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Regioselectivity and Diasteroselectivity in Pt(II)-Mediated "Green" Catalytic Epoxidation of Terminal Alkenes with Hydrogen Peroxide: Mechanistic Insight into a Peculiar Substrate Selectivity

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Abstract: Recently developed electron-poor Pt(II) catalyst **1** with the "green" oxidant 35% hydrogen peroxide displays high activity and complete substrate selectivity in the epoxidation of terminal alkenes because of stringent steric and electronic requirements. In the presence of isolated dienes bearing terminal and internal double bonds, epoxidation is completely regioselective toward the production of terminal epoxides. Insight into the mechanism is gained by means of a reaction progress kinetic analysis approach that underlines the peculiar role of **1** in activating both the alkene and H_2O_2 in the rate-determining step providing a rare example of nucleophilic oxidation of alkenes by H_2O_2.

Introduction

Highly selective oxy-functionalization of organic substrates is a rather challenging field that requires the design of specific catalysts along with tailoring many variables such as substrate, oxidant nature, and experimental conditions with the ultimate goal of achieving high activity, selectivity, and productivity under mild experimental conditions.[1] In particular, the oxidation of alkenes to the corresponding epoxides is a well-documented reaction that has been investigated for decades because epoxides represent important commodities and, at the same time, pivotal building blocks for organic synthesis, both from the industrial and academic points of view.[2] Although heterogeneous methods for the epoxidation of alkenes have been developed,[3] the highest selectivities have been observed under homogeneous conditions[4] with metal-containing or purely organic catalysts.

Several oxidants have been tested over the years for such reactions; nevertheless, in recent years the interest toward hydrogen peroxide is overcoming all the other ones because of stringent environmental concerns. In fact, as recently outlined by Beller,[5] H_2O_2[6] is characterized by unique features and advantages, such as high atom-efficiency,[7] moderate cost, safe handling and storage, and production of water as the only byproduct[8] making it the most interesting oxidant after molecular oxygen and stimulating its use in liquid-phase oxidations, especially for fine-chemicals production.[9]

The number of transition-metal complexes able to efficiently activate hydrogen peroxide toward different alkenes is relatively large.[4] Nevertheless, most of them are generally active toward a limited class of substrates such as, e.g., allylic alcohols where the presence of the hydroxyl group allows easy coordination to the metal active site,[10] or unfunctionalized alkenes, where good performance could be observed only for electron-rich C═C double bonds, or styrene derivatives where peculiar reactivity is imparted by the presence of the conjugated aromatic ring. In this framework, a lack of methods is evident for an efficient and selective epoxidation of terminal, unfunctionalized alkenes that are intrinsically poorly reactive substrates toward electrophilic oxidation. In this respect, worthy of mention are complexes of Ru(III),[11] W(VI),[12−15] Mn(II),[16,17] Re(V),[18] and

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Fe(III),[19,20] although relatively high metal loading, presence of additives, moderately high temperatures, and in many cases use of overstoichiometric amounts of hydrogen peroxide are generally required due to parallel partial decomposition of the oxidant catalyzed by the complex itself. Very recently, *bis*-(μ-hydroxo)-bridged divanadium species implemented in a peroxotungstate framework showed highly selective and efficient H_2O_2 epoxidation of alkenes, in particular toward terminal alkenes with very good regioselectivity in diene epoxidation.[21]

Thus far, catalyst design has been aimed mainly at oxidant activation and has paid little or no attention to the interaction between the metal center and the alkene. Requirement for a wider scope, successful epoxidation of simple terminal alkenes seems to be a new catalyst design activating the substrate instead of the oxidant, hence changing the role between electrophile and nucleophile in the system.

Very recently, we reported about the peculiar activity of second generation,[22] electron poor Pt(II) complexes containing a pentafluorophenyl residue with general formula $[(P-P)Pt(C_6F_5)(H_2O)]^+$ (P−P = diphosphine), and their application as selective epoxidation catalysts toward terminal unfunctionalized alkenes, with 2% mol catalyst loading, yields up to 89%, operating under mild conditions, and with the use of only 1 equiv of hydrogen peroxide.[23] The same class of complexes bearing chiral diphosphine ligands showed ee values up to 98% in the epoxidation of terminal alkenes.[24]

Focusing on the most active complex of the achiral series $[(dppe)Pt(C_6F_5)(H_2O)]OTf$ **1** (dppe = 1,2-*bis*(diphenylphosphino)ethane), herein we provide further insight into its extremely high substrate selectivity and explore in detail aspects like regioselectivity and diasteroselectivity in the oxidation of a wide range of substrates (Scheme 1). Further details into the selectivity of this catalyst are provided by a mechanistic investigation performed employing the reaction progress kinetic analysis approach.[25]

Results and Discussion

Scheme 1. Epoxidation of Terminal Olefins with 35% Hydrogen Peroxide Catalyzed by Electron-Poor Pt(II) Complex **1**

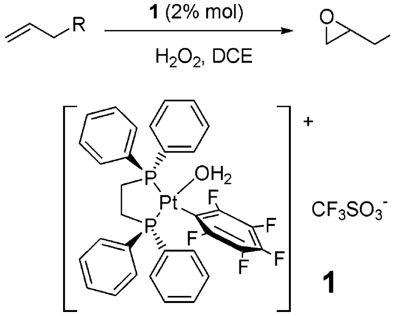
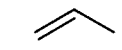
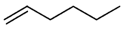
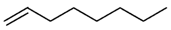
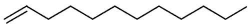
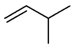
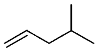
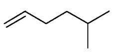
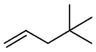
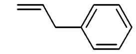
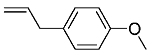
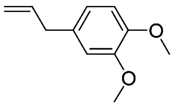
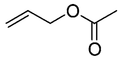
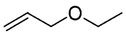
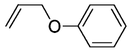


Table 1. Catalytic Epoxidation of Various Alkenes with Hydrogen Peroxide Mediated by **1**: Substrate Scope of the Reaction[a]

Entry	Substrate	Time (h)	Yield (%)[b]
1		20	78[c]
2		3.5	96
3		5	89
4		4	81
5		4	81
6		24	0
7		3	59
8		4	82
9		24	4
10		6	55
11		6	38
12		6	34
13		5	4
14		6	0
15		24	5

[a] Experimental conditions: Substrate = 0.83 mmol, H_2O_2 = 0.83 mmol, [**1**] =2% mol, solvent = 1 mL of dichloroethane (DCE) at RT. [b]Yield determined by GC analysis. [c]Reaction performed at 0 °C, [**1**] =3.5% mol; yield determined by ^1H NMR integration.

Substrate Specificity: Scope of the Epoxidation Reaction. The substrate scope of the reaction was thoroughly investigated with catalyst **1** exploring the reactivity toward different substrates bearing alkyl substitution as well as various functional groups on the alkyl chain (Table 1). In a previous paper dealing with the same catalyst[23] we discovered that disubstituted alkenes (e.g., cyclohexene, methylene cyclohexane) as well as styrene are not suitable substrates, but terminal double bonds can be efficiently epoxidized. As shown in Table 1, **1** shows high

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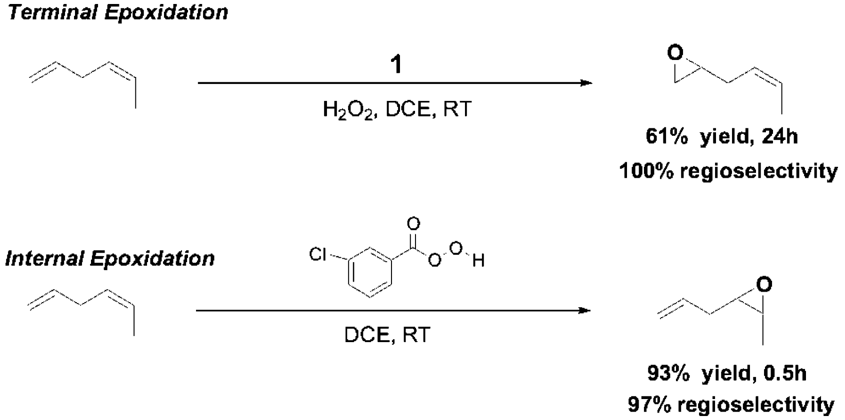
Scheme 2. Regioselective Epoxidation of *cis*-1,4-Hexadiene Bearing a Terminal and a *cis* Disubstituted Double Bond with 35% Hydrogen Peroxide Catalyzed by **1** Compared to the Stoichiometric Epoxidation Performed with *m*-CPBA



activity toward monofunctionalized linear terminal alkenes with a slight decrease in productivity with an increase in the length of the alkyl chain (entries 2−5). The smaller substrate of the series, propene (entry 1), was efficiently epoxidized in a few hours with 78% yield at low temperature with a catalyst loading as low as 3.5%. Comparing entries 3 with 7 and 8 makes it clear that a methyl substituent in the γ-position of the alkyl chain of the substrate influenced the epoxidation reaction only slightly, while methyl substitution in the β-position decreased the yield in epoxide. Further substitution in the same position hampered the reaction almost completely (entry 9) as did substitution in the α-position (entry 6). From these observations it clearly appears that the present catalytic system is specific for terminal alkenes and it is very sensitive to the steric properties of the substrate; in fact, the closer the substituent to the double bond, the lower the yield in epoxide.

Another class of suitable alkenes is based on allyl benzene derivatives, which can be considered as β-substituted terminal double bonds (entries 10−12). Substitution with methoxy residues does not influence directly the electron density on the double bond but decreased the yield in epoxide probably because of increased steric bulkiness or competition of the oxygen donor with the C═C double bond for coordination at Pt. At the same time, the system did not withstand the presence of coordinating heteroatoms in the side chain; in fact 3-butenol, 3-cyanopropene, allyl chloride, 5-hexenoic acid, and allyl imidazole are all nonreactive substrates. Even more surprisingly substitution of a methylene residue in the alkyl chain of 1-hexene with an oxygen atom as in the case of allyl ethyl ether (entries 3 and 14) caused a severe drop in reactivity, while for allyl phenyl ether the yield reached a maximum of 5% (entry 15). Analogously allyl acetate (entry 13), albeit comparable in steric hindrance with other substrates, turned out to be almost unreactive, because of the presence of heteroatoms in the side chain. These observations clearly speak for the dramatic effect of heteroatoms acting as potential ligands toward the catalytic site of the Pt(II) complex **1**, even though water present in large excess from H_2O_2 did not hamper the reaction. In this respect, it has to be pointed out that even if water may be a good competitor for coordination to the metal, its concentration in DCE is about 2 orders of magnitude lower than that of the substrate under standard reaction conditions. To have further confirmation about the detrimental effect of heteroatoms, we performed the epoxidation of 1-octene with catalyst **1** and H_2O_2 in dichloroethane as the solvent with an increasing amount of tetrahydrofurane (THF) or methanol. In a 2:1 DCE/THF solution the epoxide yield after 24 h decreased to 54%, and a reaction performed in pure THF led only to a 12% yield. Pure methanol as the solvent showed an even stronger effect yielding only 6% terminal 1,2-epoxyoctane.

Experiments with a decreasing amount of catalyst in the case of 1-hexene as the substrate were performed. A gradual decrease of yield and concomitant increase in the TON was observed (cat 2%, yield 89%, TON 45; cat 1%, yield 85%, TON 85; cat 0.4%, yield 63%, TON 158) which clearly speaks for the intrinsic robustness of the present catalyst under the strongly oxidizing experimental conditions. On the contrary, an experiment carried out in neat 1-hexene did not show product formation because of catalyst insolubility in pure alkene.

Regioselective Dienes Epoxidation. Regioselective monooxidation of dienes is a challenging oxidative step which leads to highly valuable synthons for organic synthesis, in particular good results were reported for conjugated dienes with a preference for the oxidation of more electron rich *cis*[26] and *trans*[27] double bonds.

The high regioselectivity of catalyst **1** toward terminal unfunctionalized alkenes is emphasized by the experiments reported in Scheme 2. As a typical example, *cis*-1,4-hexadiene bears both a terminal and a *cis* C═C bond and, in the presence of a stoichiometric amount of *m*-chloroperbenzoic acid (*m*-CPBA), leads mainly to *cis*-4,5-epoxy-1-hexene due to the electrophilic epoxidation of the more electron-rich internal double bond. On the contrary, when the epoxidation is performed with catalyst **1** and 1 equiv of H_2O_2, the regioselectivity of the reaction is completely inverted, favoring the product with the terminal oxirane ring (Scheme 2). In Table 2 are reported a few examples of such an inversion of regioselectivity in the epoxidation with *m*-CPBA and with H_2O_2 catalyzed by **1**. The complete regioselectivity toward unsubstituted terminal olefins observed with the former system is, to the best of our knowledge, for some substrates comparable and for others better than that observed with the best catalyst reported so far, i.e., V(III) containing polyoxometalates.[21]

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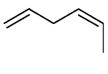
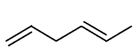
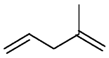
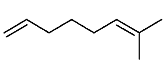
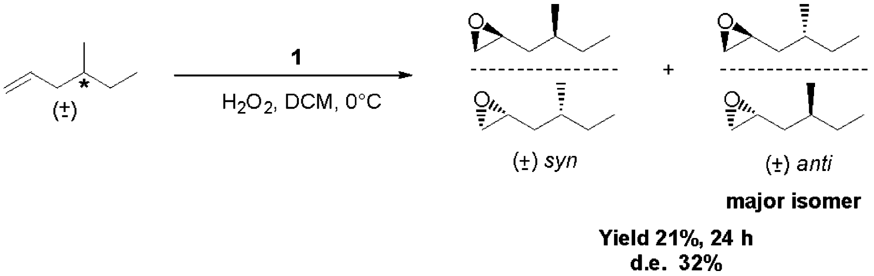
Table 2. Regioselectivity Comparison in the Epoxidation of Various Dienes with Hydrogen Peroxide Catalyzed by **1** and with a Standard Electrophilic Oxidant Like *m*-CPBA[a]

Entry	Substrate	Oxidant	Catalyst	Time (h)	Yield (%)[b]	[Terminal epox.]/ [Internal epox.][c]
1		H_2O_2	**1**	24	61	100:0
2		*m*-CPBA	-	0.5	93	3:97
3		H_2O_2	**1**	24	91	100:0
4		*m*-CPBA	-	0.5	95	4:96
5		H_2O_2	**1**	24	64	100:0[d]
6		*m*-CPBA	-	0.5	>98	7:93[d]
7		H_2O_2	**1**	1	48[e]	100:0
8		*m*-CPBA	-	0.5	96	2:98

[a] Experimental conditions: Substrate = 0.83 mmol, H_2O_2 = 0.83 mmol, [**1**] = 2% mol, solvent = 1 mL of dichloroethane (DCE) at RT. [b] Sum of epoxides. [c] Determined by GC and ^{1}H NMR analysis. [d] [Terminal monosubstituted epoxide]/[terminal disubstituted epoxide]. [e] 7% of side products.

Scheme 3. Diastereoselective Epoxidation of a Chiral Terminal Alkene with 35% Hydrogen Peroxide Catalyzed by **1** (2% mol)



Analogously to what was reported for V(III) polyoxometalates,[21] the exceptional regioselectivity observed with **1** supports the existence of stringent steric requirements although the extreme ability in substrate recognition suggests that electronic effects should also be carefully analyzed.

Diastereoselectivity in Terminal Alkenes Epoxidation. Spurred by the high selectivity showed by catalyst **1**, we investigated also the diastereoselectivity of this complex toward the epoxidation of a racemic chiral terminal alkene such as 4-methylhexene. This substrate differs from 4-methylpentene only for the longer alkyl chain (Table 1 entry 7); however, the former reacts more slowly (25% yield after 24 h at RT) compared to the shorter analogue, with 25% diastereoselectivity in favor of the epoxide product with the oxirane ring *anti* to the methyl group in the β position (Scheme 3). The low diastereoselectivity observed at room temperature increases up to 32% with a 21% yield when the reaction was performed at 0 °C.

The de observed is low, but this is no surprise because of the small steric difference between the methyl and ethyl group in the chiral alkene substrate,[28] as well as the absence of attractive interactions that often are responsible for the peculiar substrate orientation. A well-known example of such behavior is the oxidation of chiral allylic alcohols that often show a high degree of diastereoselectivity with product distribution that is dependent on catalyst/oxidant combination.[29]

In isolated terminal dienes the epoxidation of the first C=C double bond creates a stereocenter (racemic monoepoxide), and the subsequent epoxidation of the remaining alkene moiety occurs in a diastereoselective fashion. In Scheme 4 we report the results of the diastereoselective epoxidation of 1,4-pentadiene and 1,5-hexadiene with catalyst **1** and an excess of hydrogen peroxide.

At 0 °C the reaction with 1,4-pentadiene led to a lower yield in diepoxides but with a higher diastereoselectivity when compared to the reaction performed with the longer substrate for which higher yields but a lower diastereoselectivity were observed. Both effects can be probably ascribed to the strong steric sensitivity characteristic of catalyst **1**. In 1,5-hexadiene the two double bonds are remote from each other, and they react almost independently behaving similarly to isolated double bonds with a high yield in diepoxide and low reciprocal sensing as confirmed by the low de. On the contrary with the smaller 1,4-pentadiene the two double bonds are closer, and this decreases the yield in diepoxide while increasing the diastereoselectivity.

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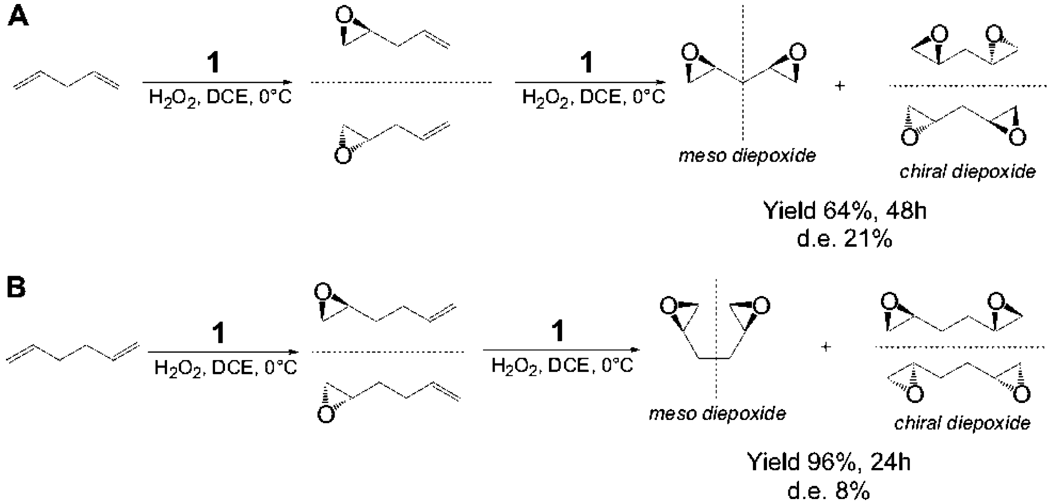
(28) For examples of diastereoselective epoxidation of chiral alkenes: (a) Yang, D.; Jiao, G.-S.; Yip, Y.-C.; Wong, M.-K. *J. Org. Chem.* **1999**, *64*, 1635. (b) Chan, W.-K.; Liu, P.; Yu, W.-Y.; Wong, M.-K.; Che, C.-M. *Org. Lett.* **2004**, *6*, 1597. (c) Chan, W.-K.; Wong, M.-K.; Che, C.-M. *J. Org. Chem.* **2005**, *70*, 4226. (d) Jensen, A. J.; Luthman, K. *Tetrahedron Lett.* **1998**, *39*, 3213.

(29) For examples of diastereoselective epoxidation of chiral allylic alcohols: (a) Adam, W.; Degen, H.-G.; Saha-Möller, C. R. *J. Org. Chem.* **1999**, *64*, 1274. (b) Adam, W.; Stegmann, V. R.; Saha-Möller, C. R. *J. Am. Chem. Soc.* **1999**, *121*, 1879. (c) Adam, W.; Mitchell, C. M.; Saha-Möller, C. R. *J. Org. Chem.* **1999**, *64*, 3699. Della Sala, G.; Giordano, L.; Lattanzi, A.; Proto, A.; Scettri, A. *Tetrahedron* **2000**, *56*, 3567. (d) Adam, W.; Alsters, P. L.; Neumann, R.; Saha-Möller, C. R.; Sloboda-Rozner, D.; Zhang, R. *J. Org. Chem.* **2003**, *68*, 1721. (e) Dusi, M.; Mallat, T.; Baiker, A. *Catal. Rev.—Sci. Eng.* **2000**, *42*, 213. (f) Adam, W.; Malisch, W.; Roschmann, K. J.; Saha-Möller, C. R.; Schenk, W. A. *J. Organomet. Chem.* **2002**, *661*, 3.

Scheme 4. Diastereoselective Oxidation of Isolated Terminal Dienes[a]



[a] (A) 1,4-Pentadiene and (B) 1,5-hexadiene with excess of hydrogen peroxide catalyzed by 1 (2% mol). Experimental conditions like those in Table 1, 2.1 equiv of H_2O_2.

Kinetic Investigation by Means of Reaction Progress Kinetic Analysis. Insight into the mechanism of epoxidation catalyzed by **1** was obtained performing a series of kinetic experiments following the approach elegantly described by Blackmond in a recent review article.[25] Starting from a small number of kinetic experiments following the reaction progress from the beginning to completion, such a kinetic method allows us to ascertain catalyst and substrate order, as well as possible inactivation phenomena like catalyst decomposition or product inhibition. According to the protocol described by Blackmond,[25] hydrogen peroxide was the reactant used in "excess". Being the reaction medium biphasic (dichloromethane/water), the concentration of H_2O_2 in dichloromethane is determined by the partition coefficient.[30] Clearly the "excess" refers rather to the amount present in the whole system than to the actual concentration of H_2O_2 present in the organic phase. As will be clear below from the order observed in H_2O_2 concentration, this does not affect the meaning of the results. As long as mass transfer of the reagents back and forth between the phases is not the rate-determining step (rds), the results observed by reaction progress kinetic analysis in the case of biphasic reactions are correct.

In the case at hand, a plot of the rate vs 1-octene concentration under standard conditions is reported in Figure 1 and shows that the reaction is first order in alkene. The plot is reproducible even changing the stirring rate (1500 and 1000 rpm), thus indicating the absence of mass transfer limitations. Actually, the plot shows a small positive intercept on the abscissa indicating that when the rate goes to zero there is still some alkene left. This may be an indication that catalyst concentration during the reaction progress is not constant,[31] and especially that partial decomposition of the catalyst may occur in the highly oxidizing conditions in which the present reaction is carried out. Nevertheless, such a detrimental side reaction does not seem to hamper the epoxidation considering the high yields in epoxide observed. Support for this view was found by carrying out an experiment with different alkene concentrations but the same [excess] showing that the new plot does not overlay to the original one (Figure 2). Indeed, deviation from overlapping is small (as is the intercept on the abscissa) indicating that catalyst deactivation might be rather limited. An alternative view to justify the positive intercept could be a possible inhibition by product. This was checked by adding some free 1,2-epoxyoctane to the reaction system. Perfect overlapping of the new set of data to the original one rules out this possibility (Figure 3).

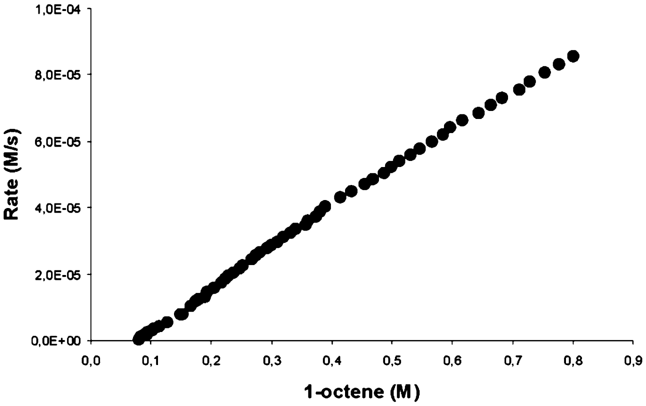


Figure 1. Rate vs 1-octene concentration, standard conditions. (●) $[\mathbf{1}]_0 = 15.3$ mM; $[\text{1-octene}]_0 = 0.82$ M; $[H_2O_2]_0 = 1.05$ M; [excess] = 0.23 M; solvent, 0.5 mL of dichloromethane (DCM); $T = 15$ °C.

A new experiment was carried out using a different [excess], keeping $[\text{alkene}]_0$ constant and increasing $[H_2O_2]_0$. The corresponding plot of rate vs [alkene] overlays the original one (Figure 4) indicating that the reaction is zero order in $[H_2O_2]$. A further increase in $[H_2O_2]_0$ up to 1.8 M provided a rate vs [alkene] profile completely overlapping the previous ones. Reaction order with respect to catalyst concentration was determined by carrying out experiments at different $[\text{catalyst}]_0$. Plots of turnover frequency (TOF) vs [alkene] clearly overlapped and prove the first-order kinetic dependence in [**1**] (Figure 5),

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(30) The partition coefficient of H_2O_2 in dichloroethane/water biphasic system DCE/H_2O = 1/367 was determined following the procedure reported in Wolfe, W. C. *Anal. Chem.* **1962**, *34*, 1328. Due to the higher polarity of DCM compared to DCE, it is likely that the partition coefficient for the former chlorinated solvent should be lower then 1/300.

(31) (a) Rosner, T.; Pfaltz, A.; Blackmond, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 4621. (b) Singh, U. K.; Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14104. (c) Shekhar, S.; Ryberg, P.; Hartwig, J. F.; Mathew, J. S.; Blackmond, D. G.; Strieter, E. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 3584.

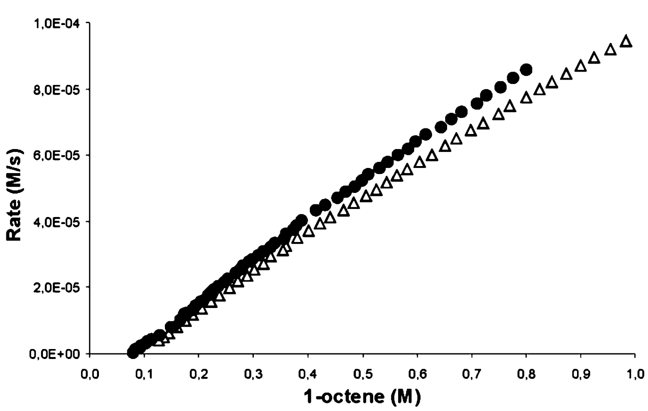

Figure 2. Rate vs 1-octene concentration under same "[excess]" conditions. (●) $[\mathbf{1}]_0 = 15.3$ mM; $[\text{1-octene}]_0 = 0.82$ M; $[H_2O_2]_0 = 1.05$ M; [excess] = 0.23 M; (△) $[\mathbf{1}]_0 = 15.3$ mM; $[\text{1-octene}]_0 = 1.09$ M; $[H_2O_2]_0 = 1.32$ mM; [excess] = 0.23 M; solvent, 0.5 mL of DCM; $T = 15$ °C.

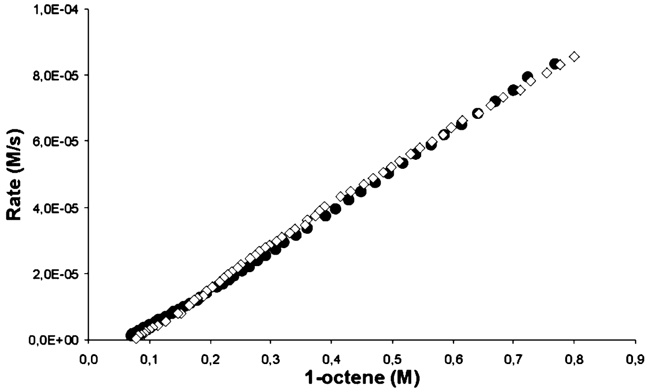

Figure 3. Rate vs 1-octene concentration for the experiment with product addition. (●) $[\mathbf{1}]_0 = 15.3$ mM; $[\text{1-octene}]_0 = 0.82$ M; $[H_2O_2]_0 = 1.05$ M; [excess] = 0.23 M; (◇) $[\mathbf{1}]_0 = 15.3$ mM; $[\text{1-octene}]_0 = 0.82$ M; $[H_2O_2]_0 = 1.05$ M; $[\text{1,2-epoxyoctane}]_0 = 0.163$ M; [excess] = 0.23 M; solvent, 0.5 mL of DCE; $T = 15$ °C.

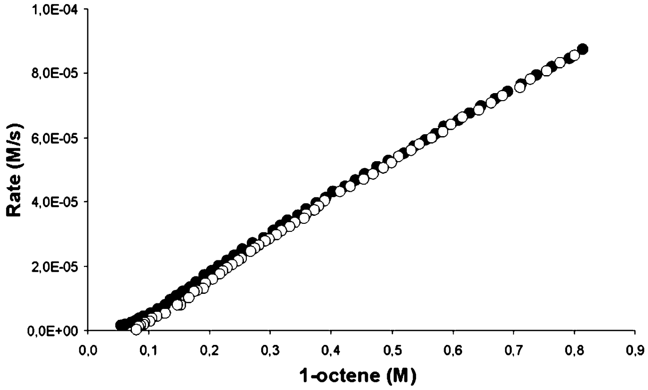

Figure 4. Rate vs 1-octene concentration under different "[excess]" conditions. (●) $[\mathbf{1}]_0 = 15.3$ mM; $[\text{1-octene}]_0 = 0.82$ M; $[H_2O_2]_0 = 1.05$ M; [excess] = 0.23 M; (○) $[\mathbf{1}]_0 = 15.3$ mM; $[\text{1-octene}]_0 = 0.82$ M; $[H_2O_2]_0 = 1.18$ M; [excess] = 0.36 M; solvent, 0.5 mL of DCM; $T = 15$ °C.

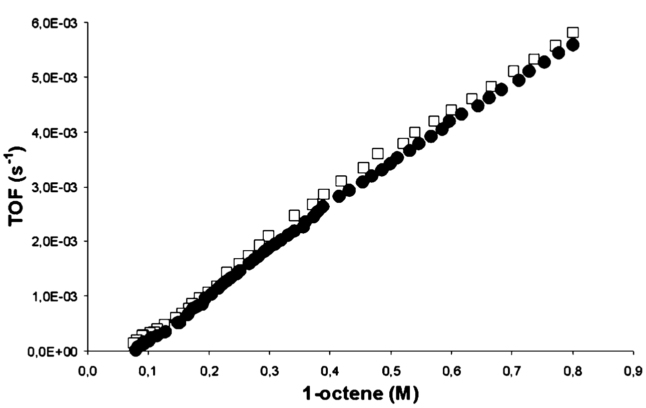

Figure 5. Turnover frequency vs 1-octene concentration with different $[\mathbf{1}]_0$. (●) $[\mathbf{1}]_0 = 15.3$ mM; $[\text{1-octene}]_0 = 0.82$ M; $[H_2O_2]_0 = 1.05$ M; [excess] = 0.23 M; (□) $[\mathbf{1}]_0 = 23.1$ mM; $[\text{1-octene}]_0 = 0.82$ M; $[H_2O_2]_0 = 1.05$ M; [excess] = 0.23 M; solvent, 0.5 mL of DCM; $T = 15$ °C.

Scheme 5. Possible Reaction Pathways for the Catalytic Epoxidation of 1-Octene with Hydrogen Peroxide Catalyzed by Complex **1**

$$\begin{aligned} &\text{Pt}^+ + \text{ol} \xrightarrow{\text{rds}} \text{Pt(ol)}^+ \\ &\text{Pt(ol)}^+ + H_2O_2 \xrightarrow{\text{fast}} \text{Pt}^+ + \text{epox} + H_2O \qquad \textbf{A} \end{aligned}$$

$$\begin{aligned} &\text{Pt}^+ + H_2O_2 \xrightarrow{\text{fast}} \text{Pt-OOH} + H^+ \\ &\text{Pt-OOH} + \text{ol} \xrightarrow{\text{rds}} \text{PtOH} + \text{epox} \qquad \textbf{B} \\ &\text{Pt-OH} + H^+ \xrightarrow{\text{fast}} \text{Pt}^+ + H_2O \end{aligned}$$

even though a negligible difference between the two profiles is present, probably due to the moderate catalyst deactivation as observed in Figure 5. The kinetic analysis reported above leads to the following rate expression:

$$\text{Rate} = \text{d[epox]}/\text{d}t = k[\text{Pt}]_0[\text{alkene}]$$

Reaction Mechanism. The above-described kinetic analysis is consistent with two possible alternative reaction schemes reported in Scheme 5, where in path A $[\text{Pt}]_0$ is equivalent to the concentration of the starting complex $[\mathbf{1}] = (\text{Pt}^+)$, whereas according to path B, $[\text{Pt}]_0$ is equivalent to the concentration of a newly formed $[(\text{dppe})\text{Pt}(C_6F_5)(\text{OOH})]$ species (Pt−OOH). The latter mechanism is suggested on the basis of previous observations with $[(\text{PP})\text{Pt}(CF_3)(\text{solv})]^+$ interaction with hydrogen peroxide leading to the formation of Pt-hydroperoxo species.[22]

In order to gain more insight into the species involved in the reaction a series of ^{31}P NMR experiments were performed under the experimental conditions of Figure 1. The spectrum of the starting complex **1** in $CDCl_3$ (Figure 6, spectrum A) shows two signals at δ 29.0 ppm $^1J_{\text{P-Pt}}$ 4353 Hz and 44.5 ppm $^1J_{\text{P-Pt}}$ 2309 Hz, the latter with evidence for P−F coupling. Addition of an excess of water to this complex (spectrum B) leads to the formation of a slightly different species ($\text{P}_{1-\text{H2Otrans}}$ 29.9 ppm $^1J_{\text{P-Pt}}$ 3474 Hz; $\text{P}_{2-\text{C6F5trans}}$ 44.9 ppm $^1J_{\text{P-Pt}}$ 2320 Hz), indicating that the latter is indeed the aquo complex whereas the initial species observed in spectrum A is most likely a solvento (CD_2Cl_2) complex. Addition of 50 equiv of H_2O_2 to a solution of **1** in CD_2Cl_2 leads to a spectrum identical to spectrum B. This observation seems to rule out pathway B, because the formation of a hydroperoxy platinum species would require a significant shift of the signal relative to P *trans* to O and a $^1J_{\text{P-Pt}}$ in the 3200−3500 Hz range.[32] On the contrary, addition of 50 equiv of 1-octene to a solution of **1** in CD_2Cl_2 caused the formation (spectrum C) of a new species characterized by signals at lower field ($\text{P}_{1-\text{C=Ctrans}}$ 46.7 ppm $^1J_{\text{P-Pt}}$ 3476 Hz; $\text{P}_{2-\text{C6F5trans}}$ 45.7 ppm $^1J_{\text{P-Pt}}$ 2146 Hz) in particular for the P atom *trans* to the neutral coordinating ligand, while P *trans* to C_6F_5 changes only slightly. The relative intensities between the original and the new species

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(32) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738.

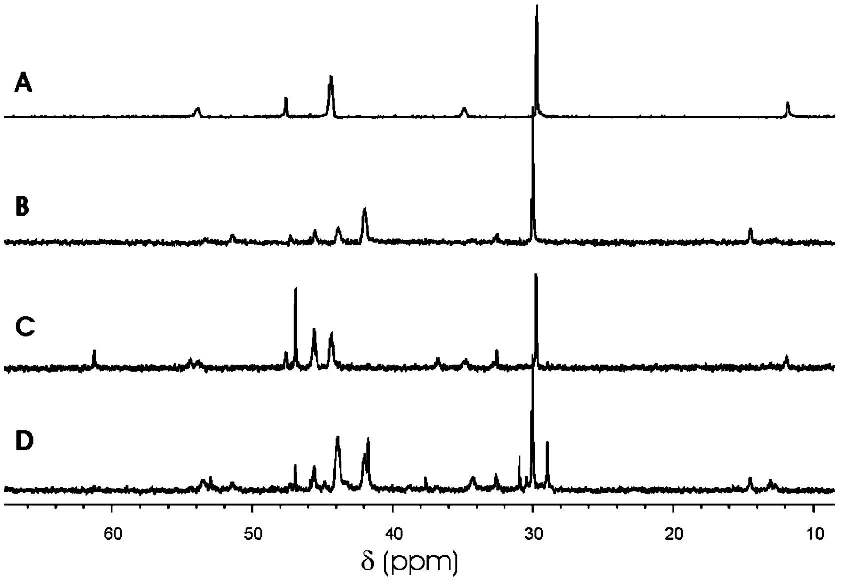
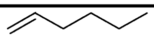
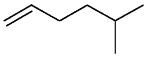
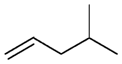
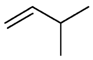


Figure 6. $^{31}P\{^1H\}$ NMR of (A) catalyst **1**; (B) **1** with H_2O; (C) **1** with addition of 50 equiv of 1-hexene; (D) **1** with addition of 50 equiv of 1-hexene and 50 equiv of H_2O_2.

Table 3. Reversible Coordination of Alkenes to **1**[a]

Entry	Substrate	Ratio[b]
1		32:68
2		24:76
3		14:86
4		0:100

[a] Experimental conditions: Substrate = 0.83 mmol, [**1**] = 2% mol, solvent = 0.5 mL of $CDCl_3$ at RT. [b] Relative ratio of [**1**·alkene]/[**1**] determined by integration of the ^{31}P NMR spectra.

are 1 to 1.6. The decrease of the $^1J_{P-Pt}$ coupling constant for P *trans* to the neutral ligand is in agreement for alkene coordination in square planar complexes.[32]

Alkene coordination is the most obvious explanation to this NMR experiment and is supported also by ^1H NMR of **1** in a solution saturated with propene where new signals at higher field compared to the free alkene are observed. ^{31}P NMR experiments performed at different temperatures showed different amounts of **1** and the low field species with coordinated propene proving the reversibility of the substrate coordination step (see Supporting Information). Moreover, if alkene coordination was the rds, the largely prevailing species in solution should be complex **1**, and as a consequence, signals of the **1**·alkene, which is a species just after the rds, should disappear when H_2O_2 is present and the epoxidation reaction occurs.

It is clear that alkene coordination is therefore a reversible pre-equilibrium that takes place rapidly and whose position is due to the steric and electronic features of the alkene. In fact, increasing steric hindrance of the substrate in closer proximity of the double C═C bond decreases alkene pre-equilibrium coordination (Table 3) and hampers the subsequent epoxidation step (see Supporting Information).

This point was further investigated by NMR analysis of metal alkene formation with substrates that proved catalytically unreactive according to Table 1. For a more hindered methylenecyclohexane and vinyl-cyclohexane, as well as styrene or *cis*-2-heptene, clearly no or negligible metal−alkene species were observed. These experiments are in agreement with the general coordination preference of Pt(II) complexes with alkenes where the presence of electron-withdrawing groups on the alkene encourages back-donation and enhances coordination, while on the contrary electron-donating groups make the alkene bind more weakly.[33] For the reaction at hand, clearly no reaction is possible in the absence of a reversible metal−alkene pre-equilibrium interaction. Such observations rules out pathway A in Scheme 5.

Addition to **1** of 50 equiv of 1-octene and excess H_2O (independently of the addition order) showed the presence of four different species (spectrum D, Figure 6). These are the solvento complex, the aquo complex (all together approximately 90% of all the Pt(II) species), the olefin complex, and a new species with signals at δ 28.7 ppm and 41.9−42.5 ppm with no evidence for P−F coupling. The latter could probably be ascribed to both olefin and water containing penta-coordinate species where one P donor is in equatorial position, the other P is in axial position, and the C_6F_5 ligand is in equatorial position. Five-coordinate Pt(II) complexes with alkene neutral ligands are known in the literature,[34] and they usually assume trigonal bipyramidal geometry. Addition of 50 equiv of H_2O_2 instead of water leads to a spectrum identical to spectrum D. Differences with respect to D after 24 h are the slow formation of traces of 1,2-bis(diphenylphosphino)ethane dioxide (39 ppm), clearly supporting the partial degradation of the catalyst, and the depletion after several hours of the olefin-containing species when free olefin concentration is decreased because of the

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(33) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: 1988. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. T.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Wallet, CA, 1987.

(34) (a) Fanizzi, F. P.; Margotta, N.; Lanfranchi, M.; Tiripicchio, A.; Pacchioni, G.; Natile, G. *Eur. J. Inorg. Chem.* **2004**, 1705. (b) Albano, V. G.; Natile, G.; Panunzi, A. *Coord. Chem. Rev.* **1994**, *133*, 67.

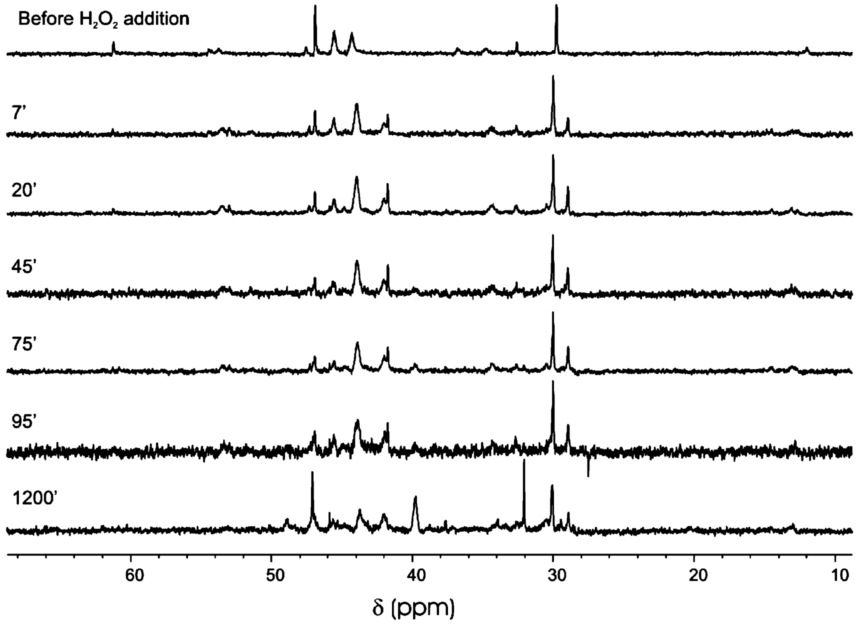

Figure 7. $^{31}P\{^1H\}$ NMR at different times taken during the reaction of 1-octene with H_2O_2 catalyzed by **1**. Experimental conditions as those in Figure 1.

catalytic reaction, again indicating that they are in equilibrium with the original catalyst **1** (Figure 7).

The apparent discrepancy between kinetic and NMR studies is not to be ascribed to different stirring or diffusional conditions because rate data calculated from ^1H NMR spectra overlay with those obtained by GC analysis (Supporting Information), at least for a significant part of the experiment. To overcome this problem a different explanation is therefore necessary.

Fluorine atoms can impart peculiar properties to molecules; for instance there are many examples of hydrogen bonding of fluorinated drugs[35] within the hydrophobic portions of proteins that enhances pharmacological activity compared to nonfluorinated ones. In catalysis, fluorinated solvents, in particular alcohols, have attracted the attention of many research groups for several years because of their intrinsic ability in the activation of H_2O_2 for oxidation reactions. In most cases such an effect allows us to perform oxidation reactions in the complete absence of any sort of metal catalysts, just exploiting the solvating and hydrogen bonding donor and acceptor ability of fluorinated moieties that act as organo-catalysts. Sound literature on fluorinated solvent effects in electrophilic activation of hydrogen peroxide in epoxidation reactions[36] and nucleophilic activation in a Baeyer−Villiger reaction[36b,37] is available. Moreover, many research groups analyzed in detail the effect of fluorine on the mechanisms of activation by means of experimental measurements[38] and theoretical calculations.[39] Spurred by this vast literature, we decided to investigate the possible effect of the perfluoro-aryl ligand present in catalyst **1** on the epoxidation reaction, in particular its interaction (if any) with H_2O_2. It is well-known that H_2O_2 is both a better hydrogen bond donor and a better acceptor than H_2O;[40] therefore, in order to investigate plausible hydrogen bonding between the oxidant and the fluorine atoms of the C_6F_5 residue,[39d] we first performed ^{19}F NMR experiments on **1** in the presence of H_2O_2, 1-octene and both reagents under catalytic conditions. Such measurements did not allow any unequivocal assignment of the resonances of the C_6F_5 moiety because addition of either 1-octene or H_2O_2 caused changes in the chemical shifts due to both direct interaction with the fluorine atoms and direct coordination to the metal center. As observed by ^{31}P NMR investigation, several species are therefore present in solution all with different ^{19}F spectra which are not easily assignable. In order to exclude the latter effect and investigate only the interaction of the reagents with the fluorine atoms, the complex $[(dppe)Pt(C_6F_5)Cl]$ was employed as a nonreactive analogue of catalyst **1**. Addition of H_2O_2 to $[(dppe)Pt(C_6F_5)Cl]$ caused a small but substantial deshielding of *meta* and *para* fluorine atoms of about 0.1 ppm that could well account for hydrogen bonding between such fluorine atoms and H_2O_2 dissolved in $CDCl_3$.[41] At the same time, no signals for the original complex are observed. It is therefore likely that H_2O_2 efficiently binds to the *meta* and *para* fluorine atoms of C_6F_5 by means of hydrogen bonding to all the different Pt(II) species present in solution as is observed by ^{31}P NMR analysis (Figure 7). Such an interaction can be described as an equilibrium strongly shifted toward the forma-

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(35) (a) Carosati, E.; Sciabola, S.; Cruciani, G. *J. Med. Chem.* **2004**, *47*, 5114. (b) Razgulin, A. V.; Mecozzi, S. *J. Med. Chem.* **2006**, *49*, 7902.

(36) (a) Berkessel, A.; Adrio, J. A.; Hüttenhain, D.; Neudörfl, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 8421. (b) Neimann, K.; Neumann, R. *Org. Lett.* **2000**, *2*, 2861. (c) van Vliet, M. C. A.; Arends, I. W. C. E.; Sheldon, R. A. *Chem. Commun.* **1999**, 263. (d) van Vliet, M. C. A.; Arends, I. W. C. E.; Sheldon, R. A. *Chem. Commun.* **1999**, 821. (e) van Vliet, M. C. A.; Arends, I. W. C. E.; Sheldon, R. A. *Synlett* **2001**, 248.

(37) (a) Berkessel, A.; Andreae, M. R. M.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4481. (b) Berkessel, A.; Andreae, M. R. M. *Tetrahedron Lett.* **2001**, *42*, 2293.

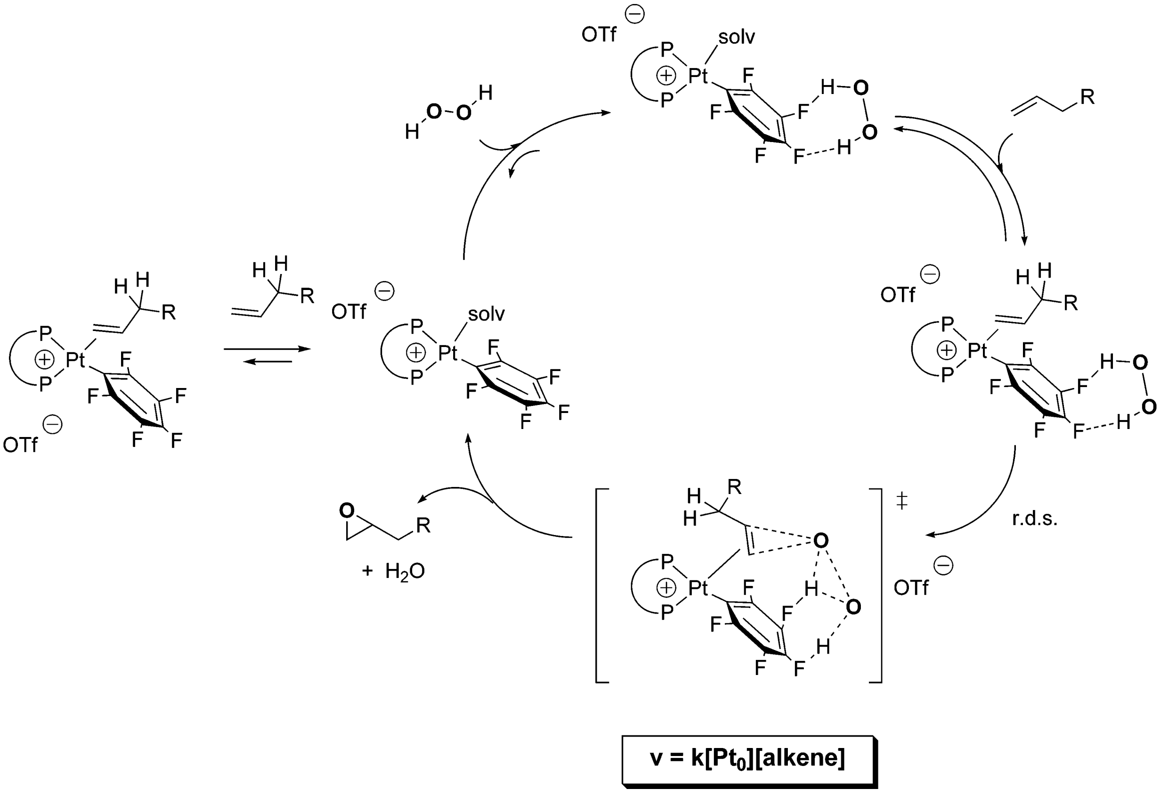
(38) (a) Ravikumar, K. S.; Zhang, Y. M.; Bégué, J. P.; Bonnet-Delpon, D. *Eur. J. Org. Chem.* **1998**, 2937. (b) Legros, J.; Crousse, B.; Bourdon, J.; Bonnet-Delpon, D.; Bégué, J. P. *Tetrahedron Lett.* **2001**, *42*, 4463. (c) ten Brink, G.-J.; Vis, J. M.; Arends, I. W. C. E.; Sheldon, R. A. *Tetrahedron* **2002**, *58*, 3977.

(39) (a) de Visser, S. P.; Kaneti, J.; Neumann, R.; Shaik, S. *J. Org. Chem.* **2003**, *68*, 2903. (b) Berkessel, A.; Adrio, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 13412. (c) Schaal, H.; Häber, T.; Suhm, M. A. *J. Phys. Chem. A* **2000**, *104*, 265. (d) Howard, J. A. K.; Hoy, V. J.; O'Hagan, D.; Smith, G. T. *Tetrahedron* **1996**, *52*, 12613. (e) Alkorta, I.; Rozas, I.; Elguero, J. *J. Fluorine Chem.* **2000**, *101*, 233.

(40) (a) Goebel, J. R.; Ault, B. S.; Del Bene, J. E. *J. Phys. Chem. A* **2001**, *105*, 11365. (b) Rankin, K. N.; Boyd, R. J. *J. Comput. Chem.* **2001**, *22*, 1590. (c) Goebel, J. R.; Ault, B. S.; Del Bene, J. E. *J. Phys. Chem. A* **2000**, *104*, 2033. (d) Mó, O.; Yáñez, M.; Rozas, I.; Elguero, J. *J. Chem. Phys.* **1994**, *100*, 2871. (e) Mó, O.; Yáñez, M.; Rozas, I.; Elguero, J. *Chem. Phys. Lett.* **1994**, *219*, 45.

(41) A typical example of an H−F hydrogen bond in organometallic complexes: Anil Kumar, P. G.; Pregosin, P. S. *Organometallics* **2004**, *23*, 5410.

Scheme 6. Mechanistic Hypothesis for Terminal Alkene Epoxidation with Hydrogen Peroxide Mediated by **1** on the Bases of the Results of Reaction Progress Kinetic Analysis and ^{31}P and ^{19}F NMR Investigation



tion of the $C_6F_5{-}H_2O_2$ adduct. In Scheme 6 is reported what we believe is the most likely mechanism of the reaction.

Such a scheme takes into account all the spectroscopic evidence on the reaction reported above, including the formation of an off-cycle metal−olefin complex, and is in agreement with the kinetic data under the assumption (confirmed by NMR data) that [Pt_0] is essentially given by the solvento and aquo complexes carrying H_2O_2 hydrogen-bound to the C_6F_5 ligand, all the other species being negligible. Scheme 6 would also account for the steric effects observed in Table 1 as metal−alkene formation precedes the rate-determining step, as well as for the nucleophilic character of the oxygen transfer step as demonstrated by the unusual regioselectivity observed in dienes epoxidation (Table 2). This is, to the best of our knowledge, a rare example of epoxidation of unfunctionalized alkenes by means of electrophilic alkene and nucleophilic oxidant activation provided by metal catalysts. In fact, this kind of oxidation characterized by a concomitant substrate and oxidant activation is much more common for electron-poor substrates, as demonstrated recently for the asymmetric nucleophilic epoxidation of chalcone with hydrogen peroxide catalyzed by polyleucine catalysts.[42]

Differences with respect to the mechanism proposed for the homologous $-CF_3$ derivatives and analyzed by initial rate kinetic experiments are likely due to the different nature of the fluorinated ligands. The trifluoromethyl residue is less sterically demanding with respect to pentafluorophenyl but more electron-withdrawing.[43] It is likely that the higher acidity of CF_3 favors also direct H_2O_2 coordination, and the reaction proceeds through a second-order kinetic dependence in catalyst concentration.[22e]

Conclusion

The use of Pt(II) complex **1** demonstrated a high activity and unusual selectivity compared to other metal-catalyzed epoxidation methods for terminal monofunctionalized alkenes with hydrogen peroxide as oxidant. In addition to (i) high activity under mild experimental conditions, (ii) catalyst loading as low as 2%, and (iii) no need of over-stoichiometric amounts of oxidant, key features of catalyst **1** are (iv) the extreme substrate selectivity and (v) the exceptional regioselectivity[21] which, in particular with some dienes, is the highest so far reported for metal mediated epoxidation. Such properties, along with the straightforward synthesis of the catalyst, allowed the development of an asymmetric and highly regioselective version of the reaction[24] whose results are well interpreted on the basis of the mechanism observed. Further development on the described class of Pt(II) catalysts is currently underway with the aim of disclosing a practical application for highly selective terminal alkene epoxidation.

Experimental Section

Reagents and Materials. The complex $[(dppe)Pt(C_6F_5)(H_2O)]OTf$ **1** was prepared following the procedure reported in the literature.[23] Hydrogen peroxide (35% Aldrich) as well as all the alkene substrates listed above and 1,2-epoxyoctane are commercial products (Aldrich) and were used without further purification.

General. ^{1}H, ^{31}P{^{1}H}, and ^{19}F{^{1}H} NMR spectra were recorded at 298 K, unless otherwise stated, on a Bruker AVANCE 300 spectrometer

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[42] Mathew, S. P.; Gunathilagan, S.; Roberts, S. M.; Blackmond, D. G. *Org. Lett.* **2005**, *7*, 4847.

[43] Acidity of alcohols: (a) Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1959**, *81*, 1050. (b) Korenaga, T.; Kadowaki, K.; Ema, T.; Sakai, T. *J. Org. Chem.* **2004**, *69*, 7340. Acidity of carboxylic acids: (c) Takahashi, S.; Cohen, L. A.; Miller, H. K.; Peake, E. G. *J. Org. Chem.* **1971**, *36*, 1205. (d) Strong, L. E.; Brummel, C. L.; Lindower, P. *J. Solution Chem.* **1987**, *16*, 105. Taft's σ^* values: ref 43b.

operating at 300.15, 121.50, and 282.38 MHz, respectively. δ values in ppm are relative to $SiMe_4$, 85% H_3PO_4, and $CFCl_3$. GLC measurement were taken on a Hewlett-Packard 5890A gas chromatograph equipped with an FID detector (gas carrier He). All reactions were monitored on a 25 m HP-5 capillary column. The concentration of hydrogen peroxide was checked iodometrically prior to use.

Oxidation Reactions. These were carried out in a 2 mL vial equipped with a screw-capped silicone septum to allow sampling. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer (700 rpm). Constant temperature was maintained by water or alcohol circulation through an external jacket connected with a thermostat. The concentration of the commercial 35% H_2O_2 solution was checked iodometrically prior to use. Typically, the proper amount of catalyst **1** (0.016 mmol, 2% mol) was placed in the vial, followed by the solvent (1 mL) and internal standard, and then the vial was thermostatted. After the mixture stirred for 10 min, the substrate (0.83 mmol) was added and the mixture stirred for another 10 min. To this 35% hydrogen peroxide was added in one portion, (0.83 mmol) and time was started. All reactions (except when the substrate was propene) were monitored with GLC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Prior quenching of the samples by adding an excess of LiCl was found to be unnecessary. Separation of the products was performed on a 25 m HP-5 capillary column with He as carrier using a flame ionization detector.

Propene Oxidation. 5 mL of DCE were placed in a vial thermostatted at the desired temperature, and to this propene was bubbled for 30 min until saturation of the solution. 1 mL of such solution was put in a vial, and catalyst **1** was added (0.016 mmol). The substrate/catalyst ratio was determined by ^1H NMR. The solution was then thermostatted, and the proper amount of internal standard followed by 35% hydrogen peroxide (1 equiv compared to propene) were added and time was started. Reaction was quenched at the desired time by LiCl addition, and the yield was determined by ^1H NMR integration.

Reaction Progress Kinetic Analysis. The experimental methodology employed for data acquisition was GC analysis of the progress of the reaction, monitoring the reactant [1-octene] and product [1,2-epoxyoctane] over time with *n*-decane as the internal standard. The concentration of H_2O_2 (the reagent in "excess") was calculated indirectly from the concentration of alkene, as a sufficient number of direct determinations during reaction progress is experimentally impossible. The mass balance for H_2O_2 was checked at the end of the reaction and found satisfactory. The experimental concentration vs time profiles for epoxide product was interpolated with a sixth grade polynomial function, which was subsequently derived to obtain a rate vs time profile.

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Supporting Information Available: ^{31}P NMR spectra for the coordination of different alkenes to **1** and temperature effect on pre-equilibrium position in the coordination of propene to **1**. Comparison of catalyst's activity by means of NMR and GC determination. This material is available free of charge via the Internet at http://pubs.acs.org.

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