Steric Effects in the Baeyer−Villiger Oxidation of Ketones Catalyzed by Platinum(II) Lewis Acid Complexes with Coordinated Electron-Donor Alkyl Diphosphines

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The synthesis and characterization of new hydroxo-bridged platinum(II) complexes of the type [Pt(μ-OH)(P−P)]$_2$[BF$_4$]$_2$ (**1a**−**d**), where P−P = R$_2$PCH$_2$CH$_2$PR$_2$ (R = Me, dmpe, **1a**; Et, depe, **1b**; *i*-Pr, dippe, **1c**; Cy, dcype, **1d**), and [Pt(P−P)(H$_2$O)$_2$][BF$_4$]$_2$) (where R= *t*-Bu, dtbpe, **1e**) are reported. These complexes were tested in the Baeyer−Villiger oxidation of 2-methylcyclohexanone, 2-methylcyclopentanone, and cyclobutanone with 35% hydrogen peroxide as oxidant. The reactions were performed at 20 and 70 °C in a chlorinated solvent/H$_2$O two-phase system. Within the above-reported series of complexes, **1e** gave the highest catalytic activity and productivity in the oxidation of cyclic ketones. The Lewis acidity of **1a**−**e** was investigated through the determination of the wavenumber shift $\Delta\bar{\nu} = \bar{\nu}(C{\equiv}N)_{coord} - \bar{\nu}(C{\equiv}N)_{free}$ of the isocyanide moiety in complexes of the type [PtCl(CN-2,6-(Me)$_2$C$_6$H$_3$)(P−P)][BF$_4$] (P−P = **2a**−**e**). The values of $\Delta\bar{\nu}$ showed that compounds **2a**−**e** have comparable Lewis acidity, thus indicating that the difference in the catalytic activity observed for **1a**−**e** must be largely ascribed to steric requirements imparted by the alkyl diphosphine ligand.

1. Introduction

The Baeyer−Villiger (BV) oxidation of ketones using organic peroxy acids is an important reaction that finds wide application in organic synthesis.[1] However, its catalytic version using other oxidants such as hydrogen peroxide or sodium hypochlorite is still rather elusive, and factors leading to high catalytic activity have not yet been completely understood. In fact, in the past 20 years the number of active homogeneous and heterogeneous catalysts discovered for such oxidation reaction is still very limited and has not allowed a thorough investigation of the factors (electronic and steric) that control the reaction.

Some years ago, we reported the successful use of a class of [(P−P)Pt(μ-OH)]$_2^{2+}$-soluble complexes (P−P = different diphosphines, including chiral ones) that proved to be the most active catalysts known to date for the BV reaction.[2] These complexes operate under very mild conditions (room temperature, atmospheric pressure), using a green oxidant such as hydrogen peroxide.[3] They also allow performing the enantioselective version of this reaction with ee's up to 80% observed in the desymmetrization of *meso*-substituted cyclohexanones.[4]

The synthetic importance of this oxidation reaction together with unique features such as the use of H$_2$O$_2$ as an environmentally friendly oxidant, the mild experimental conditions, and the possibility of performing the reaction in an enantioselective fashion prompted us toward a systematic study of the individual variables affecting the activity of this class of catalysts. In particular, in recent years, our group thoroughly investigated the effect of the bite angle of the diphosphine[4b] and more recently the effect of the Lewis acid character of the complexes. The latter factor was systematically investigated with two different approaches: (i) performing the synthesis of the Pt(II) complex bearing 1,2-bis(dimethoxyphosphino)ethane (Pom−Pom) as chelating ligand[5] and (ii) preparing a series of complexes containing differently fluorinated tetra-aryl diphosphines.[6] In the latter case, a clear correlation between the number of fluorine atoms and the catalytic activity was observed, while in the former case, enhancement of both activity and productivity due to the less electron donating character of the ligands was observed comparing isosteric ligands. Both results are consistent with the common observation that high Lewis acidity parallels high catalytic activity in oxidation reactions[7] due to better electrophilic activation of the substrate. One major problem concerning these catalysts is their limited lifetime under (strongly oxidizing) reaction conditions. In fact, during catalytic experiments the diphosphine ligand starts being oxidized in a parallel side reaction until the catalyst is completely destroyed.

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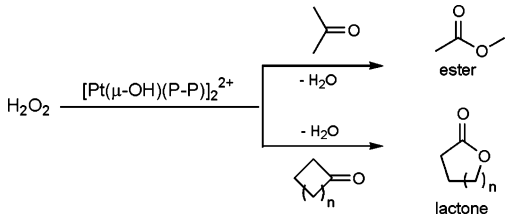
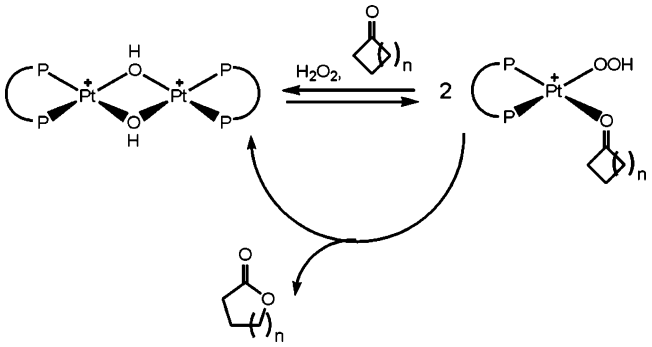
Scheme 1. Baeyer−Villiger Oxidation of Acyclic and Cyclic Ketones with H_2O_2 Catalyzed by Pt(II) Complexes



Scheme 2. Equilibrium between Dimeric and Active Monomeric Species in the BV Oxidation Mediated by Dimeric Pt(II) Complexes



Nevertheless, moderate turnover numbers (TON) up to 65 in the BV oxidation of 2-methylcyclohexanone can be attained.[6]

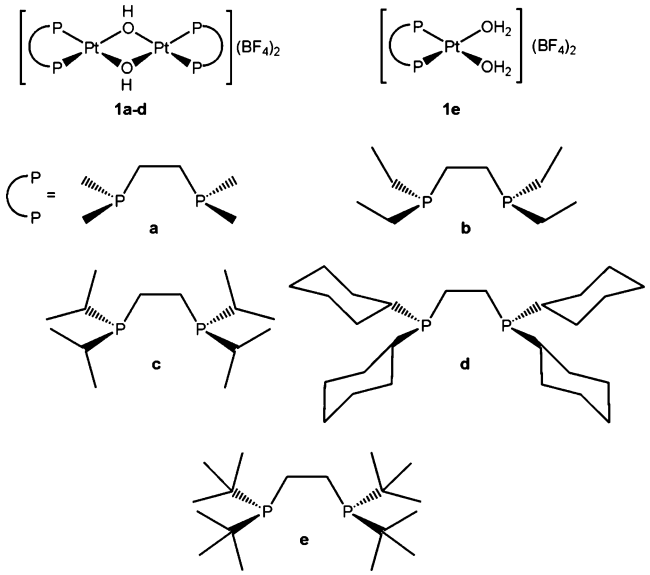
A second issue that deserves attention is related to the necessity to improve catalytic activity through the increase of the concentration of the active monomeric species according to the equilibrium depicted in Scheme 2, which, for complexes bearing aryl diphosphines, is a little shifted to the right. In fact, kinetic studies performed with this type of dimeric complexes have suggested that the most likely active species is a monomeric hydroperoxo complex derived from the bridge splitting of the μ-hydroxo dimeric complex by substrate and oxidant coordination, and consequently the Lewis acidity of the metal center is crucial for the activation of the ketone toward nucleophilic attack by the oxidant.[8]

The above points are addressed in the present paper where we report on recent studies in the BV oxidation of cyclic ketones with hydrogen peroxide using a series of dimeric complexes of the type $[(P-P)Pt(\mu\text{-}OH)]_2^{2+}$ (**1a**−**d**) and a monomeric $[(P-P)Pt(H_2O)_2]^{2+}$ (**1e**) with 1,2-bis(dialkyphosphino)ethane ligands, where the alkyl substituents at phosphorus have been systematically changed (Chart 1).

The design of complexes **1a**−**e** is based on the assumption that the use of more electron-donating alkyldiphosphines would stabilize the P−Pt bond and make it more resistant toward oxidation, as it is known that the oxidation of a Pt(II)-coordinated phosphine is a process that occurs at the P donor atoms when they dissociate from the metal.[9]

In principle, this formulation should (i) stabilize to some extent the complexes against phosphine oxidation due to a less labile P−Pt bond; (ii) allow complexes of similar Lewis acidity, with a stronger P *trans* labilizing effect compared to aryldiphosphines; and (iii) check the effect of a larger concentration of monomeric species due to the influence of the steric hindrance on the position of the equilibrium that makes the dissociation

Chart 1. Pt(II) Dimeric μ-OH Complexes 1a−d and Monomeric 1e with Coordinated Alkyl Diphosphines



of dimeric complexes more favorable (Scheme 2). On the other hand, the employment of ligands with a more pronounced donating character will also decrease the Lewis acidity at the metal center, and this, in turn, could result in a decrease of catalytic activity. An investigation on which one of the two effects will predominate is crucial for the further development of more active environmentally friendly Pt(II) complexes in the BV oxidation with hydrogen peroxide.

2. Experimental Section

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), dmpe and depe (Aldrich), and $AgBF_4$ (Aldrich) were commercial products and used without purification; $[PtMe_2(COD)]$,[10] $[PtCl_2(dcype)]$,[11] $[PtCl_2(dtbpe)]$,[12] and 1,2-bis(diisopropylphosphino)ethane[13] were synthesized according to literature methods. The complexes $[PtCl_2(dmpe)]$, $[PtCl_2(depe)]$, and $[PtCl_2(dippe)]$ were prepared following a modified procedure with respect to that previously reported.[14,15]

IR spectra were taken on a FT-IR AVATAR 320 spectrophotometer (Nicolet Instrument Corporation) in CH_2Cl_2 solution using CaF_2 windows; the wavenumbers are given in cm^{-1}. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were run at 298 K, unless otherwise stated, on a Bruker AC200 spectrometer operating at 200.13 and 81.015 MHz, respectively; δ values in ppm are relative to $SiMe_4$ and 85% H_3PO_4. GLC measurements were taken on a Hewlett-Packard 5890A gas chromatograph equipped with a FID detector (carrier gas He). Identification of products was made with GLC by

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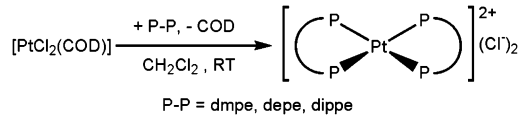
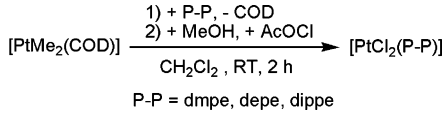
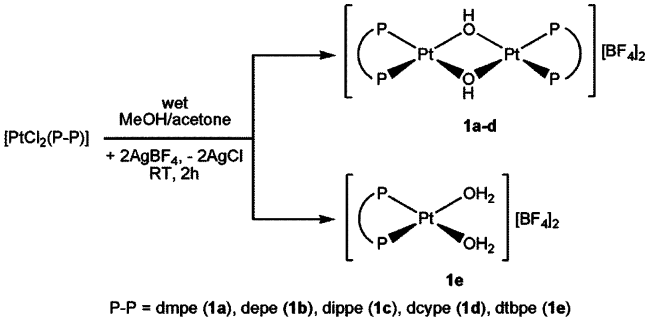
Scheme 3. Attempted Synthesis of [$PtCl_2$(P−P)] Complexes with P−P = dmpe, depe, and dippe



Scheme 4. Synthesis of the Complexes [$PtCl_2$(P−P)] with P−P = dmpe, depe, and dippe



Scheme 5. Synthesis of the Complexes 1a−e



comparison with authentic samples. The elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of the Università di Padova.

2.2. Synthesis. 2.2.1. Synthesis of [$PtCl_2$(dmpe)]. To a solution of [$PtMe_2$(COD)] (0.352 g, 1.057 mmol) in dichloromethane (20 mL) at RT was added 0.180 mL (1.079 mmol) of 1,2-bis(dimethylphosphino)ethane (dmpe). To the mixture was then added 20 mL of methanol and 0.220 mL (3.094 mmol) of acetyl chloride (evolution of CH_4). After 2 h the solution was reduced to a small volume under reduced pressure and treated with methanol to precipitate a white solid. The solid was filtered, washed with ethanol, and dried under vacuum. Yield: 0.316 g, 71.7%. Anal. Calcd for $C_6H_{16}Cl_2P_2Pt$: C, 17.32; H, 3.88. Found: C, 17.54; H, 4.12. IR ($\tilde{\nu}$, PE): 230, 280 (s, Pt−Cl). ^{1}H NMR (δ, $(CD_3)_2SO$): 2.94 (m, CH_2), 1.73 (m, CH_3). $^{31}P\{^1H\}$ NMR (δ, $(CD_3)_2SO$): 34.26 (s, $^1J_{Pt-P}$ = 3521 Hz).

2.2.2. Synthesis of [$PtCl_2$(depe)]. The procedure is similar to that reported above for the synthesis of [$PtCl_2$(dmpe)], starting from 0.403 g (1.21 mmol) of [$PtMe_2$(COD)] and 0.290 mL (1.24 mmol) of 1,2-bis(diethylphosphino)ethane (depe). Upon addition of 20 mL of methanol and 0.25 mL (3.5 mmol) of acetyl chloride, a white solid was isolated. Yield: 0.424 g, 74.1%. Anal. Calcd for $C_{10}H_{24}Cl_2P_2Pt$: C, 25.43; H, 5.12. Found: C, 25.33; H, 5.30. IR ($\tilde{\nu}$, PE): 303, 279 (s, Pt−Cl). ^{1}H NMR (δ, $CDCl_3$): 1.71−2.36 (m, CH_2-CH_3), 1.83 (m, CH_2), 1.24 (dt, CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 57.85 (s, $^1J_{Pt-P}$ = 3545 Hz).

2.2.3. Synthesis of [$PtCl_2$(dippe)]. The procedure is similar to that reported above for the synthesis of [$PtCl_2$(dmpe)], starting from 0.224 g (0.627 mmol) of [$PtMe_2$(COD)] and 0.185 g (0.694 mmol) of 1,2-bis(diisopropylphosphino)ethane (dippe). Upon addition of 20 mL of methanol and 0.10 mL (1.4 mol) of acetyl chloride, a white solid was isolated. Yield: 0.237 g, 66.6%. Anal. Calcd for $C_{14}H_{32}Cl_2P_2Pt$: C, 31.83; H, 6.10. Found: C, 31.46; H, 6.15. ^{1}H NMR (δ, $CDCl_3$): 2.54−2.73 (m, CH), 1.72−1.78 (m, PCH_2), 1.16−1.46 (m, CH_3). ^{31}P $\{^1H\}$ NMR (δ, $CDCl_3$): 72.35 (s, $^1J_{Pt-P}$ = 3571 Hz).

2.2.4. Synthesis of [Pt(μ-OH)(dmpe)]$_2$[BF_4]$_2$ (1a). To a suspension of [$PtCl_2$(dmpe)] (0.81 g, 1.00 mmol) in acetone (50 mL) and methanol (25 mL) at RT was added 2.10 mL (2.10 mmol) of a 1.0 M $AgBF_4$ solution in acetone. The reaction mixture was stirred for 2 h. Then the solid AgCl was filtered off. Upon concentration, the solution was treated with diethyl ether to give the product as a white solid. Yield: 0.84 g, 99.6%. Anal. Calcd for $C_{12}H_{34}B_2F_8O_2P_4Pt_2$: C, 16.05; H, 3.82. Found: C, 16.14; H, 3.91. IR ($\tilde{\nu}$, Nujol): 3566 (s, OH). ^{1}H NMR (δ, CD_3CN): 1.69−2.13 (m, PCH_2 + CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_3CN): 24.51 (s, $^1J_{Pt-P}$ = 3426 Hz).

2.2.5. Synthesis of [Pt(μ-OH)(depe)]$_2$[BF_4]$_2$ (1b). This compound was prepared as described for **1a** starting from [$PtCl_2$(depe)] (0.21 g, 0.24 mmol). Yield: 0.20 g, 90.7%. Anal. Calcd for $C_{20}H_{50}B_2F_8O_2P_4Pt_2$: C, 23.78; H, 4.99. Found: C, 23.74; H, 5.12. IR ($\tilde{\nu}$, Nujol): 3532 (s, OH). ^{1}H NMR (δ, $(CD_3)_2CO$): 2.02−2.17 (m, CH_2), 1.21−1.38 (m, CH_3). $^{31}P\{^1H\}$ NMR (δ, $(CD_3)_2CO$): 51.55 (s, $^1J_{Pt-P}$ = 3469 Hz).

2.2.6. Synthesis of [Pt(μ-OH)(dippe)]$_2$[BF_4]$_2$ (1c). This compound was prepared as reported for **1a** starting from [$PtCl_2$(dippe)] (0.46 g, 0.49 mmol). Yield: 0.36 g, 75.6%. Anal. Calcd for $C_{28}H_{66}B_2F_8O_2P_4Pt_2$: C, 29.96; H, 5.93. Found: C, 29.88; H, 5.90. IR ($\tilde{\nu}$, Nujol): 3512 (s, OH). ^{1}H NMR (δ, $(CD_3)_2CO$): 2.07−2.12 (m, Ar), 1.26−1.49 (m, PCH_2). $^{31}P\{^1H\}$ NMR (δ, $(CD_3)_2CO$): 68.60 (s, $^1J_{Pt-P}$ = 3488 Hz).

2.2.7. Synthesis of [Pt(μ-OH)(dcype)]$_2$[BF_4]$_2$ (1d). This compound was prepared as reported for **1a** starting from [$PtCl_2$(dcype)] (0.20 g, 0.29 mmol). Yield: 0.18 g, 87.1%. Anal. Calcd for $C_{52}H_{98}B_2F_8O_2P_4Pt_2$: C, 43.28; H, 6.85. Found: C, 43.24; H, 6.72. IR ($\tilde{\nu}$, Nujol): 3540 (s, OH). ^{1}H NMR (δ, DMSO-d_6): 3.46 (s, OH), 2.52 (m, PCH_2), 1.31−2.11 (m, Cy). $^{31}P\{^1H\}$ NMR (δ, DMSO-d_6): 59.31 (s, $^1J_{Pt-P}$ = 3470 Hz).

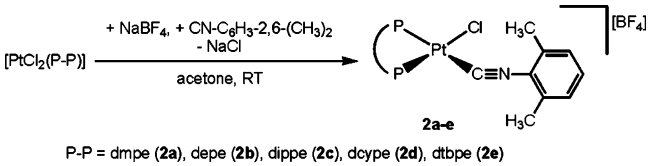
2.2.8. Synthesis of [Pt(dtbpe)(H_2O)$_2$][BF_4]$_2$ (1e). To a suspension of [$PtCl_2$(dtbpe)] (0.12 g, 0.20 mmol) in acetone (20 mL) and methanol (10 mL) at RT was added 0.41 mL (0.41 mmol) of a 1.0 M $AgBF_4$ solution in acetone. The reaction mixture was stirred for 2 h. Then the solid AgCl was filtered off. Upon concentration, the solution was treated with diethyl ether to precipitate the product as a white solid. Yield: 0.048 g, 38.1%. Anal. Calcd for $C_{18}H_{44}B_2F_8O_2P_2Pt$: C, 29.90; H, 6.13. Found: C, 29.54; H, 6.12. ^{1}H NMR (δ, $CDCl_3$): 3.48 (s, OH), 2.19−2.55 (m, PCH_2), 1.55 (s, *t*-Bu). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 78.17 (s, $^1J_{Pt-P}$ = 3926 Hz).

2.2.9. Synthesis of [PtCl(CN-2,6-(CH_3)$_2$$C_6H_3$)(dmpe)][$BF_4$] (2a). To a solution of [$PtCl_2$(dmpe)] (0.084 g, 0.201 mmol) in acetone (20 mL) was added 0.12 g (1.10 mmol) of $NaBF_4$ under stirring. A solution of 1,6-dimethylphenyl isocyanide (0.027 g, 0.205 mmol) in 12 mL of acetone was added by dropping in 20 min. Then the mixture was stirred for 1 h and the solid NaCl was filtered off. Upon concentration, the solution was treated with diethyl ether to give a white solid, which was filtered, washed with Et_2O, and dried under vacuum. Yield: 0.10 g, 86.9%. Anal. Calcd for $C_{15}H_{25}BClF_4NP_2Pt$: C, 30.10; H, 4.21; N, 2.34. Found: C, 30.24; H, 4.13; N, 2.29. IR ($\tilde{\nu}$, CH_2Cl_2): 2202 (s, C≡N). ^{1}H NMR (δ, $CDCl_3$): 7.35−7.17 (m, Ph); 2.32 (m, CH_2); 1.98 (m, CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 30.74 (s, $P_{Cl-trans}$, $^1J_{Pt-P}$ = 3051 Hz); 41.09 (s, $P_{C-trans}$, $^1J_{Pt-P}$ = 2729 Hz).

2.2.10. Synthesis of [PtCl(CN-2,6-(CH_3)$_2$$C_6H_3$)(depe)][$BF_4$] (2b). This compound was prepared according to a procedure similar to that described above for **2a** starting from [$PtCl_2$(depe)] (0.15 g, 0.32 mmol). Yield: 0.19 g, 89.9%. Anal. Calcd for $C_{19}H_{33}BClF_4NP_2Pt$: C, 34.85; H, 5.08; N, 2.14. Found: C, 34.64; H, 4.82; N, 2.19. IR ($\tilde{\nu}$, CH_2Cl_2): 2199 (s, C≡N). ^{1}H NMR (δ, $(CD_3)_2CO$): 7.17−7.36 (m, Ph); 2.11−2.46 (m, PCH_2); 1.19−1.38 (s, CH_3). $^{31}P\{^1H\}$ NMR (δ, $(CD_3)_2CO$): 60.10 (s, $P_{Cl-trans}$, $^1J_{Pt-P}$ = 3061 Hz); 63.24 (s, $P_{C-trans}$, $^1J_{Pt-P}$ = 2751 Hz).

2.2.11. Synthesis of [PtCl(CN-2,6-(CH_3)$_2$$C_6H_3$)(dippe)][$BF_4$] (2c). This compound was prepared according to a procedure similar to that reported for **2a** starting from [$PtCl_2$(dippe)] (0.11 g, 0.20 mmol). Yield: 0.13 g, 91.4%. Anal. Calcd for $C_{23}H_{41}BClF_4NP_2Pt$: C, 38.86; H, 5.81; N, 1.97. Found: C, 38.74; H, 5.92; N, 1.99%. IR ($\tilde{\nu}$, CH_2Cl_2): 2198 (s, C≡N). ^{1}H NMR (δ, $CDCl_3$): 7.18−7.40

Scheme 6. Synthesis of the Complexes [PtCl(CN-2,6-$(CH_3)_2C_6H_3$)(P−P)](BF_4), 2a−e



(m, Ph); 2.11−2.82 (m, PCH_2 + PCH); 1.26−1.47 (s, CH_3). $^{31}P\{^1H\}$ NMR (δ,$CDCl_3$): 81.47 (s, $P_{Cl-trans}$, $^1J_{Pt-P}$ = 3098 Hz); 76.37 (s, $P_{C-trans}$, $^1J_{Pt-P}$ = 2807 Hz).

2.2.12. Synthesis of [PtCl(CN-2,6-$(CH_3)_2C_6H_3$)(dcype)]$_2$[BF_4]$_2$ (2d). This compound was prepared according to a procedure similar to that reported for **2a** starting from [$PtCl_2$(dcype)] (0.099 g, 0.144 mmol). Yield: 0.106 g, 84.4%. Anal. Calcd for $C_{27}H_{49}BClF_4NP_2Pt$: C, 42.28; H, 6.44; N, 1.83. Found: C, 42.22; H, 6.32; N, 1.92. IR ($\tilde{\nu}$, CH_2Cl_2): 2196 (s, C≡N). ^1H NMR (δ, $CDCl_3$): 7.19−7.38 (m, Ph); 1.32−2.45 (m, PCH_2 + Cy). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 73.18 (s, $P_{Cl-trans}$, $^1J_{Pt-P}$ = 3102 Hz); 68.77 (s, $P_{C-trans}$, $^1J_{Pt-P}$ = 2798 Hz).

2.2.13. Synthesis of [PtCl(CN-2,6-$(CH_3)_2C_6H_3$)(dtbpe)]$_2$[BF_4]$_2$ (2e). This compound was prepared using a procedure similar to that described above for **2a** starting from [$PtCl_2$(dtbpe)] (0.030 g, 0.052 mmol). Yield: 0.039 g, 98.4%. Anal. Calcd for $C_{35}H_{57}BClF_4NP_2Pt$: C, 48.26; H, 6.59; N, 1.61. Found: C, 48.34; H, 6.52; N, 1.59. IR ($\tilde{\nu}$, CH_2Cl_2): 2198 (s, C≡N). ^1H NMR (δ, $CDCl_3$): 7.17−7.36 (m, Ph); 2.21−2.57 (m, PCH_2); 1.44 (s, CH_3); 1.73 (s, CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 93.33 (s, $P_{Cl-trans}$, $^1J_{Pt-P}$ = 3164 Hz); 81.44 (s, $P_{C-trans}$, $^1J_{Pt-P}$ = 2884 Hz).

2.3. Catalytic Studies. 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. Constant temperature (20 or 70 °C) was maintained by water circulation through an external jacket connected with a thermostat. The possible presence of diffusional problems was determined by the dependence of conversion versus time plots on the stirring rate. The concentration of the commercial 35% H_2O_2 solution was checked iodometrically prior to use.

The following general procedure was followed: the required amount of catalyst was placed in the reactor. Subsequently the substrate was added followed by the required amount of 1,2-dichloromethane. Then the vial was thermostatted at the required temperature for 10 min, and subsequently the appropriate amount of 35% H_2O_2 solution was injected through the septum and time was started.

All reactions were monitored with GLC by quick direct injection of samples taken periodically from the reaction mixtures with a microsyringe employing *n*-decane as internal standard. Prior quenching of the samples by adding an excess of LiCl was found unnecessary. Initial rate data were determined from conversion versus time plots. Separation of the products was performed on a 25 m HP-5 capillary column using a flame ionization detector.

3. Results and Discussion

3.1. Synthesis and Characterization of the Complexes. The synthesis of the new hydroxo-bridged Pt(II) complexes [Pt(μ-OH)(P−P)]$_2$[BF_4]$_2$ (**1a**−**d**) involved the initial preparation of the dichloro derivatives [$PtCl_2$(P−P)]. While compounds with P−P = dcype and dtbpe were prepared according to general routes based on metathesis of L_2 ligand(s) in [$PtCl_2L_2$] complexes (L_2 = COD, 2 PhCN)[11,12] by the alkyl diphosphines, those with P−P = dmpe, depe, and dippe required an alternative synthetic procedure. In fact, the metathesis reactions carried out in dichloromethane with 1 equiv of dmpe, depe, and dippe lead always to the precipitation of a white solid, as also reported by Andersen,[14] which was only soluble in polar solvents such as acetone or methanol. The $^{31}P\{^1H\}$ NMR spectra show in each case a singlet resonance flanked by ^{195}Pt satellites with $^1J_{P-Pt}$ values in the range 2200−2300 Hz, considerably lower than those expected for [Pt(μ-OH)(P−P)]$_2$[BF_4]$_2$ complexes and in agreement with similar Pt(II) bis-chelated complexes.[16] On the other hand, the NMR and far-IR analysis of the complexes are in accordance with the formation of bis-chelate diphosphine complexes probably due to the high nucleophilicity of the ligands employed (Scheme 3).

Table 1. $^{31}P\{^1H\}$ NMR Data for $^1J_{P-Pt}$ (Hz) of the [(P−P)Pt(μ-OH)]$_2^{2+}$ Hydroxo-Bridging Complexes (1a−d) and of [(dppe)Pt(μ-OH)]$_2^{2+}$ for Comparison Purposes

complex	diphosphine	$^1J_{P-Pt}$ (Hz)
	dppe	3624
1a	dmpe	3426
1b	depe	3469
1c	dippe	3488
1d	dcype	3470

In order to avoid undesired secondary reactions, dimethyl Pt(II) complex [$PtMe_2$(COD)] was employed in order to prevent bis-chelation by the diphosphine ligands, and it was reacted with the appropriate P−P ligands to form the dimethyl diphosphine complexes [$PtMe_2$(P−P)] by displacement of COD (Scheme 4). These latter complexes were then converted in good yields to the final [$PtCl_2$(P−P)] derivatives upon treatment *in situ* with a solution of acetyl chloride in methanol as *in situ* source of HCl (Scheme 4).

The final μ-hydroxo-bridged dimeric Pt(II) catalysts were then synthesized according to a general procedure[2b] (Scheme 5) starting from the dichloro complexes by abstraction of the chlorides with $AgBF_4$ in a wet solvent mixture.

The IR spectra in Nujol mulls of **1a**−**d** show a medium-intensity O−H stretching band in the range 3566−3512 cm^{-1}, typical for this class of complex, and a strong broad band at ca. 1060 cm^{-1} due to the BF_4 group. Selected $^{31}P\{^1H\}$ NMR data are reported in Table 1. It is observed that there is a steady increase in the value of the P−Pt coupling constant from 3426 Hz for **1a** to 3488 Hz for **1c**. This behavior can be associated with an increasing weakening of the Pt−O bond *trans* to the P atom probably ascribed to the increasing steric hindrance of the diphosphine ligand. Because of overlap with other resonances, ^1H NMR spectra the OH signal cannot be detected except for **1d**.

The synthesis performed starting from dtbpe led to the formation of complex **1e**, whose spectroscopic properties are markedly different from those of the series of dimeric complexes **1a**−**d**. In fact, **1e** shows a ^{31}P NMR spectrum characterized by a singlet at 78.17 ppm flanked by ^{195}Pt satellites with $^1J_{P-Pt}$ of 3926 Hz. The value of the coupling constant is much higher than that expected for a classical μ-OH dimeric structure, being more typical for a neutral coordinating ligand like a molecule of an organic solvent or a molecule of water.[17] This suggests that the diphosphine dtbpe is too bulky to allow the formation of the dimeric μ-OH species, and simple monomeric bis-aquo complex [(dtbpe)Pt(H_2O)$_2$]$^{2+}$ is preferentially obtained. The latter species was confirmed, observing via NMR that exactly the same spectra were obtained by addition of other silver salts (e.g., $AgPF_6$, AgOTf) to dtbpe$PtCl_2$.

(16) Berning, D. E.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 11432−11447.
(17) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738−747.

Table 2. Selected IR Data[a] and $^{31}P\{^1H\}$ NMR $^1J_{Pt-P(trans-C)}$ for the Isocyanide Complexes 2a−e and $[PtCl(CN\text{-}2,6\text{-}(CH_3)_2C_6H_3)\ (dppe)]^+$ as Reference

complex	ligand	$\bar{\nu}_{C\equiv N\ coord}$ (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})	$^1J_{Pt-P(trans-C)}$ (Hz)
	dppe[b]	2207	85	2844
2a	dmpe	2202	80	2729
2b	depe	2199	77	2751
2c	dippe	2198	76	2807
2d	dcype	2196	74	2798
2e	dtbpe	2198	76	2884

[a] Values taken in CH_2Cl_2 solution. $\bar{\nu}_{CN}$ for free CN-2,6-$(Me_2)C_6H_3$ 2122 cm^{-1}. [b] See ref 6.

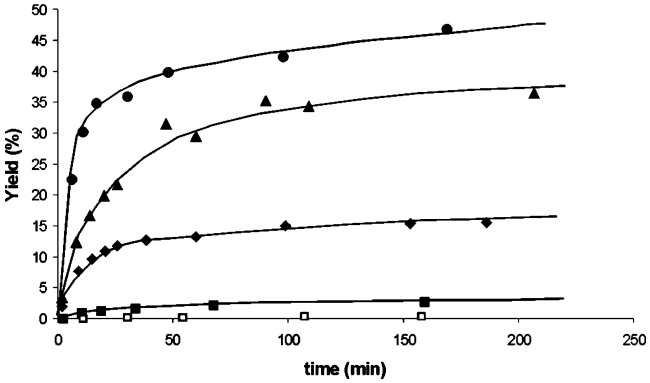


Figure 1. Oxidation of 2-methylcyclohexanone catalyzed by catalysts **1a** (□), **1b** (■),**1c** (▲),**1d** (◆), and **1e** (●). Reaction conditions: Pt, 0.017 mmol; ketone, 1.7 mmol; H_2O_2, 1.7 mmol; dichloroethane (DCE) 3 mL as solvent; *T*, 20 °C.

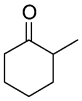
3.2. Lewis Acidity Measurements. It is known that the value of the C≡N stretching (or the wavenumber shift $\Delta\bar{\nu} = \bar{\nu}(C\equiv N)_{coord} - \bar{\nu}(C\equiv N)_{free}$) of a transition metal coordinated isocyanide provides information about the electrophilicity of the isocyanide carbon atom, which in turn is related to the electron density and hence to the Lewis acidity of the metal center.[18] This approach was previously tested successfully and provided a qualitative correlation between activity and Lewis acid character when applied to a class of homologous complexes containing differently fluorinated diphosphines.[6]

Following the same approach, we prepared a homologous series of model isocyanide complexes **2** of the general formula $[PtCl(CN\text{-}2,6\text{-}(Me)_2C_6H_3)(P-P)]^+$ (P−P = dmpe (**2a**), depe (**2b**), dippe (**2c**), dcype (**2d**), and dtbpe (**2e**)). They were obtained as reported in Scheme 6 starting from the corresponding $[PtCl_2(P-P)]$ derivatives by initial halide abstraction and subsequent reaction with 2,6-dimethylphenyl isocyanide in the presence of $NaBF_4$ in acetone.

Complexes **2a**−**e** were characterized by IR and multinuclear NMR spectroscopies. Selected IR and $^{31}P\{^1H\}$ NMR data are reported in Table 2.

Complexes **2a**−**e** display the $\bar{\nu}(C\equiv N)$ absorption in the range 2202−2196 cm^{-1} and the $\Delta\bar{\nu}$ values in the range 80−74 cm^{-1} in CH_2Cl_2 solution (Table 2). The average $\Delta\bar{\nu}$ value displayed by the alkyl-diphosphine complexes is ca. 8 cm^{-1} lower than that observed for the *tetra*-aryl dppe derivative (Table 2) and even lower than that reported for the corresponding fluorinated aryl diphosphine compounds, which displayed $\Delta\bar{\nu}$ values in the range 99−85 cm^{-1}.[6] This feature supports that dialkyl diphosphine complexes here reported display a lower Lewis acidity that decreases with increasing steric bulkiness of the alkyl moieties, thus indicating that complexes **1a**−**e** are characterized by similar Lewis acid character. As a consequence of the IR study described above, it appears reasonable to ascribe the differences in the catalytic activity shown by the series of μ-OH complexes **1a**−**e** in the Baeyer−Villiger oxidation (see later) mainly to the different steric properties of the diphosphines. It is likely that an increase of the steric bulkiness of the ligand determines a shift to the right of the equilibrium depicted in Scheme 2, thus increasing the concentration of the monomeric active species.

Table 3. Catalytic Baeyer−Villiger Oxidation of Cyclic Ketones with Hydrogen Peroxide Catalyzed by Dimeric Pt(II) Catalysts 1a−e[a]

Substrate	Catalyst	Time (h)	Yield %
	**1a**	2	36
	1b	2	57
	1c	2	60
	1d	2	42
	1e	2	72
	**1a**	3	0.5
	1b	3	1
	1c	3	17
	1d	3	13
	1e	3	16
	1a[b]	1	1
	1b[b]	1	1
	1c[b]	1	15
	1d[b]	1	13
	1e[b]	1	16
	**1a**	4	1
	1b	4	3
	1c	4	35
	1d	4	15
	1e	4	46
	1a[b]	0.5	4
	1b[b]	0.5	7
	1c[b]	0.5	34
	1d[b]	0.5	20

[a] Reaction conditions: Pt, 0.017 mmol; ketone, 1.7 mmol; H_2O_2, 1.7 mmol; dichloroethane (DCE) 3 mL as solvent; *T*, 20 °C. [b] Experiment carried out at 70 °C.

3.3. Baeyer−Villiger Oxidation of Cyclic Ketones. Catalytic tests performed with **1a**−**e** were carried out on cyclobutanone, 2-methylcyclopentanone, and 2-methylcyclohexanone either at 20 or 70 °C using 1 mol % [Pt] catalyst in all cases. Some typical reaction profiles for the room-temperature oxidation of 2-methylcyclohexanone with the different catalysts are collected in Figure 1. As shown, the reactions are virtually finished after about 4−5 h, and conversions and initial rates follow similar trends for each individual catalyst. As a consequence, the conversion after a certain time can be reasonably assumed as an indication of the overall activity as well as the lifetime of the catalysts (TON).

(18) (a) Michelin, R. A.; da Silva, M. F. C. G.; Pombeiro, A. J. L. *Coord. Chem. Rev.* **2001**, *218*, 75−112. (b) Belluco, U.; Michelin, R. A.; Uguagliati, P.; Crociani, B. *J. Organomet. Chem.* **1983**, *250*, 565−587.

A summary of the conversions obtained with the different substrates and the different combinations of substrate and catalyst is reported in Table 3. As can be seen, high activities for all complexes are observed only in the case of cyclobutanone. This is no surprise, as the four-membered cyclobutanone ring is intrinsically reactive, while the other substrates better show the differences in activity of the catalysts. As a general observation, with methylcyclopentanone and methylcyclohexanone all the catalysts **1a**−**e** led to the regioselective formation of the normal lactone due to migration of the more substituted carbon atom.

A positive trend in catalytic activity and TON was observed with increasing steric bulkiness in the series of complexes employed, with a maximum for the monomeric **1e**. This behavior associated with increasing size of the diphosphine alkyl moiety is evident also in the case of cyclobutanone, albeit more moderate. Performing the reaction at 70 °C had a substantial effect only on the rate of the reaction but not on the productivity and robustness of the catalysts, and yields comparable to the reactions performed at 20 °C were observed. Complex **1c** was more active also than the corresponding complex $[Pt(\mu\text{-}OH)(dppe)]_2(BF_4)_2$ bearing aryl diphosphines.[8] This observation clearly speaks for the prevailing positive effect of alkyldiphosphines in enhancing catalyst lifetime as well as catalytic activity, and the detrimental effect on activity due to decreased Lewis acidity can be efficiently overcome by increasing steric bulkiness.

4. Conclusion

This work represents a further step in the investigation and optimization of the properties of Pt(II) complexes that favor high activity and high productivity in the BV oxidation of cyclic ketones. Although catalytic activity and TON's are in general relatively moderate, no better catalysts have been reported so far. We systematically changed the steric bulkiness of a homologous series of cationic Pt(II) catalysts by acting on the size and branching degree of alkyl diphosphine ligands that were employed for the synthesis of μ-hydroxo complexes. Similar Lewis acidity was proved by means of spectroscopic evidence by analyzing the C≡N stretching mode of coordinated 2,6-dimethylphenyl isocyanide used as a probe molecule.

We observed a systematic increase in activity and productivity with increasing steric bulkiness of the ligand in complexes **1a**−**d** likely due to a more favorable dissociation of the dimeric into monomeric catalyst structure, the latter being the active catalytic species, as confirmed by the highest activity of **1e**. These results represent key information for the development of new catalysts for the "green" BV oxidation of ketones with hydrogen peroxide and prompt us toward the development of Pt(II) complexes implementing bulky ligands in order to attain high activity. In particular, new strategies to favor the formation of monomeric species in solution are currently underway and will be shortly reported.

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