

# Synthesis, characterization and Baeyer–Villiger oxidation of ketones by the bis-cationic platinum(II) complex $[\text{Pt}(\mu\text{-OH})(\text{Pom-Pom})]_2[\text{BF}_4]_2$ [Pom-Pom = $(\text{OMe})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OMe})_2$ ]

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Received 26 May 2006; accepted 2 August 2006

Available online 8 September 2006

## Abstract

The synthesis and spectroscopic characterization of the new hydroxo-bridged platinum(II) complex  $[\text{Pt}(\mu\text{-OH})(\text{Pom-Pom})]_2[\text{BF}_4]_2$  (**3**) containing the electron-poor P–P ligand 1,2-bis(dimethoxyphosphino)ethane,  $(\text{OMe})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OMe})_2$  (Pom-Pom), is reported. This compound has been used in the Baeyer–Villiger oxidation of a series of cyclic ketones using 35% hydrogen peroxide as oxidant. The reactions were performed at 25 °C and at 70 °C in chlorinated solvent/H<sub>2</sub>O biphasic system. The catalytic activity and the Lewis acidity of the complex (**3**) has been compared to other Pt(II) complexes previously investigated.

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**Keywords:** Catalytic oxidation; Hydrogen peroxide; Electron-poor diphosphine; Platinum complex; Baeyer–Villiger

## 1. Introduction

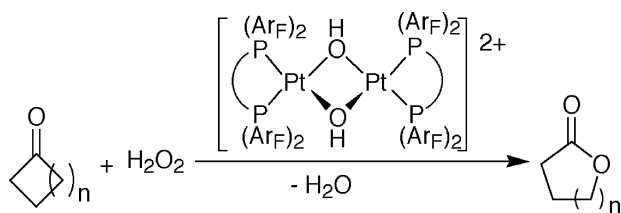
Catalytic oxidation reactions are among the most useful organic transformation [1], and analogously to other reactions, key goals are productivity, selectivity and broad substrate scope of the catalyst employed. Moreover, in the recent years oxidation reactions are experiencing the shift from hazardous to more environmentally friendly terminal oxidants. Among all, hydrogen peroxide is emerging as a promising choice because of its easy handling, relatively low cost and production of only water as by-product [2]. The homogeneous oxidation of organic substrates by hydrogen peroxide can be performed with several transition metal complexes [3], in particular over the past two decades some of us focused their attention to the employment of cationic Pd(II) and Pt(II) complexes due to the peculiar Lewis acid character of such complexes that allows both nucleophilic and electrophilic oxidation as a direct consequence of

the ligands coordinated to the metal [4]. The hydroxo-bridged dimeric cationic compounds of the type  $\{[\text{Pt}(\mu\text{-OH})(\text{P-P})]_2\}^{2+}$  (P–P = chelating diphosphine) have been found [4,5] to promote the Baeyer–Villiger (BV) oxidation of cyclic and acyclic ketones in the presence of H<sub>2</sub>O<sub>2</sub> to give esters and lactones, respectively. In a recent work [6] we have systematically changed the electrophilicity of a homologous series of dimeric cationic Pt(II) centres (and hence their Lewis acidity) by acting on the degree of fluorine substitution of a series of tetraaryl diphosphine ligands that were employed for the synthesis of  $\mu$ -hydroxo complexes of the type  $[\text{Pt}(\mu\text{-OH})(\text{P-P})]_2[\text{BF}_4]_2$ , where  $\text{P-P} = (\text{C}_6\text{H}_5\text{-}_n\text{F}_n)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5\text{-}_n\text{F}_n)_2$  ( $n = 2\text{--}5$ ) (Scheme 1). As a result, we have observed a systematic increase in activity in the catalytic Baeyer–Villiger oxidation of ketones with hydrogen peroxide when the Lewis acidity of the metal center increases.

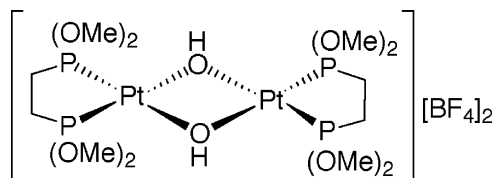
Such behaviour, in agreement with a general observation common to oxidation reactions and recently reviewed [7], prompted us to explore the use of new Lewis acidic Pt(II) complexes with the aim to develop more active and selective catalysts. In this work we report the synthesis and characterization of the complex  $[\text{Pt}(\mu\text{-OH})(\text{Pom-Pom})]_2[\text{BF}_4]_2$  containing the

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Scheme 1. Baeyer–Villiger oxidation of cyclic ketones with  $\text{H}_2\text{O}_2$  catalyzed by electron-poor fluorinated dimeric Pt(II) complexes.



Scheme 2. Dimeric structure of the electron-poor complex  $[\text{Pt}(\mu\text{-OH})(\text{Pom-Pom})]_2[\text{BF}_4]_2$  (**3**).

electron-poor diphosphine 1,2-bis(dimethoxyphosphino)ethane,  $(\text{OMe})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OMe})_2$  (Pom-Pom) (Scheme 2). The catalytic activity of the above reported derivative was tested in the Baeyer–Villiger oxidation of cyclic and acyclic ketones using hydrogen peroxide as oxidant and its activity and Lewis acidity discussed.

## 2. Experimental

### 2.1. General procedures and materials

All work was carried out with the exclusion of atmospheric oxygen under a dinitrogen atmosphere using standard Schlenk techniques. 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),  $\text{HBF}_4$  54% in diethyl ether (Aldrich) and all the ketone substrates were commercial products and used without purification. IR spectra were taken on a FT-IR AVATAR 320 of the Nicolet Instrument Corporation spectrophotometer in  $\text{CH}_2\text{Cl}_2$  solution using  $\text{CaF}_2$  windows; the wavenumbers are given in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR and  $^{31}\text{P}\{^1\text{H}\}$  spectra were run at 298 K, unless otherwise stated, on a Bruker AC200 spectrometer operating at 200.13 and 81.015 MHz, respectively;  $\delta$  values in ppm are relative to  $\text{SiMe}_4$  and 85%  $\text{H}_3\text{PO}_4$ . GLC measurement were taken on a Hewlett-Packard 5890A gas chromatograph equipped with a FID detector (gas carrier He). Identification of products was made with GLC by comparison with authentic samples. The elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of the Università di Padova. The compounds Pom-Pom [8],  $[\text{PtCl}_2(\text{COD})]$  [9] (COD 1,5-cyclooctadiene) and  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  [10] were prepared according to published procedures.

### 2.2. Kinetic studies

These were carried out in a 10 mL round-bottomed flask equipped with a stopcock for vacuum/ $\text{N}_2$  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. Constant temperature ( $20 \pm 0.1$  or  $70 \pm 0.1$  °C) was maintained by water circulation through an external jacket connected with a thermostat. The concentration of the commercial 35%  $\text{H}_2\text{O}_2$  solution was checked iodometrically prior to use. The following general procedure was used: the solid catalyst (0.017 mmol) was placed in the reactor, which was evacuated and filled with  $\text{N}_2$  and then 1,2-dichloroethane (3 mL) was added under  $\text{N}_2$  flow, followed by purified  $\text{N}_2$ -saturated substrate (1.7 mmol). After thermostating at the required temperature for a few minutes, the  $\text{H}_2\text{O}_2$  solution in the appropriate amount (1.7 mmol) was injected through the septum and time was started. All reactions were monitored with GLC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Prior quenching of the samples by adding an excess of LiCl was found to be unnecessary. Initial rate data were determined from conversion vs time plots. Separation of the products was performed on a 25 m HP-5 capillary column using a flame ionization detector.

### 2.3. Synthesis of $[\text{PtCl}_2(\text{Pom-Pom})]$ (**1**)

$[\text{PtCl}_2(\text{COD})]$  (2.03 g, 5.42 mmol) was suspended in chloroform (100 mL) at room temperature and subsequently treated with Pom-Pom (1.16 mL, 5.42 mmol) under nitrogen. The reaction mixture was stirred until complete dissolution of the solid. The solution was then concentrated to 10 mL under reduced pressure and diethyl ether was added. The white solid precipitate was filtered off, washed with diethyl ether and dried under vacuum. Yield 1.79 g, 69%. Anal. calc. for  $\text{C}_6\text{H}_{16}\text{Cl}_2\text{O}_4\text{P}_2\text{Pt}$ : C, 15.01; H, 3.36. Found: C, 15.03; H, 3.11%. IR ( $\bar{\nu}$ , PE): 311, 290 (s, Pt-Cl).  $^1\text{H}$  NMR ( $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): 4.04 (d,  $\text{OCH}_3$ ,  $^3J_{\text{P-H}} = 13.0$  Hz); 1.84 (m,  $\text{PCH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): 136.4 (s,  $^1J_{\text{Pt-P}} = 4645$  Hz).

### 2.4. Synthesis of $[\text{PdCl}_2(\text{Pom-Pom})]$ (**2**)

A suspension of  $[\text{PdCl}_2(\text{MeCN})_2]$  (0.31 g, 1.19 mmol) in chloroform (50 mL) at room temperature was treated with Pom-Pom (0.27 mL, 1.25 mmol) under nitrogen. The reaction mixture was stirred overnight until complete dissolution of the solid to afford a yellow solution, which was concentrated to ca. 5 mL under reduced pressure and diethyl ether was added. The white solid precipitate was filtered off, washed with diethyl ether and dried under vacuum. Yield 0.46 g, 98%. Anal. calc. for  $\text{C}_6\text{H}_{16}\text{Cl}_2\text{O}_4\text{P}_2\text{Pd}$ : C, 18.41; H, 4.42. Found: C, 18.70; H, 3.81%. IR ( $\bar{\nu}$ ,  $\text{cm}^{-1}$ , PE): 317, 289 (s, Pd-Cl); 1060 (s,  $\text{BF}_4$ ).  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ): 4.10 (d,  $\text{OCH}_3$ ,  $^3J_{\text{P-H}} = 13.0$  Hz); 1.92 (m,  $\text{PCH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ): 165.9 (s).

### 2.5. Synthesis of $[\text{Pt}(\mu\text{-OH})(\text{Pom-Pom})]_2[\text{BF}_4]_2$ (**3**)

To a suspension of **1** (0.30 g, 0.62 mmol) in methanol (15 mL) at room temperature was added 1.46 mL (1.25 mmol) of a 0.9 M acetone solution of  $\text{AgBF}_4$ . The reaction mixture was stirred under nitrogen for 3 h and then the solid  $\text{AgCl}$  formed was filtered off. After concentration, the solution was

treated with diethyl ether to give a white solid, which was filtered off and dried under vacuum. Yield 0.30 g, 94.0%. Anal. calc. for  $C_{12}H_{34}B_2F_4O_{10}P_4Pt_2$ : C, 14.05; H, 3.34. Found: C, 14.00; H, 3.11%. IR ( $\bar{\nu}$ ,  $cm^{-1}$ , Nujol): 3500 (s, OH); 1060 (s,  $BF_4$ ).  $^1H$  NMR ( $\delta$ ,  $CD_2Cl_2$ ): 4.14 (s, OH); 3.90 (d,  $OCH_3$ ,  $^3J_{P-H} = 12.5$  Hz); 1.92 (m,  $CH_2$ ).  $^{31}P\{^1H\}$  NMR ( $\delta$ ,  $CD_2Cl_2$ ): 123.5 (s,  $^1J_{Pt-P} = 4762$  Hz).

## 2.6. Synthesis of $[PtCl(CN-2,6-(CH_3)_2C_6H_3)(Pom-Pom)][BF_4]$ (4)

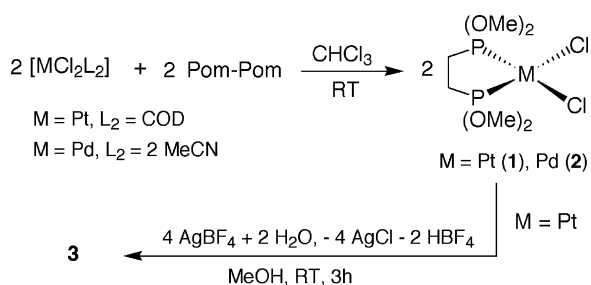
To a suspension of **1** (0.48 g, 1.00 mmol) in dichloromethane (70 mL) was added, under stirring, 1.25 mL (1.07 mmol) of an acetone solution of  $AgBF_4$ . The reaction mixture was stirred under nitrogen for 30 min and then the solid  $AgCl$  formed was filtered off. To the solution was added 2,6-dimethylphenyl isocyanide (0.11 g, 0.83 mmol) and stirred for 5 min. It was then concentrated under vacuum and diethyl ether was added. The yellowish solid precipitated was filtered off, washed with diethyl ether and dried under vacuum. Yield 0.49 g, 74%. Anal. calc. for  $C_{15}H_{25}BClF_4NO_4P_2Pt$ : C, 27.19; H, 3.80; N, 2.11%. Found: C, 27.81; H, 3.60; N, 2.48%. IR ( $\bar{\nu}$ ,  $cm^{-1}$ ,  $CH_2Cl_2$ ): 2219 (s,  $C\equiv N$ ). IR ( $\bar{\nu}$ ,  $cm^{-1}$ , PE): 319 (s, Pt-Cl).  $^1H$  NMR ( $\delta$ ,  $CDCl_3$ ): 7.4–7.0 (m, Ph); 3.98, 4.08 (d,  $OCH_3$ ,  $^3J_{P-H} = 12.7$  Hz); 2.45 (m,  $PCH_2$ ); 2.50 (s,  $CH_3$ ).  $^{31}P\{^1H\}$  NMR ( $\delta$ ,  $CDCl_3$ ): 138.1 (d,  $P_{Cl-trans}$ ,  $^1J_{Pt-P} = 4253$  Hz,  $^2J_{P-P} = 13.4$  Hz); 144.4 (d,  $P_{C-trans}$ ,  $^1J_{Pt-P} = 3830$  Hz,  $^2J_{P-P} = 13.4$  Hz).

## 3. Results and discussion

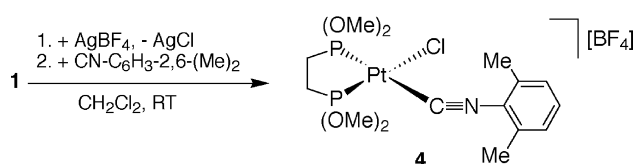
### 3.1. Synthesis of the complexes

The dichloro complexes  $[MCl_2(Pom-Pom)]$  ( $M = Pt$  (**1**);  $Pd$  (**2**)) were readily prepared by ligand exchange from the precursors  $[MCl_2L_2]$  as illustrated in Scheme 3. The Pt(II) bridging hydroxo dimer  $[Pt(\mu-OH)(Pom-Pom)]_2[BF_4]_2$  (**3**) was prepared in high yield according to a general method reported in the literature [11] and previously experienced in the preparation of the catalysts for the Baeyer–Villiger oxidation of cyclic and acyclic ketones [5], which involves chloride abstraction from **1** by treatment with  $AgBF_4$  in wet methanol/acetone solution.

The analogous reaction starting from the Pd(II) derivative (**2**) did not give the corresponding  $\mu$ -hydroxo complex, but instead the formation of black metallic decomposition products was observed.



Scheme 3. Synthetic pathway for the synthesis of the catalyst (**3**).



Scheme 4. Preparation of the isocyanide complex (**4**).

The complexes (**1**)–(**3**) are new compounds and they have been characterized by IR, multinuclear NMR and elemental analysis. The IR spectra of (**1**) and (**2**) show typical M–Cl stretchings around  $300\text{ cm}^{-1}$ . The  $^{31}P\{^1H\}$  NMR spectrum of (**1**) shows a singlet at 136.4 ppm flanked by  $^{195}Pt$  satellites ( $^1J_{P-Pt}$  4645 Hz), while (**2**) shows the  $^{31}P$  resonance at 165.9 ppm. The IR spectrum of (**3**) shows a medium-intensity O–H stretching band at  $3500\text{ cm}^{-1}$  and a strong broad band at ca.  $1060\text{ cm}^{-1}$  typical of the  $BF_4$  group. The  $^{31}P\{^1H\}$  NMR spectrum gives rise to a singlet at  $\delta$  123.5 ppm ( $^1J_{P-Pt}$  4762 Hz). In the  $^1H$  NMR spectrum in anhydrous  $CD_2Cl_2$  the OH resonance was observed at 4.14 ppm, a value which is a clear indication of the bridging nature of the anionic ligand [11a]. The high values of the Pt–P coupling constants of (**1**) and (**3**) with respect to those observed for alkyl and aryl-substituted diphosphines, which are reported to be ca. 1000 Hz lower [12], may be explained with the presence of the strong electron-withdrawing methoxy groups directly bonded to the P atoms giving rise to low *trans*-influence. Thus, for instance, the complex *cis*- $[PtCl_2\{P(OPh)_3\}]$  containing the even more electron-withdrawing phenoxy groups, shows the  $^1J_{Pt-P}$  of 5793 Hz [13].

The isocyanide complex (**4**) was specifically prepared in order to correlate the catalytic activity of (**3**) with the Lewis acidity of the metal center arising from the withdrawing ability of the coordinated electron-poor diphosphine. The (**4**) was prepared as previously described for similar isocyanide complexes [6] of the type  $[PtCl(C\equiv N-R)(P-P)][BF_4]$  ( $R = 2,6-(Me)_2C_6H_3$ ;  $P-P =$  various fluorinated diphosphines) by initial halide abstraction from (**1**) with an equivalent amount of  $AgBF_4$  in  $CH_2Cl_2$  and subsequent treatment with a stoichiometric amount of the 2,6-dimethylphenyl isocyanide ligand (Scheme 4).

It is known [14] that the value of the  $C\equiv N$  stretching (or the wavenumber shift  $\Delta\bar{\nu} = (\bar{\nu}(C\equiv N))_{coord} - \bar{\nu}(C\equiv N)_{free}$  of a transition metal coordinated isocyanide gives information about the electrophilicity of the isocyanide carbon atom, which in turn is related to the electron density and hence to the Lewis acidity of the metal center. Thus, it is expected that a larger electron-withdrawing effect by the metal will give rise to a larger wavenumber shift. The general assumption is confirmed by the  $\Delta\bar{\nu}$  observed for (**4**) ( $92\text{ cm}^{-1}$ ) which is a rather high value, comparable to that observed for partially fluorinated aryl diphosphine complexes with the same general dimeric structure [6], and generally higher than analogous complexes bearing normal alkyl diphosphine ligands [15]. This electronic effect positively influences the catalytic activity, as reported later on.

### 3.2. Catalytic studies

Catalytic studies were performed in the oxidation of a series of cyclic and acyclic ketones with commercial 35% hydrogen

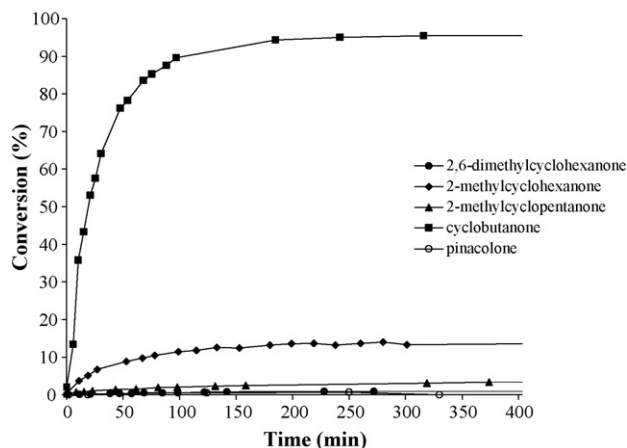


Fig. 1. Oxidation of ketones catalyzed by  $[\text{Pt}(\mu\text{-OH})(\text{Pom-Pom})]_2[\text{BF}_4]_2$  (**3**) with 35% hydrogen peroxide. Reaction conditions: Pt, 0.017 mmol; ketone, 1.7 mmol;  $\text{H}_2\text{O}_2$ , 1.7 mmol; 1,2-dichloroethane as solvent, 3 mL;  $T$ , 25 °C.

peroxide using (**3**) as catalyst. The reactions were carried out in two-phase solvent systems (1,2-dichloroethane/water) at two different temperatures (25 and 70 °C). Some typical reaction profiles (% conversion versus time) are reported in Fig. 1, while initial rates and conversions are collected in Table 1.

Fig. 1 shows that reactions generally began with relatively fast rates but tend to level off rather quickly. Reactions performed at 25 °C were generally finished in about 200 min, with yield from moderate to good. The only acyclic ketone 3,3-dimethyl-2-butanone (pinacolone) was not oxidized, while for 2,6-dimethylcyclohexanone, the steric hindrance of the substrate hampered the oxidation and reaction was sluggish under the experimental conditions employed. Increasing the reaction temperature logically resulted in a significant increase in both the initial rate and the maximum conversion. At 70 °C reactions may be controlled by the diffusion of  $\text{H}_2\text{O}_2$  from the aqueous to the organic phase, as was found for example in the case of 2-methylcyclohexanone and 2-methylcyclopentanone or in the case of cyclobutanone, even at 25 °C. The latter ketone showed very high conversions and rates, but this is not surprising as ring strain makes it by

Table 1  
Summary of the kinetic data for the oxidation of ketones at 25 and 70 °C with 35% hydrogen peroxide catalyzed by  $[\text{Pt}(\mu\text{-OH})(\text{Pom-Pom})]_2[\text{BF}_4]_2$  (**3**)

Ketone	Temperature (°C)	Initial rate ( $\times 10^5 \text{ M s}^{-1}$ )	Conversion (%)
2,6-Dimethylcyclohexanone	25	0.03	1
	70	1.3	2
2-Methylcyclohexanone	25	2.2	16
	70	22	29
2-Methylcyclopentanone	25	1.7	4
	70	7.8	14
Cyclobutanone	25	24	95
Pinacolone	25	–	0
	70	–	0

Experimental conditions: Pt, 0.017 mmol; ketone, 1.7 mmol;  $\text{H}_2\text{O}_2$ , 1.7 mmol; 1,2-dichloroethane as solvent, 3 mL.

far the most reactive substrate. The electron-withdrawing effect of the oxygen atoms on the Pt(II) metal center exerts a positive effect on the catalytic activity analogously to what observed with aryl diphosphines [4]. In fact the productivity towards all the substrates for complex (**3**) is more than twice as much as that of the isosteric but less electron-poor complex  $[\text{depePt}(\mu\text{-OH})]_2(\text{BF}_4)_2$  (depe = bis-diethylphosphino ethane) [15]. Fig. 1 shows that the leveling off in conversion is practically complete after about 100 min at 25 °C and about 60 min at 70 °C. Some randomly performed analyses of the residual hydrogen peroxide in the final reaction mixture indicate that the consumed oxidant corresponds to the maximum conversion observed. In other words, there are no side reactions leading to consumption of the oxidant. These observations imply that reactions stop because of catalyst deactivation.

In order to check this point, a  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR study was performed with the aim of investigating the mechanism by detecting the active species involved in the catalytic process. The complex  $[\text{Pt}(\mu\text{-OH})(\text{Pom-Pom})]_2[\text{BF}_4]_2$  (**3**) (8.6 mg) was dissolved in  $\text{CD}_2\text{Cl}_2$  and the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum was run showing a singlet at 123.5 ppm flanked by  $^{195}\text{Pt}$  satellites with a  $^1J_{\text{P-Pt}}$  coupling constant of 4762 Hz. Addition of 91  $\mu\text{L}$  of 2-methylcyclohexanone did not change the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, while in the  $^1\text{H}$  NMR spectrum a series of multiplets at 2.39–1.38 ppm ( $\text{CH}_2$ ) and a doublet at 1.022 ppm ( $\text{CH}_3$ ) of the ketone were observed. Further addition of 73  $\mu\text{L}$  35% hydrogen peroxide (Pt:ketone: $\text{H}_2\text{O}_2$  = 5:100:100) produced right after a new species, which gives rise in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum a downfield resonance at 130.6 ppm with a  $^1J_{\text{P-Pt}}$  coupling constant of 4572 Hz. On the other hand, the  $^1\text{H}$  NMR spectrum showed the presence of a growing multiplet at 4.42 ppm ( $\text{OCH-Me}$ ) for the product lactone and a new doublet at 1.15 ppm ( $\text{OCH-CH}_3$ ). After 140 min the singlet present in the  $^{31}\text{P}\{^1\text{H}\}$  NMR disappeared as well as the signals of the catalyst at 1.92 ppm (m,  $\text{CH}_2$ ) and 3.96 ppm (d,  $\text{OCH}_3$ ,  $^3J_{\text{Pt-H}} = 12.8 \text{ Hz}$ ) in  $^1\text{H}$  NMR spectrum and the water phase assumed a yellow color. This speaks for the progressive transition of the Pt(II) complex from the organic to the aqueous phase, aided by the presence of oxygen atoms in the ligand. This was confirmed by running a  $^{31}\text{P}\{^1\text{H}\}$  spectrum of the supernatant aqueous phase, after addition of a small volume of  $\text{D}_2\text{O}$ , that showed initially the presence of a singlet at 119 ppm flanked by satellites signals with  $^1J_{\text{P-Pt}}$  5120 Hz attributed to  $[\text{Pt}(\mu\text{-OH})(\text{Pom-Pom})]_2[\text{BF}_4]_2$  dissolved in water, together with a small singlet at 34 ppm with no satellite signals, attributed to the free oxidized ligand Pom-Pom $\text{O}_2$  by comparison with an authentic sample prepared by direct oxidation of the ligand with  $\text{H}_2\text{O}_2$ . Over the time, the latter signal increases and that of the Pt complex decreases as indication of degradation of the catalyst by ligand oxidation.

In summary, the presence of the oxidant in solution transforms the dimeric complex into a new symmetric species with equivalent P atoms, but still nothing can be said at present about the monomeric or dimeric nature of such species. Nevertheless, the decrease in the  $^1J_{\text{P-Pt}}$  coupling constant is indicative of a slightly higher *trans*-effect compared to the original  $\mu\text{-OH}$  ligand, which could be at first interpreted by the formation of a symmetric monomeric or dimeric species bearing



anionic  $\text{HOO}^-$  ligands. During the reaction progress, such active species migrates into the aqueous phase because of the intrinsic hydrophilic nature of the ligand, while concomitant degradation of the catalyst by oxidation of Pom-Pom to phosphonic methyl ester causes the progressive inactivation of the catalyst and brings the reaction to stop. The electronic properties of the complex seems peculiar for the nucleophilic oxidation of ketones to lactones, in fact, attempts to perform epoxidation, which is a typical electrophilic oxidation, of cycloctene with catalyst (**3**) and 35% hydrogen peroxide at 25 and 70 °C were unsuccessful.

#### 4. Concluding remarks

The present work reports the synthesis of new monomeric Pd(II) and Pt(II) dichloro complexes and the dimeric Pt(II) complex bearing 1,2-bis(dimethoxyphosphino)ethane (Pom-Pom) as chelating ligand and the use of the latter complex as catalyst in the Baeyer–Villiger oxidation of ketones with the environmentally friendly oxidant hydrogen peroxide. Key features are the high Lewis acidity of the complex as confirmed by the IR shift of the isocyanide moiety stretching for the corresponding complex. Such peculiar electronic character is responsible for the enhanced catalytic activity compared to analogous alkyl diphosphine complexes. The water solubility of (**3**) prompts us towards the development of new water soluble electron-poor Pt(II) complexes with the aim of developing more green catalytic processes characterized by the employment of eco-friendly oxidant like  $\text{H}_2\text{O}_2$  as well as replacement of organic solvent with water as inert and inexpensive reaction medium.

#### Acknowledgements

RAM and GS thank MIUR, the University of Padova and University of Venice for financial support (PRIN and COFIN 2003). RAM thanks CIRCC (Consorzio Interuniversitario Reattività Chimica e Catalisi) for a fellowship to EP. GS wishes to thank Johnson-Matthey for the loan of platinum.

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