Epoxidation versus Baeyer−Villiger Oxidation: The Possible Role of Lewis Acidity in the Control of Selectivity in Catalysis by Transition Metal Complexes

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The synthesis of a series of cationic complexes of Pt^{II} containing triphos or triphosPO and either a solvent, a hydroxo or a hydroperoxo as the fourth ligand is reported. The complexes are characterized by IR and $^{31}P\{^{1}H\}$ NMR spectroscopy and by molar conductivity data, and their Lewis acid characteristics determined by NMR techniques. All complexes are good catalysts for the epoxidation of olefins and the Baeyer–Villiger oxidation of ketones under mild conditions using hydrogen peroxide as oxidant. The latter reaction is more Lewis-acid demanding in terms of the electronic characteristics of the catalysts. The use of Lewis-acidic metal centers allows the selective oxidation of unsaturated ketones to the corresponding unsaturated esters without oxidation of the carbon-carbon double bond, indicating that a strong Lewis-acid character of the catalyst can be an important feature in the design of catalysts capable of separating the two processes.

Introduction

In transition metal chemistry, the idea of Lewis acidity is generally associated with electron-deficient metal centers such as the early metals in their highest oxidation state or the first row late metals such as Cu^{II} and Zn^{II}. This simple notion is supported by a huge number of applications in organic synthesis.[1] Within this framework, the idea of associating Lewis acidity with electron-rich metal centers like Pd^{II} and Pt^{II} for catalytic applications is a relatively recent one, the necessary condition to exploit the Lewis acidity of the latter systems being the presence of at least one positive charge on the complex. In the past few years, the number of applications of these systems in catalysis has been increasing, although, among the examples reported,[2] none refers to oxidation reactions.

Several years ago we reported the first example of transition metal catalysis in the Baeyer−Villiger (BV) oxidation of ketones, with H_2O_2 as the oxidant, and using a cationic complex of Pt^{II} as the catalyst.[3] The mechanism of the reaction[3b] (Figure 1) clearly indicates that, having no role in the activation of the oxidant, the major function of Pt in the catalytic cycle is to behave as a Lewis acid for the activation of the ketone. This view is strengthened by the analogies (Figure 1) between the quasi-peroxymetallacyclic intermediate **1** and the Criegee intermediate involved in the purely organic reaction using peracids (Pt replaces H^+). More recently, typical Lewis acids such as Al^{III},[4] Mg^{II},[5] and Sn^{IV} [6] have also been reported in the BV oxidation of ketones, emphasizing the importance of having a Lewis-acid center to promote the reaction by activation of the ketone.

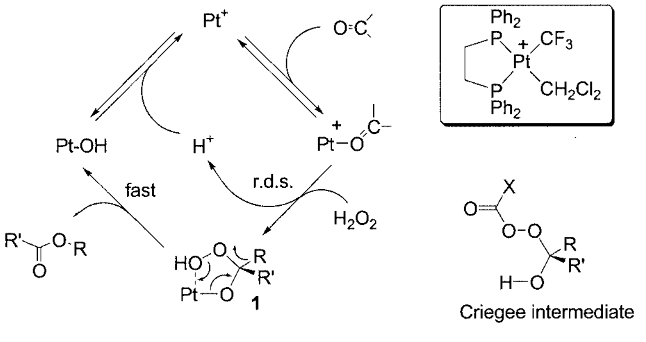

Figure 1. Reaction mechanism for the Baeyer−Villiger oxidation of ketones with hydrogen peroxide catalyzed by $[Pt(CF_3)(P\text{-}P)(solv)]^+$-type complexes

The same complex reported in Figure 1 was also recognized to be an efficient catalyst for the epoxidation of olefins with H_2O_2 under mild conditions,[7] although in this case the mechanism of the reaction (Figure 2) indicates that the function of the catalyst is more complex[7d] as it activates both the olefin towards nucleophilic attack and, at the

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same time, hydrogen peroxide, increasing its nucleophilicity by coordination.

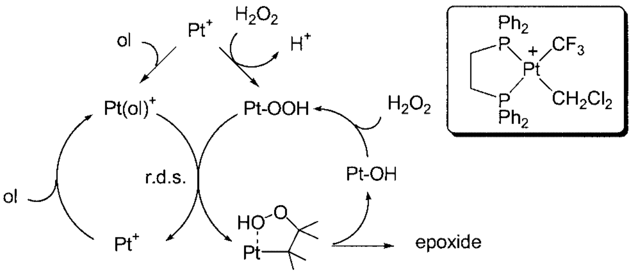
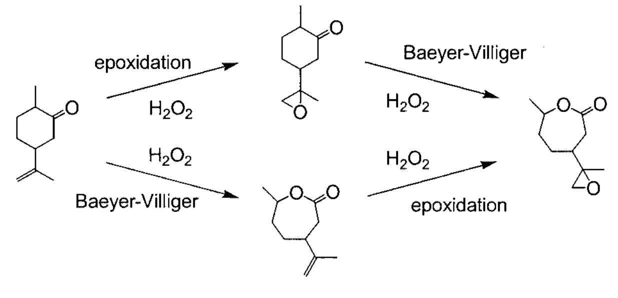


Figure 2. Reaction mechanism for the epoxidation of olefins with hydrogen peroxide catalyzed by $[Pt(CF_3)(P\text{-}P)(solv)]^+$-type complexes

Platinum complexes are the only catalysts known in the literature that catalyze both the BV and the epoxidation reactions with high activity. Moreover, they do so using hydrogen peroxide as the oxidant, i.e. a cheap, environmentally friendly oxidant, but also an elusive one for selective, non-radical-type oxidations. The versatility of these systems offers a unique opportunity to investigate in more detail the electronic properties of the metal center that allow us to separate the BV reaction from the epoxidation reaction. This aspect is crucial for selectivity whenever a bifunctional molecule is oxidized, and may have an important impact in organic synthesis, as both the BV and the epoxidation reactions are widely used as intermediate steps in complex synthetic procedures, leading to the preparation of pharma, agro and fine chemicals. As an example, Scheme 1 shows the theoretical case of dihydrocarvone where both parallel and consecutive reactions are possible leading to the unselective formation of the epoxy lactone. The aim of the present work is to establish whether the Lewis acidity of the metal center is of importance for controlling the relative rates of the BV and epoxidation reactions.



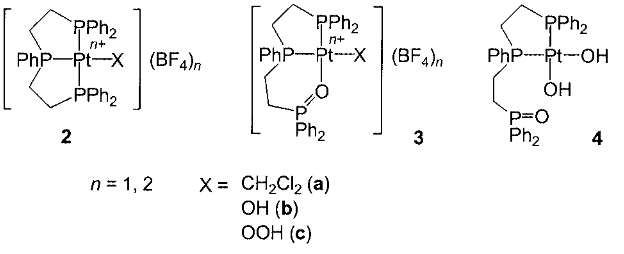
Scheme 1

Results and Discussion

Synthesis of Complexes

To address the problem exposed above, one has to design a class of cationic homologous complexes of platinum(II) with very similar geometric constraints, but differing in the electron density of the metal. Since the presence of a coordinated diphosphane seems to be a crucial requirement to promote the activity of these complexes,[3,7,8] to achieve this goal we chose tridentate ligands of the type P-P-P and P-P-P=O, bearing, respectively, three P donors and two P and one O donors. This would ensure the formation of bis-cationic complexes possessing, in principle, a significant Lewis acidity.

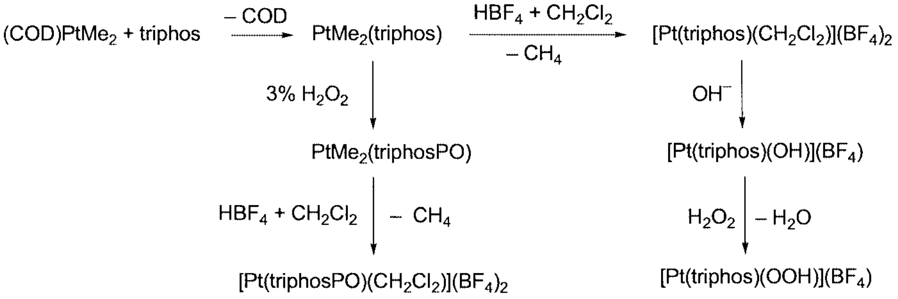
Square planar Pt^{II} complexes such as **2** and **3** containing tridentate ligands (Scheme 2) were synthesized following the procedure outlined in Scheme 3. This was already published for solvento complexes by Bergamini et al.[9] although the species were characterized in situ (NMR evidence) but never isolated. The isolation of the hydroxo and hydroperoxo complexes of **2** could be easily accomplished by addition of, respectively, OH^- to the corresponding solvento complex or H_2O_2 to the hydroxo complex. Conversely, in the case of **3**, given the lability of the oxygen donor, the same procedure led to the formation of a different species that was characterized in situ by NMR spectroscopy. Attempts to isolate this species synthetically using the procedure adopted for **2b** (i.e. addition of a stoichiometric amount of OH^- in acetone/H_2O) led to the formation of a complex mixture showing a different NMR spectrum. Isolation of a species (albeit in moderate yield) with the same NMR spectrum as observed in the in situ experiment could be accomplished in CH_2Cl_2 by adding an excess of OH^- in water. This species is most likely a neutral bis-hydroxo complex of the type $[Pt(OH)_2(P\text{-}P\text{-}P{=}O)]$ (**4**) as seems to be indicated by the full spectroscopic characterization (see below).



Scheme 2

Characterization of Complexes

All complexes were characterized by IR and $^{31}P\{^1H\}$ NMR spectroscopy, and molar conductivity measurements. A summary of the characterization data is reported in Table 1. For the purpose of simplicity, and with reference to Scheme 2, in reporting the NMR spectroscopic data P_a refers to the phosphorus *trans* to P (or to O in complexes **3**), P_b to the phosphorus *trans* to X and (only in complexes **3**) P_c to the oxidized phosphorus. As shown in Table 1, in the IR spectrum all complexes display the broad band characteristic of non-coordinated BF_4^- in the 1100−960 cm^{-1} range. Additionally, complexes **2b** and **2c** show typical weak O−H stretching frequencies at 3620 and 3483 cm^{-1}, respectively, in agreement with previously reported hydroxo



Scheme 3

Table 1. Characterization data for complexes **2** and **3**[a]

Complex	IR (cm^{-1})	$^{31}P\{^1H\}$ NMR (δ in ppm, J in Hz)	Molar conductivity ($\Omega^{-1}mol^{-1}cm^2$)
2a	1100−960 (b)	P_a 50.6 (s), $^1J_{P,Pt} = 2452$	115−120
		P_b 80.2 (s), $^1J_{P,Pt} = 3475$	
2b	3620 (w)	P_a 77.7 (d), $^2J_{P,P} = 3.7$, $^1J_{P,Pt} = 2575$	79.6
	1100−960 (b)	P_b 39.6 (t), $^2J_{P,P} = 3.7$, $^1J_{P,Pt} = 2625$	
2b[b]		P_a 75.2 (d), $^2J_{P,P} = 4.1$, $^1J_{P,Pt} = 2592$	
		P_b 39.2 (t), $^2J_{P,P} = 4.1$, $^1J_{P,Pt} = 2620$	
2c	3483 (w)	P_a 70.9 (d), $^2J_{P,P} = 4.3$, $^1J_{P,Pt} = 2385$	90.3
	1100−960 (b)	P_b 42.4 (t), $^2J_{P,P} = 4.3$, $^1J_{P,Pt} = 2811$	
3a	1100−960 (b)	P_a 38.2 (s), $^1J_{P,Pt} = 3753$	172
	1124 (s)	P_b 42.9 (s), $^1J_{P,Pt} = 3890$	
		P_c 55.1 (d), $^3J_{Pb,Pc} = 9.0$	
4[b]	1178 (s)	P_a 33.4 (d), $^2J_{Pa,Pb} = 11.0$, $^1J_{P,Pt} = 3477$	8−10
	3599 (w)[c]	P_b 39.4 (dd), $^2J_{Pa,Pb} = 11.0$, $^3J_{Pb,Pc} = 52.5$, $^1J_{P,Pt} = 3480$	
		P_c 31.2 (d), $^3J_{Pc,Pb} = 52.5$	
2d[d]		P_a 48.4 (s), $^1J_{P,Pt} = 2459$	
		P_b 82.2 (s), $^1J_{P,Pt} = 3434$	
3d[d]		P_a 37.9 (d), $^2J_{Pa,Pb} = 6.8$, $^1J_{P,Pt} = 3900$	
		P_b 43.2 (s), $^1J_{P,Pt} = 3714$	
		P_c 55.1 (d), $^3J_{Pb,Pc} = 11.1$	

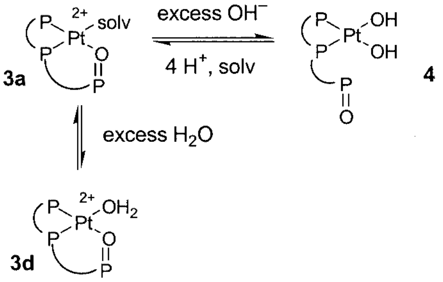
[a] IR in nujol; NMR in [D$_6$]acetone at 25 °C; molar conductivity: 10^{-3} M solution in EtOH. [b] NMR spectrum recorded in CD_2Cl_2. [c] In 1,2-dichloroethane solution. [d] NMR spectra recorded in acetone at −70 °C.

and hydroperoxo complexes of Pt^{II}.[7e,10] Similarly, in complex **3a** the P=O stretching frequency of the oxygen-coordinated ligand is observed at 1124 cm^{-1}.[11]

The NMR spectroscopic data were taken in [D$_6$]acetone. Complexes **2a** and **3a** give very broad signals in CD_2Cl_2 so a more coordinating solvent was necessary in order to observe a relatively static spectrum at room temperature. The signals are moderately broad so that P−P coupling constants cannot be determined. In general, P_b when it is *trans* to a solvent (as in **2a** and **3a**), displays higher P−Pt coupling constants. The same happens to P_a in **3a** where it is *trans* to the labile oxygen ligand. It should be noted that the P_b−Pt coupling constants for **2b** and **2c** are significantly smaller than in the case of mononuclear diphosphane complexes of platinum[7e,10a,12] where they fall in the 3000−3400 Hz range, reflecting the moderate *trans* effect of the -OH (-OOH) ligand, as was suggested by Appleton and Bennett.[12] The data reported for **2a**, **2b** and **3a** are identical to those observed in situ by Bergamini et al.[9]

Conductivity data for **2a**, **3a**, and **2b**, **2c** taken in 10^{-3} M MeOH solutions are in the range generally accepted for 1:2 and 1:1 electrolytes, respectively.[13]

At variance with the NMR spectra mentioned above, the addition of an excess of OH$^-$ to **3a** results in the formation of a more static species (**4**) in which P−P coupling constants can be observed. The signal assigned to P_c is strongly shifted (about 20 ppm) to higher fields with respect to the parent compound, indicating that the O donor is probably no longer in the coordination sphere of the metal. This view seems to be confirmed by the observation that in the IR spectrum of the isolated species the P=O stretching frequency shifts from 1124 cm^{-1} in **3a** to 1178 cm^{-1} in **4**.[11] Additionally, the P_a−Pt and P_b−Pt coupling constants are practically identical (3477 and 3480 Hz respectively). The IR spectrum of **4** in dichloroethane solution also shows a weak band at 3599 cm^{-1}, typical of hydroxo complexes of Pt^{II}.[7d,7e,8a,10a] On this basis two possibilities are possible, both in agreement with the NMR spectroscopic data but neither corresponding to **3b**: the complex might be either a mononuclear bis-hydroxo complex or a dinuclear μ-hydroxo complex. The latter class of complexes is very stable and is relatively common in the literature in the case of Pt^{II}.[14] A possible formulation of **4** as a dinuclear μ-hydroxo complex might be supported by the values of the $^1J_{P,Pt}$ coupling constants that fall in the 3200−3600 Hz range typical for this class of complexes.[14] Addition of an excess (4:1) of HBF_4 in Et_2O (Scheme 4) allows us to observe the corresponding solvento complex **3a**, while the further addition of an excess of water leads to the formation of the aquo complex (see below and **3d** in Table 1). These observations would be consistent with **4** being both a bis-hydroxo complex (as formulated in Scheme 4) and also a dinuclear μ-hydroxo complex. Conclusive evidence for the nature of **4** as a mononuclear bis-hydroxo complex comes from IR spectroscopy, where the broad strong BF_4^- band is not observed, and from molar conductivity data. As shown in Table 1, the conductivity of a 10^{-3} M solution of **4** in MeOH is practically negligible, indicating that the complex is neutral.



Scheme 4

Acidity Measurements

A critical point for the purpose of the present work is the determination of the Lewis acid characteristics of the homologous complexes **2a** and **3a**. This was initially investigated by IR spectroscopy, following addition to solutions of **2a** and **3a** of CO, acetonitrile and 2,6-dimethylphenyl isocyanide, all of which can easily displace the CH_2Cl_2 from the coordination sphere of the metal. It is well-known that both the CO, CN and NC stretching frequencies of the above coordinated molecules are sensitive to the electron density of the metal[14] and hence might be a valuable tool for understanding the Lewis acid nature of the metal center. Experiments were carried out in 1,2-dichloroethane (DCE). In the case of CO, solutions of the complexes were saturated with the gas prior to recording the IR spectrum, while with acetonitrile or 2,6-dimethylphenyl isocyanide variable amounts of reactant could be added. This allowed us to distinguish between the free and coordinated ligand. Table 2 summarizes the results obtained. As can be seen, in all cases the coordinated ligand vibrates at higher frequencies with respect to the free ligand (CO 2143 cm^{-1}; MeCN 2255 cm^{-1}; 2,6-dimethylphenyl isocyanide 2121 cm^{-1}), which is a good indication that the complexes are indeed Lewis acids. However, the addition of CO or CH_3CN results in negligible differences between the complexes, only with 2,6-dimethylphenyl isocyanide could a 5 cm^{-1} shift to higher frequency be observed in the case of **3b**. It has to be pointed out that with the latter complex the addition of an excess of isocyanide determines a further shift of the band maximum to higher frequencies as a result of the formation of a shoulder at about 2225 cm^{-1}, indicative of the presence of a second ligand in the coordination sphere of the metal causing the likely displacement of the labile O donor. Since the above IR data did not provide a clear answer as to which of the complexes was more Lewis acidic (common chemical sense would indicate **3a**) it was decided to turn to a different technique.

Table 2. IR data of **2a** and **3a** after reaction with CO, acetonitrile or 2,6-dimethylphenyl isocyanide[a]

Complex	ν(CO) (cm^{-1})	ν(CN) (cm^{-1})	ν(NC) (cm^{-1})
2a	2150	2295, 2324	2204
2b	2152	2296, 2326	2209

[a] In DCE solution; resolution 0.5 cm^{-1}.

Recently, Zhong et al.[16] have faced a similar problem in the study of a homologous series of cationic bis(aryl)diimine-ligated methyl complexes of Pt^{II} where the substituents on the aromatic rings were varied systematically. The aim of these authors was to determine the electronic effects of the ligands on the metal center and possibly find a correlation with respect to their properties in the C−H activation of alkanes. The problem was addressed by studying the equilibrium shown in Scheme 5 by ^1H NMR spectroscopy, where water is used as a Lewis base. The extent of this equilibrium can be taken as a measure of the Lewis acidity of the metal center. Although this method was developed for a different class of homologous complexes of Pt^{II}, it seems reasonable to apply it, at least semi-quantitatively, also to the present case. The ratio between Pt-solv and $Pt-OH_2$ complexes can be easily determined by $^{31}P\{^1H\}$ NMR spectroscopy at −70 °C {NMR spectroscopic data for $[Pt(H_2O)(P\text{-}P\text{-}P)](BF_4)_2$ (**2d**) and $[Pt(H_2O)(P\text{-}P\text{-}P{=}O)](BF_4)_2$ (**3d**) are reported in Table 1}. By applying mass balance to Pt and H_2O one can easily solve a four-equation system, which allows us to calculate the equilibrium constant (Scheme 5). This was found to be 110 for **2a** and 1400 for **3a** indicating that the latter is considerably more Lewis acidic than the former. Indeed, as the NMR experiments were carried out in acetone the solvento species are not exactly **2a** and **3a**, as in Scheme 2, but more correctly the corresponding acetone derivatives. The limitations of these

$$\text{Pt-solv} \;+\; H_2O \;\underset{-70^{\circ}C}{\overset{K_a}{\rightleftharpoons}}\; \text{Pt-OH}_2 \;+\; \text{solv}$$

$$\text{solv} = [D_6]\text{acetone}$$

$$\left\{\begin{array}{l} [Pt(H_2O)]/[Pt(solv)] = n \\ [H_2O] + [Pt(H_2O)] = C^{\circ}_b \\ [Pt(H_2O)] + [Pt(solv)] = C^{\circ}_a \\ [solv] = 15.2\ \text{M} \end{array}\right. \qquad K_a = \frac{[Pt(H_2O)]\,[solv]}{[Pt(solv)]\,[H_2O]} \qquad K_a = \frac{n\,(n+1)\,[solv]}{n\,(C^{\circ}_b - C^{\circ}_a) + C^{\circ}_b}$$

Scheme 5

NMR experiments when used for the interpretation of the catalytic reactions that will be considered below are numerous: (i) the technique was developed for a different class of complexes, although the principle is quite general; (ii) the equilibrium constants are determined at −70 °C, while the catalysis is carried out at higher temperatures; (iii) the solvento complexes considered are actually Pt(acetone) instead of Pt(dichloromethane). Even with these limitations we believe that the overall meaning of the experiment is quite clear, i.e. **3a** is more acidic than **2a**.

Catalytic Activity

Having ascertained that **2a** and **3a** differ significantly in their Lewis acidity, their activity in the BV oxidation and in the epoxidation of olefins with hydrogen peroxide was compared. 2-Methylcyclohexanone and cyclooctene were chosen as prototype substrates and a substrate/H_2O_2/catalyst ratio equal to 100:100:1 was chosen. Reactions were carried out in DCE.

In both processes **2a** was found to be inactive at 20 °C, whereas at 70 °C a moderate activity was observed. In Figure 3 a comparison between **2a**, **2b** and **2c** in the epoxidation of cyclooctene is reported. As can be seen the homologous complexes display a very similar catalytic behavior: their maximum activity (expressed as zero-order rate constant) is essentially the same: a very short induction time is observed with **2b** and **2c**, indicating a relatively quick conversion into the catalytically active species, and only the amount of epoxide formed seems to differ markedly. The reactions are in any case very selective as the epoxide was the only product observed, with no evidence for glycol or further oxidation products. It has to be pointed out that under these experimental conditions a certain degree of irreproducibility was observed (approximately ±10% of the maximum activity and ±25% of the maximum conversion) as the result of a deactivation process that will be considered more thoroughly below. Similar results (Table 3) were observed for the oxidation of 2-methylcyclohexanone (2-heptalactone was the only oxidation product) both in terms of activity and conversion. Like in epoxidation, the reaction must be carried out at 70 °C, and deactivation of the catalyst is evident.

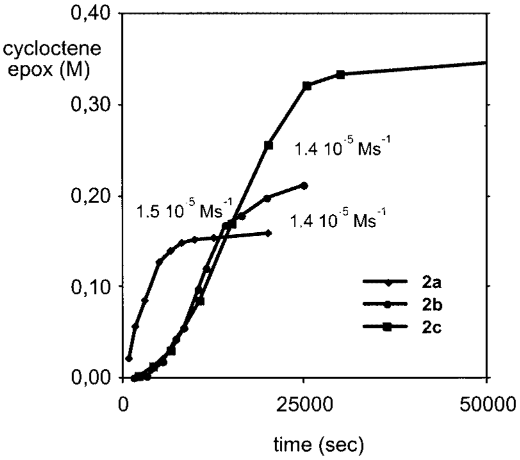


Figure 3. Reaction profiles for the epoxidation of cyclooctene with hydrogen peroxide catalyzed by homologous Pt^{II} complexes: $[(triphos)Pt(solv)]^{2+}$ (**2a**), diamonds; $[(triphos)Pt(OH)]^{+}$ (**2b**), circles; $[(triphos)Pt(OOH)]^{+}$ (**2c**), squares; numbers on the curves indicate the rate expressed as a zero-order rate constant; reaction conditions: catalyst 0.017 mmol; substrate 1.7 mmol; 35% H_2O_2 1.7 mmol; DCE 3 ml; N_2 1 atm.

The activity of **3a** is significantly different, although the reaction profile has the same shape as that shown for **2a** in Figure 3. As can be seen from Table 3, this catalyst is already active at 20 °C especially in the oxidation of 2-methylcyclohexanone, while the activity is very poor in the epoxidation of cyclooctene. At 70 °C it is approximately as active as **2a** in the epoxidation reaction and more active in the BV oxidation (Table 3), but seems to deactivate more quickly.

The reactivity shown by **2a** with respect to cyclooctene is observed also in the epoxidation of other olefins (Table 4). Even in this case a similar activity between **2a** and **2b** is observed. However, by the end of the epoxidation reactions, some epoxide hydrolysis occurs with formation of the corresponding glycol, probably promoted by the acid catalyst and due to the lower stability of these epoxides with respect to cyclooctene epoxide. Internal olefins are epoxidized more efficiently than terminal olefins (1-octene) and this contrasts with the behavior observed for other cationic Pt^{II} complexes {e.g. $[Pt(CF_3)(P\text{-}P)(solv)]^{+}$}, which are specific for the epoxidation of terminal olefins.[7] The α,β-unsatu-

Table 3. Catalytic activity of complexes **2** and **3** in the epoxidation of cyclooctene and the Baeyer−Villiger oxidation of methylcyclohexanone[a]

Catalyst	Substrate	Temp. (°C)	$10^5 \times$ max. rate (Ms^{-1})	Max. conv. (%)
2a	cyclooctene	70	1.5	20
2b		70	1.4	40
2c		70	1.4	25
2a	2-methylcyclohexanone	70	1.5	11
2b		70	1.6	13
3a	cyclooctene	20	0.05	2
3a		70	1.2	11
3a	2-methylcyclohexanone	20	2.0	40
3a		70	7.0	25

[a] Experimental conditions: catalyst 0.017 mmol; substrate 1.7 mmol; 35% H_2O_2 1.7 mmol; DCE 3 ml; N_2 1 atm.

Table 4. Catalytic activity of complexes **2** and **3** in the oxidation of other substrates[a]

Catalyst	Substrate	Temp. (°C)	$10^5 \times$ max. rate (Ms^{-1})	Max. conv. (%)
2a	cyclohexene	70	1.0	20
2b		70	1.3	20
2a	1-octene	70	0.3	10
2b		70	0.4	15
2b	4-methyl-2-pentene	70	1.0	10
2a	2-cyclohexen-1-one	70	2.0	15
2b		70	1.5	12
3a	cyclopentanone	20	0.5	5
3a		70	4.5	15
3a	cyclohexanone	20	0.5	5
3a		70	6.2	11
3a	3,3-dimethyl-2-butanone	20	0.2	5
3a		70	5	6
3a	2-allylcyclohexanone	20	0.8	11

[a] Experimental conditions: catalyst 0.017 mmol; substrate 1.7 mmol; 35% H_2O_2 1.7 mmol; DCE 3 ml; N_2 1 atm.

rated ketone 2-cyclohexen-1-one is selectively epoxidized in agrement with previous findings with Pt^{II} complexes.[17]

Complex **3a** is less effective than **2a** in the epoxidation of olefins, but far more efficient in the BV oxidation of ketones (Table 4). Notably, the oxidation of open-chain ketones is also possible, a unique ability among the BV oxidation catalysts known in the literature, that is shared only with [Pt(μ-OH)(P-P)]$_2^{2+}$ complexes.[8a]

Competition Reactions and the Possible Role of Lewis Acidity

The overall picture that emerges from an analysis of the catalytic activity of **2a** and **3a** is that the latter is far more active in the BV oxidation, whereas **2a** is probably a better epoxidation catalyst, although in this case the differences are less evident. This seems to confirm the considerations made in the Introduction, where the reactions were compared mechanistically and indicate that the BV oxidation is more Lewis acid demanding as far as the catalyst properties are concerned.

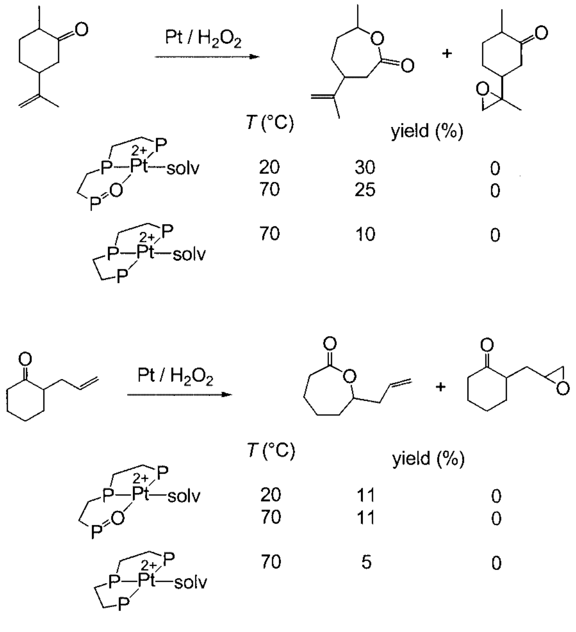
To clarify this point and possibly answer the main question raised — "can we exploit the Lewis acidity of the catalyst to control the selectivity of the reaction?" — some competition experiments and reactions on bifunctional substrates were carried out.

Table 5. Competition experiments in the oxidation of a mixture of cyclooctene and 2-methylcyclohexanone[a]

Catalyst	Product	Temp. (°C)	$10^5 \times$ max. rate (Ms^{-1})	Max. conv. (%)
2a	cyclooctene epoxide	20	–	–
	2-heptalactone			
2a	cyclooctene epoxide	70	0.8	20
	2-heptalactone		1.5	20
3a	cyclooctene epoxide	20	0.05	2
	2-heptalactone		1.5	30
3a	cyclooctene epoxide	70	1.0	10
	2-heptalactone		7.0	25

[a] Experimental conditions: catalyst 0.017 mmol; substrates 0.85 +0.85 mmol; 35% H_2O_2 1.7 mmol; DCE 3 ml; N_2 1 atm.

Initially, **2a** and **3a** were tested in the oxidation of a 1:1 mixture of cyclooctene and 2-methylcyclohexanone; the results are collected in Table 5. As can be seen, in the case of **3a** the reactivity observed seems to be simply the addition of the results observed in the reactions with the individual substrates. Conversely, the behavior of **2a** is somehow surprising and in contrast to the results observed with the individual substrates. In fact, some preference for the BV reaction seems to be evident at 70 °C. This trend becomes quite clear in the oxidation of unsaturated ketones. Scheme 6 summarizes the results observed with dihydrocarvone and 2-allylcyclohexanone. In both cases the exclusive product is the lactone, independently of the catalyst used. This might



Scheme 6

be partly due to the moderate activity of **2a** observed with terminal olefins. However, we believe that other factors might cooperate to explain the results of this competitive experiment. For example, if the complex is sufficiently Lewis acidic, even a metal center like Pt^{II} becomes more oxophilic and, in the presence of a molecule containing a C=C double bond and a C=O double bond, it becomes more prone to interact with a simple donor like oxygen and more reluctant to undergo back-bonding to the olefin. In other words, the discrimination may arise both from the intrinsic catalytic activity and from the coordinating ability of the metal, both properties being determined by the Lewis acidity of the central metal atom.

Deactivation of the Catalyst

As was mentioned above, a deactivation process is evident when reactions are carried out at 70 °C. This limits significantly the reproducibility of the catalytic experiments and seems to be independent both of the catalyst and of the oxidation reaction studied. When the metal species are isolated at the end of a catalytic reaction they can be recognized either as $[PtCl(P\text{-}P\text{-}P)](BF_4)$ (from **2a**) or, at least partly, as $[PtCl_2(P\text{-}P\text{-}P{=}O)]$ (from **3a**). In the case of **3a** the situation is more complex as some free, fully oxidized phosphane is also observed in the $^{31}P\{^1H\}$ NMR spectrum of the isolated material and therefore some phosphorus-free Pt species must also be formed. The most likely source of chloride is the solvent and it was demonstrated that the same chloro derivatives could be obtained by simply boiling the starting complexes in DCE, $CHCl_3$ or CH_2Cl_2. In the case of **3a** the observation that only the chloro complex is formed is a good indication that the other decomposed species are most likely generated in the catalytic reactions by hydrogen peroxide, which is responsible for the full oxidation of the phosphane. These observations imply that during the catalytic processes there is a parallel reaction between the catalyst and the solvent that leads to the complete conversion into catalytically inactive chloro derivatives. The inactivity of the chloro complexes was demonstrated by blank catalytic tests. The moderate stability of boiling DCE or chloroform and their tendency to form traces of HCl, which would explain our results, are quite well-known, although we have used DCE as solvent in Pt^{II}-catalyzed oxidations with hydrogen peroxide for the past 20 years and never observed such problems. The case of dichloromethane is less straightforward as this solvent boils at 42 °C and is recognized to be quite stable. We may speculate that a possible explanation for the above behavior may rely on a direct attack on the C−Cl bond by the strongly Lewis acidic Pt^{2+} metal centers.

Conclusions

In this work we have synthesized two classes of homologous cationic complexes of Pt^{II} containing tridentate ligands and bearing only one potentially vacant coordination site: one class contains three phosphorus donors while the other contains two phosphorus and one oxygen donors. Spectroscopic characterization indicates that the solvento derivative of the latter class of complexes (**3a**) is a stronger Lewis acid than its counterpart **2a**, although both are rather strong. Their use as catalysts in the BV oxidation of ketones and in the epoxidation of olefins has shown that the former reaction is quite Lewis-acid demanding with respect to the properties of the catalyst. This has allowed the complete control of the parallel oxidation processes in the oxidation of bifunctional substrates such as dihydrocarvone or 2-allylcyclohexanone, where the exclusive formation of the BV oxidation product was observed. The views presented in this work may probably be generalized and could be of help in the design of a new generation of selective, more active catalysts.

Experimental Section

Apparatus: IR spectra were recorded on a Nicolet 750 spectrophotometer either in nujol mulls using KBr plates or in CH_2Cl_2 solution using CaF_2 windows. $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded on a Bruker AC200 spectrometer, operating in FT mode, using as external reference 85% H_3PO_4 and TMS, respectively. Negative chemical shifts are upfield from the reference. GLC measurements were taken on a Hewlett−Packard 5890A gas chromatograph equipped with a FID detector (gas carrier He). Identification of products was made by GLC by comparison with authentic samples. Molar conductivity measurements were made on 10^{-3} M solutions in MeOH with a CDM 83 Radiometer Copenhagen instrument, equipped with a CDC 334 immersion cell.

Materials: Solvents were dried and purified according to standard methods. Substrates were purified by passing through neutral alumina and stored in the dark at low temperature. Hydrogen peroxide (35% Fluka), triphos (Aldrich), HBF_4 (54% in diethyl ether; Aldrich) are commercial products and were used without purification.

The following compounds were prepared according to literature procedures: $[PtCl_2(COD)]$,[18] $[PtMe_2(COD)]$,[19] $[PtMe_2(triphos)]$,[9] $[PtMe_2(triphosPO)]$.[9] The preparation of new complexes was performed under dry N_2 by using Schlenk techniques, although all of them were found to be air stable once isolated.

Preparation of Complexes: Some of the complexes reported here were previously observed by in situ NMR spectroscopy, but never isolated and fully characterised.

$[(triphos)Pt(CH_2Cl_2)](BF_4)_2$ (2a): Triphos (0.3 g, 0.56 mmol) was dissolved in dry N_2-saturated CH_2Cl_2 (5 mL) and a solution of $[PtMe_2(COD)]$ (0.19 g, 0.57 mmol) in dry N_2-saturated CH_2Cl_2 (5 mL) was added to this solution. The mixture was stirred for 2 hours under N_2 and then 200 μL of 54% HBF_4 was slowly added to the solution. This was stirred for 20 minutes, during which time rapid CH_4 evolution was observed. Water was added to the solution to eliminate traces of acid, the two phases were separated and the organic one was dried with anhydrous Na_2CO_3. The solvents were slowly evaporated from the solution in vacuo to give a white-yellow solid. This was recrystallized from CH_2Cl_2/Et_2O (0.46 g, yield 82%). $C_{35}H_{35}B_2Cl_2F_8P_3Pt$: calcd. C 42.54, H 3.57; found C 42.27, H 3.39.

$[(triphosPO)Pt(CH_2Cl_2)](BF_4)_2$ (3a): Triphos (0.80 g, 1.50 mmol) was dissolved in dry N_2-saturated CH_2Cl_2 (10 mL) and a solution of [PtMe$_2$(COD)] (0.48 g, 1.44 mmol) in dry N$_2$-saturated CH$_2$Cl$_2$ (5 mL) was added to this solution. The mixture was stirred for 2 hours under N$_2$ and then a 3% solution of H$_2$O$_2$ (5 mL, 2 mmol) was added; after vigorously stirring for one hour the mixture was filtered. The two phases were separated and the organic phase was washed with water and dried with anhydrous Na$_2$CO$_3$, filtered and reduced to a small volume. 500 μL of 54% HBF$_4$ was then slowly added to the solution. This was stirred for 20 minutes during which rapid time CH$_4$ evolution was observed. Water was added to the solution to eliminate traces of acid, the two phases were separated and the organic one was dried with anhydrous Na$_2$CO$_3$. The solvents were slowly evaporated from the solution in vacuo to obtain a white-yellow solid. This was recrystallized from CH$_2$Cl$_2$/Et$_2$O (1.15 g, yield 80%). C$_{35}$H$_{35}$B$_2$Cl$_2$F$_8$OP$_3$Pt: calcd. C 41.86, H 3.51; found C 41.57, H 3.42.

[(triphos)Pt(OH)]BF$_4$ (2b): Compound **2a** (0.50 g, 0.51 mmol) was suspended in CDCl$_3$ (15 mL). A solution of NaOH (0.1 M) was added (15 mL) and the mixture was vigorously stirred for 30 minutes. The organic phase was separated, washed with water and dried with anhydrous Na$_2$CO$_3$, filtered and slowly evaporated in vacuo to obtained a white solid. This was recrystallized from CH$_2$Cl$_2$/Et$_2$O (0.37 g, yield 87%). C$_{34}$H$_{34}$BF$_4$OP$_3$Pt: calcd. C 49.00, H 4.11; found C 49.17, H 4.03.

[(triphos)Pt(OOH)]BF$_4$ (2c): Compound **2b** (0.62 g, 0.74 mmol) was suspended in CDCl$_3$ (5 mL). A 3.5% solution of H$_2$O$_2$ (1.5 mL, 1.5 mmol) was added and the mixture was vigorously stirred for 30 minutes. The white precipitate obtained was filtered off, washed with Et$_2$O and recrystallized from CH$_2$Cl$_2$/Et$_2$O (0.35 g, yield 55%). C$_{34}$H$_{34}$BF$_4$O$_2$P$_3$Pt: calcd. C 48.07, H 4.03; found C 48.15, H 4.11.

[(triphosPO)Pt(OH)$_2$] (4): Compound **3a** (0.30 g, 0.30 mmol) was dissolved in CH$_2$Cl$_2$ (4 mL) under N$_2$. A 4 M solution of NaOH (3 mL) in water was added and the mixture was stirred for one hour. The organic phase was separated, washed with water and dried with anhydrous Na$_2$CO$_3$. The solvents were slowly evaporated from the solution in vacuo to obtain a white solid. This was redissolved in warm acetone and kept at −15 °C for 24 hours. The white solid obtained was washed with diethyl ether and dried (0.070 g, yield 30%). C$_{34}$H$_{35}$O$_3$P$_3$Pt: calcd. C 52.38, H 4.52; found C 52.12, H 4.33.

Determination of the Acidity of the Complexes. NMR Method: In these experiments **1a** and **2a** were generated in an NMR tube from a known amount of precursor. The use of the isolated complexes **2a** and **3a** was found to be less reproducible as they contain traces of water. Typically 4.5×10^{-5} mol of [PtMe$_2$(triphos)] or [PtMe$_2$(triphosPO)] were dissolved in dry [D$_6$]acetone (0.7 mL). A stoichiometric quantity of 54% HBF$_4$ (12 μL, 0.9×10^{-4} mol) was added and, after evolution of methane, the ^{31}P{^{1}H} NMR spectrum was registered at −70 °C. Then, increasing volumes of H$_2$O (1, 1.5, 2, 3 μL) were introduced into the tube, and the ^{31}P{^{1}H} NMR spectrum at −70 °C was registered each time. A new species formed (**2d** or **3d**). By comparing the intensity of the signals at δ = 56 (**3a**, at −70 °C the signal shifts to lower fields) and 55 ppm (**3d**) and at δ = 51 (**2a**) and 48.5 ppm (**2d**) the equilibrium constant could be calculated as shown in Scheme 5.

Catalytic Reactions: These were carried out in a 10 mL round-bottomed flask equipped with a stopcock for vacuum/N$_2$ operations and a sidearm fitted with a screw-capped silicone septum to allow sampling. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer. Reactions at 70 °C were carried out using an oil bath connected with a thermostat. The concentration of the commercial 35% H$_2$O$_2$ solution was checked iodometrically prior to use.

The following general procedure was followed: the required amount of catalyst was placed in solid form (0.017 mmol) in the reactor, which was evacuated and filled with N$_2$. Purified, N$_2$-saturated olefin/ketone was added under N$_2$ flow, followed by the required amount of 1,2-dichloroethane (3 mL). After thermostating at the required temperature for a few minutes, the H$_2$O$_2$ solution in the appropriate amount was injected through the septum and the time was started.

All reactions were monitored by GLC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Separation of the products was performed on a 25 m HP-5 capillary column using a flame ionization detector. The maximum rate was expressed as a zero-order rate constant from analysis of conversion vs. time curves.

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[1] *Lewis Acids in Organic Synthesis* (Ed.: H. Yamamoto), Wiley-VCH: Weinheim, **2000**.

[2] [2a] K. Hori, J. Ito, T. Ohta, I. Furukawa, *Tetrahedron* **1998**, *54*, 12737. [2b] D. Ferraris, B. Young, T. Dudding, T. Lectka, *J. Am. Chem. Soc.* **1998**, *120*, 4548. [2c] A. K. Ghosh, H. Matsuda, *Org. Lett.* **1999**, *1*, 2157. [2d] S. Oi, E. Terada, K. Ohuchi, T. Kato, Y. Tachibana, I. Inoue, *J. Org. Chem.* **1999**, *64*, 8660. [2e] K. Hori, H. Kodama, T. Ohta, I. Furukawa, *J. Org. Chem.* **1999**, *64*, 5017. [2f] K. Pignat, J. Vallotto, F. Pinna, G. Strukul, *Organometallics* **2000**, *19*, 5160. [2g] J. Hao, M. Hatano, K. Mikami, *Org. Lett.* **2000**, *2*, 4059. [2h] T. Hattori, Y. Suzuki, O. Uesugi, S. Oi, S. Miyana, *Chem. Commun.* **2000**, 73. [2i] A. Fürstner, D. Voigtländer, W. Schrader, D. Giebel, M. Reetz, *Org. Lett.* **2001**, *3*, 417. [2j] N. M. Brunkan, P. S. White, M. R. Gagné, *Organometallics* **2002**, *21*, 1565. [2k] N. M. Brunkan, M. R. Gagné, *Organometallics* **2002**, *21*, 1576.

[3] [3a] M. Del Todesco Frisone, R. Giovanetti, F. Pinna, G. Strukul, *Stud. Surf. Sci. & Catal.* **1991**, *66*, 405. [3b] M. Del Todesco Frisone, F. Pinna, G. Strukul, *Organometallics* **1993**, *12*, 148.

[4] C. Bolm, O. Beckmann, C. Palazzi, *Can. J. Chem.* **2001**, *79*, 1593.

[5] C. Bolm, O. Beckmann, A. Cosp, C. Palazzi, *Synlett* **2001**, 1461.

[6] A. Corma, L. T. Nemeth, M. Renz, S. Valencia, *Nature* **2001**, *412*, 423.

[7] [7a] G. Strukul, R. A. Michelin, *J. Chem. Soc., Chem. Commun.* **1984**, 1538. [7b] G. Strukul, R. A. Michelin, *J. Am. Chem. Soc.* **1985**, *107*, 7563. [7c] R. Sinigalia, R. A. Michelin, F. Pinna, G. Strukul, *Organometallics* **1987**, *6*, 728. [7d] A. Zanardo, F. Pinna, R. A. Michelin, G. Strukul, *Inorg. Chem.* **1988**, *27*, 1966. [7e] A. Zanardo, F. Pinna, R. A. Michelin, G. Strukul, *Inorg. Chem.* **1989**, *28*, 1648.

[8] [8a] R. Gavagnin, M. Cataldo, F. Pinna, G. Strukul, *Organometallics* **1998**, *17*, 661. [8b] C. Paneghetti, R. Gavagnin, F. Pinna, G. Strukul, *Organometallics* **1999**, *18*, 5057.

[9] [9a] G. Annibale, P. Bergamini, V. Bertolasi, E. Bosco, M. Cattabriga, R. Rossi, *Inorg. Chim. Acta* **2002**, *333*, 116. [9b] G. Annibale, P. Bergamini, M. Cattabriga, *Inorg. Chim. Acta* **2001**, *316*, 25.

[10] [10a] G. Strukul, R. Ros, R. A. Michelin, *Inorg. Chem.* **1982**, *21*, 495. [10b] M. T. Atlay, M. Preece, G. Strukul, B. R. James, *J. Chem. Soc., Chem. Commun.* **1982**, 406.

[11] [11a] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd edition, Wiley, New York, **1970**, p. 115. [11b] R. M. Silverstein, F. X. Webster, *Spectrometric Identification of Organic Compounds*, 6th ed., Wiley, New York, **1998**, p. 109.

[12] T. G. Appleton, M. A. Bennett, *Inorg. Chem.* **1978**, *17*, 738.

[13] W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81.

[14] [14a] G. W. Bushnell, K. R. Dixon, R. G. Hunter, J. J. McFarland, *Can. J. Chem.* **1972**, *50*, 3694. [14b] B. Longato, B. Corain,

G. M. Bonora, G. Pilloni, *Inorg. Chim. Acta* **1987**, *137*, 75. [14c] A. L. Bandini, G. Banditelli, F. Demartin, M. Manassero, G. Minghetti, *Gazz. Chim. Ital.* **1993**, *23*, 417. [14d] J. J. Li, P. R. Sharp, *Inorg. Chem.* **1996**, *35*, 604.

[15] J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Transition Metal Chemistry*, University Science Books, Mill Valley, **1987**, p. 110.

[16] H. A. Zhong, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2002**, *124*, 1378.

[17] C. Baccin, A. Gusso, F. Pinna, G. Strukul, *Organometallics* **1995**, *14*, 1161.

[18] J. X. McDermott, J. F. White, G. M. Whitesides, *J. Am. Chem. Soc.* **1976**, *98*, 6521.

[19] R. Bassan, K. H. Bryars, L. Judd, A. W. G. Platt, P. G. Pringle, *Inorg. Chim. Acta* **1986**, *121*, L41.

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