertiary alkyl > vinyl > secondary alkyl > phenyl > primary alkyl

This is in agreement with the series found for the organic reaction.[1] The results here reported represent the first observation of the Baeyer–Villiger oxidation of an acyclic ketone under catalytic conditions using a transition-metal complex.

The oxidation of methyl vinyl ketone represents also an interesting example of chemoselectivity. It is known[1]

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Scheme 2

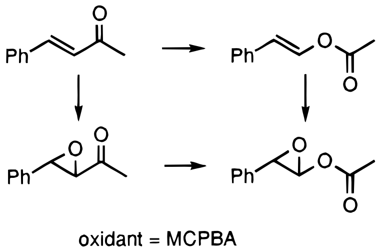

Table 1. Summary of the Kinetic Data for the Oxidation of 2-Methylcyclohexanone with Hydrogen Peroxide Catalyzed by $[(dppb)Pt(\mu\text{-}OH)]_2(BF_4)_2$[a]

$10^3[Pt_2]$ (M)	[ketone] (M)	$10^3[H_2O_2(org)]$ (M)	$10^5 \times$ init rate ($M\ s^{-1}$)
0.10	0.50	53	0.48
0.50	0.50	53	1.01
1.0	0.50	53	1.30
2.5	0.50	53	2.13
5.0	0.50	53	2.49
0.50	0.10	53	0.20
0.50	0.20	53	0.39
0.50	1.0	53	2.23
0.50	2.0	53	3.57
0.50	0.50	3.31	0.06
0.50	0.50	8.98	0.13
0.50	0.50	20.2	0.28
0.50	0.50	82	1.96
0.50	0.50	140	2.82

[a] Reactions performed in DCE at 10 °C.

that with unsaturated ketones the Baeyer–Villiger oxidation is accompanied by some epoxidation of the carbon–carbon double bond. A stoichiometric reaction using *m*-chloroperbenzoic acid (MCPBA) as the oxidant, under conditions similar to those reported for the catalytic reaction in Figure 4, indicates that the unsaturated ester forms initially, followed by the epoxy ketone and finally by the epoxy ester (Scheme 2). In contrast, the catalytic reaction with hydrogen peroxide and **2d** yields only the unsaturated ester. This result is at variance with some previous findings obtained with other Pt(II) complexes of the type $[(P{-}P)Pt(CF_3)(CH_2Cl_2)]^+$ or (P–P)Pt(2-van) + $HClO_4$ (P–P = various diphosphines; 2-van = the dianion of 2-vanillin), with which a variety of α,β-unsaturated ketones could be conveniently epoxidized.[16]

Kinetic Studies. A kinetic study was performed by analyzing the initial rate of reaction for the oxidation of 2-methylcyclohexanone with hydrogen peroxide using **2d** as catalyst. The reaction was performed in a two-phase DCE/H_2O solvent system at 10 °C, a temperature that seems to constitute a good compromise between activity and the accuracy of rate data.

A summary of the kinetic data is reported in Table 1. Since the reaction occurs in the organic phase, the concentration of H_2O_2 in DCE was calculated by determining the partition curve of H_2O_2 between H_2O and DCE using aqueous solutions ranging from 1.0 to 20 M. The effect of the individual reactants on the reaction rate is shown in Figures 5 and 6.

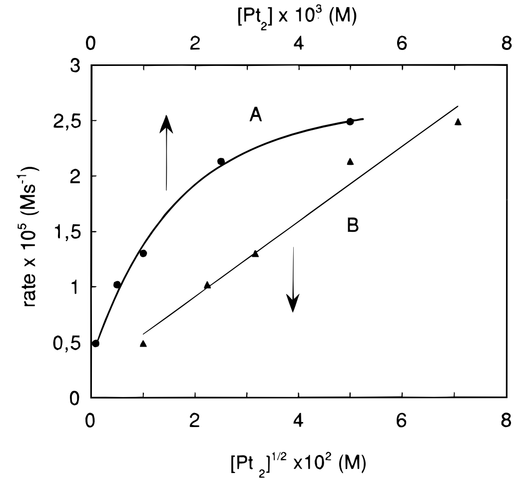

Figure 5. Kinetic analysis of the oxidation of 2-methylcyclohexanone with hydrogen peroxide using $[(dppb)Pt(\mu\text{-}OH)]_2^{2+}$ as catalyst: effect of catalyst concentration.

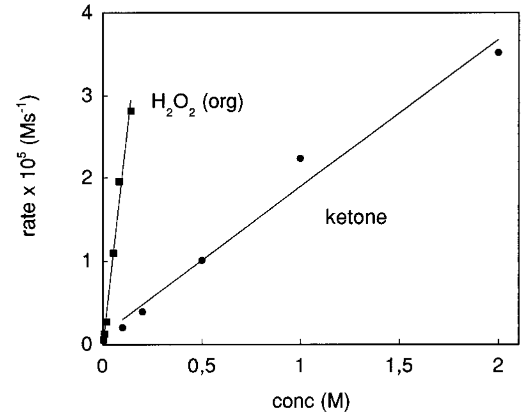

Figure 6. Kinetic analysis of the oxidation of 2-methylcyclohexanone with hydrogen peroxide using $[(dppb)Pt(\mu\text{-}OH)]_2^{2+}$ as catalyst: effect of ketone (circles) and hydrogen peroxide (squares) concentrations.

The effect of Pt concentration (Figure 5) is of fractional order, and a linear relationship is observed between the initial rate and the square root of the Pt dimer concentration. This observation is an indication that the coordinatively saturated bridging hydroxy dimer opens up to yield a catalytically active monomeric species. A first-order dependence is observed for both the ketone and hydrogen peroxide concentrations (Figure 6).

Mechanism. A simple mechanism that accounts for the above experimental observations is shown in Scheme 3. A fast dissociation equilibrium in which the ketone and hydrogen peroxide are actively involved is suggested as the initial step. This is followed by the rate-determining intramolecular nucleophilic attack in **3d** between the coordinated hydroperoxy ligand and the carbonyl carbon, the electrophilic character of which is increased by coordination. This step is described as a two-stage process leading to the formation of a quasi-peroxymetallacyclic intermediate (**4d**), in which a simple rearrangement yields the lactone and a monomeric, coordinatively unsaturated $Pt^+{-}OH$ species that quickly dimerizes to form the starting complex.

A scheme of this type yields the following mathematical expression for the reaction rate:

$$d[\text{lactone}]/dt = kK^{1/2}[\text{ketone}][H_2O_2][Pt_2(OH)_2]^{1/2}$$

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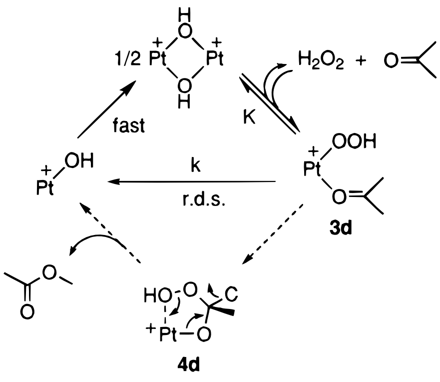
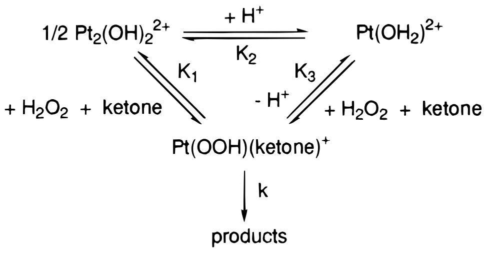
[16] Baccin, C.; Gusso, A.; Pinna, P.; Strukul, G. *Organometallics* **1995**, *14*, 1161.

Scheme 3



Scheme 4



We have tried to determine the mass balance for Pt through $^{31}P\{^1H\}$ NMR experiments. The catalyst **2d** (40 mg) was dissolved in CD_2Cl_2, and the spectrum was run, showing a singlet at δ 5.1 ppm flanked by Pt satellites exhibiting a $^1J_{P-Pt}$ coupling constant of 3546 Hz. Addition of 200 μL of 2-methylcyclohexanone did not change the spectrum nor did the further addition of 100 μL of hydrogen peroxide. A second experiment in which the order of addition of the two reactants was reversed gave the same results, indicating that the only platinum species macroscopically present in the system is the starting compound, the concentration of which is just the initial **2d** concentration. Under these circumstances, the above expression also becomes the rate law and is in full agreement with the experimental observations reported in Figures 5 and 6.

Scheme 3 is a simplified view of the actual mechanism. The initial equilibrium might be a fast, kinetically indistinguishable, stepwise process, in which the hydroxy bridge is initially cleaved by the weak acid H_2O_2, as has been observed by ourselves[8] and others[17] for other weak acids, followed by coordination of the ketone to the vacant coordination site of the monomeric hydroperoxyplatinum species. An alternative view, still kinetically indistinguishable, might be the initial cleavage of the hydroxy bridge by the ketone, followed by external nucleophilic attack of free hydrogen peroxide on the resulting Pt(OH)(ketone) species, as suggested for the Baeyer−Villiger oxidation of ketones with Pt-(CF_3) derivatives.[3b] However, this posibility seems unlikely because of the ease with which diphosphine hydroxyplatinum complexes undergo exchange with hydrogen peroxide, a pathway that has been exploited for the preparation of stable hydroperoxy complexes.[18]

Effect of Acidity. Since commercial 35% hydrogen peroxide is stabilized with acid (apparent pH 2.0), the possible active role of H^+ in the catalysis has been considered. It is known[10,14,19] that bridging hydroxy complexes of Pt(II) can be protonated to give the corresponding aquo complexes, and this would modify the catalytic cycle according to Scheme 4.

The effect on the initial rate of formation of ϵ-heptalactone in the catalytic system, following the addition of different amounts of either perchloric acid or potassium hydroxide to the aqueous phase, was studied. The addition of OH^- or H^+ in excess (up to 10 times) with respect to the catalyst showed no effect on the reaction rate. This seems to be in agreement with Scheme 4, where the equilibrium characterized by K_1 (the only one considered in Scheme 3) is mathematically equivalent to the sum of the two equilibria characterized by K_2 and K_3. From a kinetic point of view, the rate law will hold, again provided that the mass balance with respect to the different platinum species does not change.

The step by step $^{31}P\{^1H\}$ NMR experiment reported above was repeated by dissolving **2d** in CD_2Cl_2 (step 1) and then adding a 10-fold excess of $HClO_4$ (step 2) and finally a large excess of 2-methylcyclohexanone and H_2O_2 (step 3). The results are summarized in Figure 7, where spectra A−C correspond to steps 1−3, respectively. As can be seen, the addition of an excess of acid to **2d** (spectrum A) produces a new species (spectrum B) that was identified as $[(dppb)Pt(OH_2)_2]^{2+}$ by comparison with an authentic sample prepared by following the method reported by Bandini et al.[14] for $[(dppe)Pt(OH_2)_2]^{2+}$ (see Experimental Section). The addition of the ketone and hydrogen peroxide (spectrum C) restores the initial compound **2d** and produces a small amount of a new species showing two nonequivalent phosphorus nuclei (δ_{P1} 3.7 ppm, $^2J_{P-P}$ 28.5 Hz, $^1J_{P-Pt}$ 3181 Hz; δ_{P2} 2.4 ppm, $^2J_{P-P}$ 28.5 Hz, $^1J_{P-Pt}$ 3887 Hz). The presence of this species does not change significantly the platinum mass balance and seems to support the mechanism proposed, as it can be consistent with the existence of either **3d** or **4d** on the basis of the P−Pt coupling constants, with P1 being trans to a σ-bonded oxygen and P2 trans to a neutral oxygen donor.

In conclusion, the interpretation given above for the effect of H^+ in the system seems correct and the possible involvement of the additional equilibria shown in Scheme 4 appears to have no influence on the course of the catalytic reaction.

Nature of the Oxygen Transfer Step. As is shown in Scheme 3, the oxygen transfer is suggested to occur via a two-stage process in which the formation of a *quasi*-peroxymetallacyclic species (**4d**) is involved. Although species of this type have never been isolated, since the early report of Mimoun[20] they have been often implied in the oxidation of unsaturated substrates,[21]

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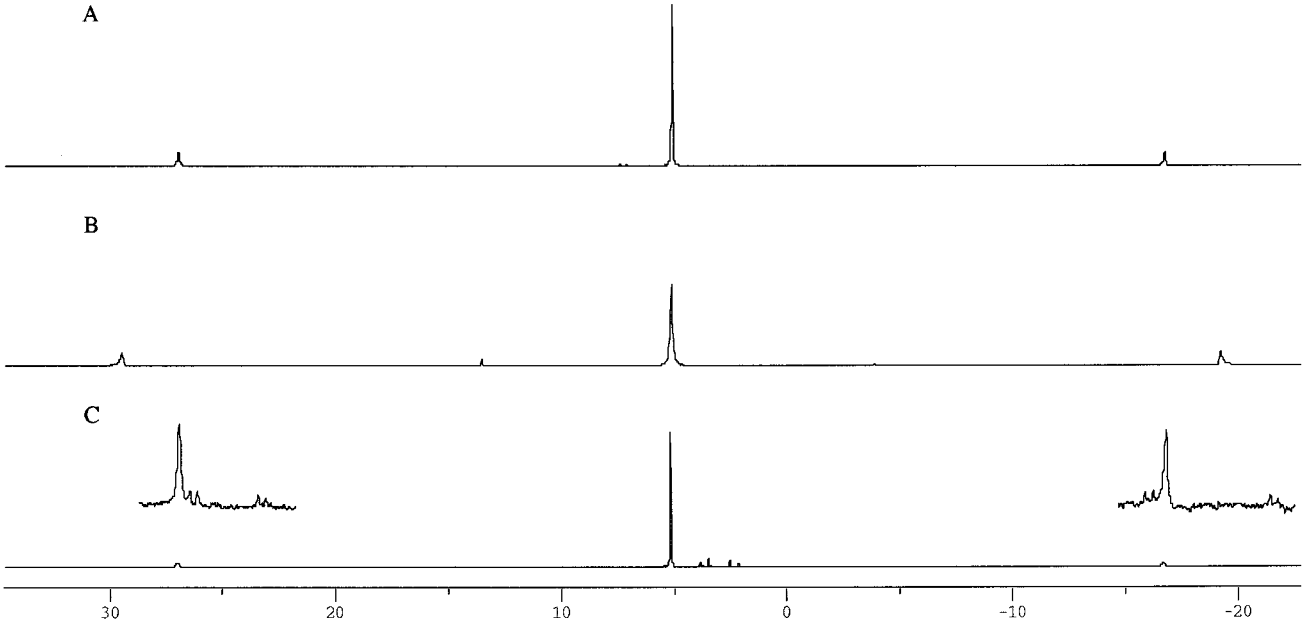
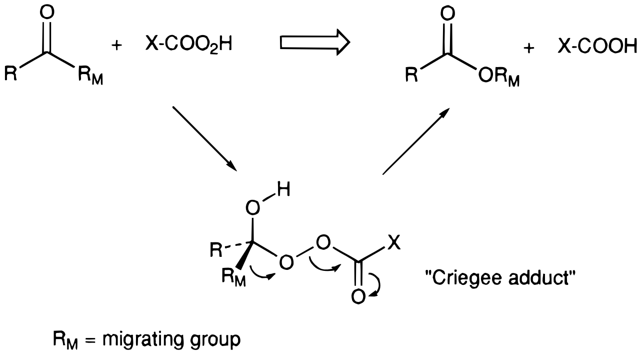


Figure 7. $^{31}P\{^1H\}$ NMR experiment in CD_2Cl_2: (A) $[(dppb)Pt(\mu\text{-}OH)]_2^{2+}$; (B) excess $HClO_4$ added; (C) excess 2-methylcyclohexanone and excess H_2O_2 added. The inset shows the satellite region of spectrum C.

Scheme 5



including ketones.[3] Clearly, the simple kinetic analysis reported above does not distinguish between a single-stage process and a two-stage process, as the rate equation would be the same in both cases. Although not required by the rate law, the suggestion that the rate-determining step is a two-stage process has the advantage of being similar to the well-known mechanism of the stoichiometric Baeyer–Villiger oxidation using peracids.[1] It is known that this reaction proceeds (Scheme 5) through the formation of a peroxidic intermediate (the so-called "Criegee intermediate"[22]), from which the ester product forms via a simple rearrangement. Of the two stages, the second is generally considered to be rate determining,[1e,g] as this is in agreement with both the order of reactivity of different peracids (which parallels the properties of $X-COO^-$ as a leaving group) and the order of migratory aptitude for different alkyl (aryl) groups.

As can be seen, the quasi-peroxyplatinacyclic intermediate bears strong similarities to the Criegee intermediate (with Pt^+ instead of H^+). However, the role of the platinum complex in the overall reaction is not simply that of a Lewis acid, as it plays two other important functions: (i) it increases the nucleophilicity of hydrogen peroxide (a very poor oxidant in noncatalyzed reactions) and (ii) it provides a facile pathway for loss of HO^- from the intermediate. The latter in particular seems crucial, as the poor reactivity of hydrogen peroxide in this reaction is generally related to HO^- being a poor leaving group. This argument, supported by the experimental evidence that the order of migratory aptitude is the same as in the organic reaction, seems to suggest that in the present Pt-catalyzed reaction the actual rate-determining step is most likely the rearrangement of the quasi-peroxyplatinacyclic intermediate species.

Conclusions

The comparison between the Pd and Pt homologous species shows that the latter are more active and stable in the Baeyer–Villiger oxidation of ketones. Although an analogous result had been previously observed in the epoxidation of olefins,[21c] it is still somehow surprising because it is contrary to the commonly observed superior catalytic properties of Pd, particularly in oxidation reactions.

The systematic change of the size of the diphosphine–metal ring led to catalyst **2d** which, for the first time, is capable of oxidizing open-chain ketones. Although the structural reasons are not understood, this represents a useful application of transition-metal catalysis to this important organic transformation.

The order of migratory aptitude for different alkyl/aryl groups in methyl ketones is in agreement with the organic transformation using peracids.

The mechanistic study points to the following important factors in the catalysis: (i) the ability of the complex to increase both the electrophilicity of the carbonyl carbon and the nucleophilicity of hydrogen peroxide and (ii) the assistance given by the metal center to dissociation of HO^- from the peroxymetallacyclic intermediate, thus making a typically "green" reagent like hydrogen peroxide a valuable oxidant for the reaction.

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Experimental Section

Apparatus. IR spectra were taken on a Nicolet FTIR Magna 750 and on a Digilab FTS 40 interferometers either in solid (KBr pellets) or in CH_2Cl_2 solution using CaF_2 windows. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 200 spectrometer operating in FT mode, using as external references TMS and 85% H_3PO_4, respectively. Negative chemical shifts are upfield from the reference. UV−vis spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. Conductivity measurements were performed on a Radiometer instrument using 10^{-3} M solutions in MeOH at 25 °C. GC measurements were taken on a Hewlett-Packard 5790A gas chromatograph equipped with a 3390 automatic integrator. GC−MS measurements were performed on a Hewlett-Packard 5971 mass selective detector connected to a Hewlett-Packard 5890 II gas chromatograph. Identification of products was made with GC or GC−MS by comparison with authentic samples.

Materials. Solvents were dried and purified according to standard methods. Ketone substrates were purified by passing through neutral alumina, prior to use. Hydrogen peroxide (35% from Acros, 60% from Degussa), *m*-chloroperbenzoic acid (MCPBA, 75% from Janssen), carbamide peroxide (CP, from Peroxid Chemie), *t*-BuOOH (80% from Fluka), Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, from Janssen), dppm, dppe, diphoe, dppp, and dppb (all from Strem), and most of the synthetic reagents were commercial products and were used without purification.

The following compounds were prepared according to literature procedures: $[(dppm)Pt(\mu\text{-}OH)]_2(BF_4)_2$,[13,14] $[(dppe)Pt(\mu\text{-}OH)]_2(BF_4)_2$,[13] $[(dppp)Pt(\mu\text{-}OH)]_2(BF_4)_2$,[13,14] $[(dppb)Pt(\mu\text{-}OH)]_2(BF_4)_2$,[13,14] $[(dppe)Pd(\mu\text{-}OH)]_2(BF_4)_2$,[23] $[(dppp)Pd(\mu\text{-}OH)]_2(BF_4)_2$.[10a]

[(dppb)PdCl$_2$]. To a solution of the complex $(MeCN)_2PdCl_2$ (0.50 g, 1.93 mmol) in N_2-saturated $C_2H_4Cl_2$ (50 mL) was added solid dppb (0.822 g, 1.93 mmol). The resulting solution was stirred at room temperature for 24 h. Then it was concentrated to small volume under reduced pressure and the resulting pale yellow solid was filtered, washed with Et_2O, and dried in vacuo (yield 94%).

Anal. Calcd (found) for $C_{28}H_{28}Cl_2P_2Pd$: C, 55.69 (55.07); H, 4.64 (4.45). IR (KBr pellet): 306, 289 cm^{-1} (PdCl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 29.8 ppm (s).

[(dppb)Pd(μ-OH)]$_2$(BF$_4$)$_2$ (1d). The complex [(dppb)PdCl$_2$] (0.50 g, 0.828 mmol) was placed in a round-bottomed flask, to which CH_2Cl_2 (70 mL) and reagent grade acetone (55 mL) were added. After the pale yellow solution was saturated with N_2, 1.69 mL (1.66 mmol) of a $AgBF_4$ solution in acetone was added. The mixture was stirred in the dark for 1 h, and then AgCl was filtered off. The resulting yellow solution was concentrated to small volume under reduced pressure, and the addition of Et_2O resulted in the precipitation of a pale yellow solid that was filtered, washed with Et_2O, and dried in vacuo (Yield 92%).

Anal. Calcd (found) for $C_{56}H_{58}O_2P_4PdB_2F_8$: C, 58.72 (59.07); H, 4.55 (4.42). IR ($C_2H_4Cl_2$ solution): 3353 cm^{-1} (OH). IR (KBr pellet): 1100−995 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 37.1 ppm (s). Conductivity (10^{-3} M in MeOH): 207 Ω^{-1} mol^{-1} cm^2.

[(dppb)Pt(OH$_2$)$_2$](BF$_4$)$_2$. The complex **1d** (0.50 g, 0.34 mmol) was dissolved in N_2-saturated CH_2Cl_2 (5 mL). To the solution was added a large excess of 11 M $HClO_4$ (0.313 mL, 3.4 mmol) under N_2. The mixture was stirred for 1 h and then brought to dryness in vacuo. The residue was treated with benzene and evaporated to dryness a few times until a white solid was obtained. This was suspended in Et_2O, filtered, washed with Et_2O, and dried in vacuo (yield 75%).

Anal. Calcd (found) for $C_{28}H_{32}O_2P_2PtB_2F_8$: C, 40.47 (40.23); H, 3.85 (3.57). IR (KBr pellet): 1100−990 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 4.6 ppm (s); $^1J_{P-Pt}$ 3930 Hz.

Synthesis of Lactones. Lactones used as standards for gas chromatography determinations in the individual catalytic reactions were synthesized from the starting ketone (20 mmol) in 25 mL of CH_2Cl_2, to which 20 mmol of MCPBA was added under N_2 with stirring. After a few hours the solid MCBA was filtered off and the solution containing the ester/lactone was used for qualitative identification in the GC analysis.

Catalytic Reactions. These were carried out in a 25 mL round-bottomed flask equipped with a stopcock for vacuum/N_2 operations and a side arm fitted with a screw-capped silicone septum to allow sampling. Constant temperature (±0.1 °C) was maintained by water circulation through an external jacket connected with a thermostat. For reactions carried out at temperatures >25 °C the reaction vessel was equipped with a reflux condenser. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer. The absence of diffusional problems was determined by the conversion vs time plot independence of the stirring rate in randomly selected catalytic experiments. The concentration of the commercial H_2O_2 solution was checked iodometrically prior to use.

The following general procedure was followed.

The required amount of catalyst was placed as a solid in the reactor, which was evacuated and filled with N_2. Purified, N_2-saturated ketone was added under N_2 flow, followed, if necessary, by the required amount of solvent. After thermostating at the required temperature for a few minutes, the H_2O_2 solution in the appropriate amount was injected through the septum and time was started.

All reactions were monitored with GLC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Initial rate data were determined from conversion vs time plots. Separation of the products was performed on a 25 m HP-5 capillary column using a flame ionization detector.

The amount of residual H_2O_2 at different times was determined by sampling 10 μL aliquots from the aqueous phase. These were diluted in water and titrated iodometrically.

Determination of H$_2$O$_2$ Concentration in C$_2$H$_4$Cl$_2$. This was performed according to a modified procedure of the method described by Wolfe.[24] To a typical blank reaction mixture (5 mL of $C_2H_4Cl_2$ + 0.25 mL of 2-methylcyclohexanone) was added 1.0 mL of aqueous H_2O_2 of known concentration. After the mixture was stirred for a few minutes, a 4 mL portion of the organic phase was separated. To this was added an equal amount of a 2.1 M solution of $TiCl_4$ in 6 N HCl, and the mixture was stirred for 10 min. A 3.0 mL portion of the orange aqueous phase was separated and diluted to 25 mL with the same 2.1 M solution of $TiCl_4$ in 6 N HCl. Spectrophotometric analysis was carried out at 416 nm (ϵ 583 cm^{-1} M^{-1}). The Lambert−Beer law was obeyed in the concentration range explored.

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