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Baeyer−Villiger Oxidation of Ketones Catalyzed by Platinum(II) Lewis Acid Complexes Containing Coordinated Electron-Poor Fluorinated Diphosphines

Rino A. Michelin,*,† Erika Pizzo,† Alessandro Scarso,‡ Paolo Sgarbossa,†
Giorgio Strukul,*,‡ and Augusto Tassan†

Dipartimento di Processi Chimici dell'Ingegneria, Università di Padova,
Via F. Marzolo 9, 35131 Padua, Italy, and Dipartimento di Chimica,
Università di Venezia, Dorsoduro 2137, 30123 Venice, Italy

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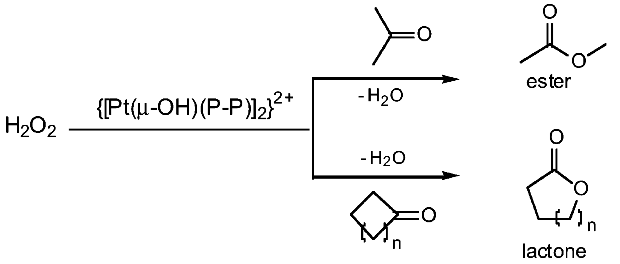
The synthesis and characterization of new hydroxo-bridged platinum(II) complexes of the type $[P(\mu\text{-OH})(P-P)]_2[BF_4]_2$ (**1**−**4**), where P−P = $(C_6H_{5-n}F_n)_2PCH_2CH_2P(C_6H_{5-n}F_n)_2$ (n = 2 (2Fdppe) (**1**), 3 (3Fdppe) (**2**), 4 (4Fdppe) (**3**), 5 (dfppe) (**4**), are reported. These compounds have been used in the Baeyer−Villiger oxidation of 2-methylcyclohexanone using 35% hydrogen peroxide as oxidant. The reactions were performed at 25, 50, and 70 °C in a chlorinated solvent/H_2O two-phase system. Among the fluorinated catalysts, complex **4** was found to be the best one in the oxidation of cyclic ketones; however, it is ineffective toward acyclic ketones. The Lewis acidity of the platinum(II) complexes with coordinated fluorinated diphosphines 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 group in complexes of the type $[PtCl(CN\text{-}2,6\text{-}(CH_3)_2C_6H_3)(P-P)][BF_4]$ (P−P = 2Fdppe, 3Fdppe, 4Fdppe, dfppe, dppe). This latter parameter, which represents a measure of the electrophilicity of the metal center, was then correlated to the catalytic activity of complexes **1**−**4** in the Baeyer−Villiger oxidation of ketones.

1. Introduction

The oxidation of organic substrates by hydrogen peroxide is a process attracting great interest from both the scientific and industrial points of view, because it is in principle environmentally safe, as the reduction product of H_2O_2 is water. Key steps in the oxygen transfer process are the activation of hydrogen peroxide and/or the substrate. Most homogeneous catalysts reported so far behave as Lewis acids, usually containing transition metals in a high oxidation state with free or easily accessible coordination sites at the metal center.[1]

In the past two decades some of us have extensively studied the properties of cationic Pd(II) and Pt(II) complexes in a variety of oxidation reactions using hydrogen peroxide as oxidant.[2] A typical feature displayed by the metal in the latter reactions is the ability to increase the reactivity of the substrate by coordination, thereby making it more susceptible to nucleophilic attack by the peroxidic oxidant. An essential requirement to promote this kind of reactivity is the presence of a positive charge on the metal, which therefore possesses a significant Lewis acidity.

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



[a] P-P = $Ph_2P(CH_2)_nPPh_2$, n = 1−4.

A class of catalytically active complexes is represented by OH-bridged dimeric cationic compounds of the type $\{[Pt(\mu\text{-OH})(P-P)]_2\}^{2+}$, where P−P is a chelating diphosphine which may be also chiral. These complexes are able to promote the Baeyer−Villiger (BV) oxidation of cyclic and acyclic ketones in the presence of H_2O_2 (Scheme 1)[3].

Recently, we have also observed that the BV oxidation is very Lewis acid demanding. Thus, the use of highly acidic $[(P-P-O)Pt]^{2+}$ type complexes (P−P−O = triphos monoxide) has allowed driving the selectivity toward BV

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† Università di Padova.
‡ Università di Venezia.

[1] (a) Jørgensen, K. A.; *Chem. Rev.* **1989**, *89*, 431. (b) Strukul, G., Ed. *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*; Kluwer: Dordrecht, The Netherlands, 1992. (c) Jones, C. W. *Applications of Hydrogen Peroxide and Derivatives*; Royal Society of Chemistry: Cambridge. U.K., 1999.

[2] See for example: (a) Strukul, G.; Michelin, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 7563. (b) Marsella, A.; Agapakis, S.; Pinna, F.; Strukul, G. *Organometallics* **1992**, *11*, 3578. (c) Del Todesco Frisone, M.; Pinna, F.; Strukul, G. *Organometallics* **1993**, *12*, 148. (d) Baccin, C.; Gusso, A.; Pinna, F.; Strukul, G. *Organometallics* **1995**, *14*, 1161. (e) Strukul, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 1198.

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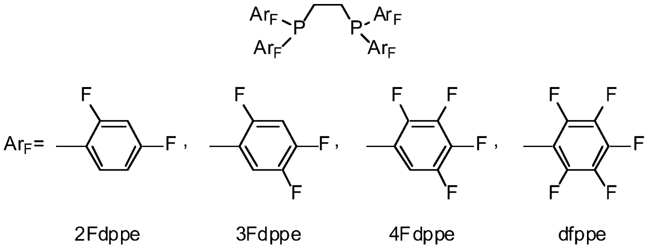
10.1021/om049264a CCC: $30.25

Chart 1. Fluorinated 1,2-Bis(diphenylphosphino)ethane Ligands



products vs epoxides in the oxidation of unsaturated ketones.[4] This observation prompted us to explore the use of other Lewis acidic Pt(II) complexes with the aim of developing more active and selective catalysts.

In this work we will report the effect of the presence of electron-withdrawing substituents at the phosphorus atoms of the P–P ligands on the Lewis acidity of the Pt(II) metal center in the complexes $\{[\mathrm{Pt}(\mu\text{-OH})(\mathrm{P-P})]_2\}^{2+}$. To this purpose, electron-poor diphosphines formally derived from progressive substitution of phenyl hydrogen of dppe (1,2-bis(diphenylphosphino)ethane) with electronegative fluorine atoms were employed.

Their catalytic activity was tested in the Baeyer–Villiger oxidation of 2-methylcyclohexanone and, in the case of the dfppe complex, of other cyclic and acyclic ketones using hydrogen peroxide as oxidant.

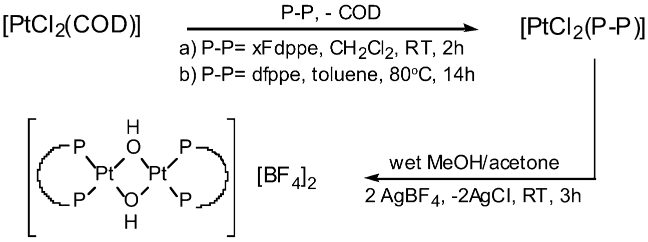
Finally, we will also report preliminary results on the correlation between the observed catalytic activity and the Lewis acidity of the synthesized complexes using 2,6-dimethylphenyl isocyanide as a probe molecule, taking advantage of the sensitivity of the C≡N stretching mode to the Lewis acidity of the metal center in complexes of the type $[\mathrm{PtCl(CN\text{-}2,6\text{-}(CH_3)_2\text{-}C_6H_3)(P-P)}][\mathrm{BF_4}]$.[5]

2. Results and Discussion

Synthesis and Characterization of the Catalysts. The partially fluorinated diphosphines (Chart 1) 2Fdppe and 3Fdppe and also 4Fdppe, which was not previously reported, were all prepared according to a published procedure[6] involving the reaction of 1,2-bis(dichlorophosphino)ethane, $\mathrm{Cl_2PCH_2CH_2PCl_2}$, with the corresponding $\mathrm{LiAr_F}$ species ($\mathrm{Ar_F} = \mathrm{C_6H_3F_2}$, $\mathrm{C_6H_2F_3}$, $\mathrm{C_6HF_4}$). The perfluorinated diphosphine dfppe is a commercially available product and was used as received.

The spectroscopic characterization of the new 4Fdppe ligand is reported in the Experimental Section. In particular, its $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum exhibits an absorption at −32.8 ppm, which is upfield from the resonance reported for the unsubstitued dppe (−12.5 ppm),[7] as also observed for 2Fdppe, 3Fdppe, and dfppe (−31.9, −30.2, and −44.5 ppm, respectively).[6]

Scheme 2[a]



1-4

[a] P-P = 2Fdppe (**1**), 3Fdppe (**2**), 4Fdppe (**3**), dfppe (**4**).

Table 1. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR Data of $[(\mathrm{P\text{-}P})\mathrm{Pt}(\mu\text{-OH})]_2^{2+}$ Bridging Hydroxo Complexes

complex	diphosphine	$^1J_{\mathrm{P-Pt}}$ (Hz)
	dppe	3624
1	2Fdppe	3685
2	3Fdppe	3694
3	4Fdppe	3721
4	dfppe	3754

The catalysts were prepared according to the general method reported in the literature[8] and previously employed in the preparation of those reported in ref 3 for the Baeyer–Villiger oxidation of cyclic and acyclic ketones (Scheme 2). The procedure involves the initial substitution of cyclooctadiene (COD) from $[\mathrm{PtCl_2(COD)}]$ by the diphosphine ($\mathrm{P{-}P} = (\mathrm{C_6H_{5-\mathit{n}}F_\mathit{n}})_2\mathrm{PCH_2CH_2P}(\mathrm{C_6H_{5-\mathit{n}}F_\mathit{n}})_2$, $n = 2{-}5$) to afford the corresponding complexes $[\mathrm{PtCl_2(P{-}P)}]$ in ca. 70–90% yield. Subsequent chloride abstraction from $[\mathrm{PtCl_2(P{-}P)}]$ by treatment with 2 equiv of $\mathrm{AgBF_4}$ in wet MeOH/acetone solutions affords the bridging hydroxo dimers $[\mathrm{Pt}(\mu\text{-OH})(\mathrm{P\text{-}P})]_2[\mathrm{BF_4}]_2$, which were isolated in high yield (>90%) as white solids upon addition of diethyl ether.

The complexes $[\mathrm{PtCl_2(4Fdppe)}]$, $[\mathrm{Pt}(\mu\text{-OH})(x\mathrm{Fdppe})]_2[\mathrm{BF_4}]_2$ (x = 2 (**1**), 3 (**2**), 4 (**3**)), and $[\mathrm{Pt}(\mu\text{-OH})(\mathrm{dfppe})]_2[\mathrm{BF_4}]_2$ (**4**) are new compounds, and they have been characterized by IR, multinuclear NMR, and elemental analysis (see Experimental Section).

The IR spectrum of $[\mathrm{PtCl_2(4Fdppe)}]$ shows typical Pt–Cl stretchings at 325 and 335 $\mathrm{cm^{-1}}$, while in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum the P atoms appear as a singlet resonance at δ 42.7 ppm flanked by $^{195}\mathrm{Pt}$ satellites ($^1J_{\mathrm{Pt-P}}$ = 3650 Hz). The IR spectra of **1**–**4** show a medium-intensity O–H stretching band in the range 3480–3369 $\mathrm{cm^{-1}}$, typical for this class of complex,[8] and a strong broad band at ca. 1060 $\mathrm{cm^{-1}}$ due to the $\mathrm{BF_4}$ group. Their $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR data along with those known for $[(\mathrm{dppe})\mathrm{Pt}(\mu\text{-OH})]_2^{2+}$ are reported in the Experimental Section. As can be seen, there is a steady increase in the value of the P–Pt coupling constant, which shifts from 3624 Hz for $[(\mathrm{dppe})\mathrm{Pt}(\mu\text{-OH})]_2^{2+}$ to 3754 Hz for **4** (Table 1). This behavior can be associated with an increasing polarization of the Pt–O bond trans to the phosphine, as was suggested by Appleton and Bennett many years ago,[9] and seems to reflect the increasing electron-withdrawing character of the diphosphine ligand. The OH resonance could be detected in the ^{1}H NMR spectra only at low temperature because of overlapping with $\mathrm{CH_2}$ multiplets at room temperature.

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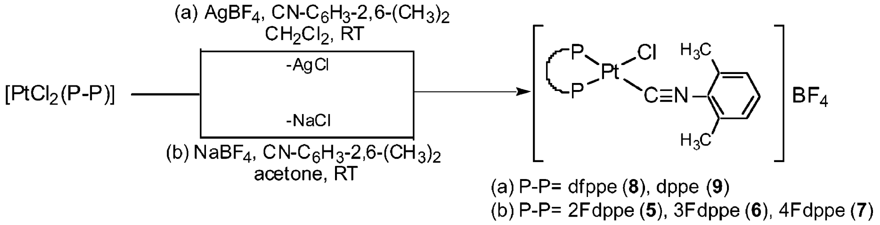
Scheme 3[a]



[a] P-P = 2Fdppe (**5**), 3Fdppe (**6**), 4Fdppe (**7**), dfppe (**8**), dppe (**9**).

Table 2. Selected IR Data[a] **of the Isocyanide Complexes [Pt(P-P)(CN-2,6-(CH$_3$)$_2$C$_6$H$_3$)Cl]$^+$**

complex	ligand	$\bar{\nu}_{C\equiv N,coord}$ (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})
9	dppe	2207	85
5	2Fdppe	2211	89
6	3Fdppe	2213	91
7	4Fdppe	2215	93
8	dfppe	2221	99

[a] Values found in CH$_2$Cl$_2$ solution. $\bar{\nu}_{CN}$(CN-2,6-(CH$_3$)$_2$C$_6$H$_3$ free) 2122 cm^{-1}.

Determination of the Lewis Acidity of the Complexes. We tried to correlate the catalytic activity of complexes **1**–**4** with the Lewis acidity of the metal center arising from the withdrawing ability of the coordinated electron-poor diphosphine. It is known[5] 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 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. On this basis, using 2,6-dimethylphenyl isocyanide as a probe molecule, we have synthesized a homologous series of isocyanide complexes of the general formula [PtCl(CN-2,6-(CH$_3$)$_2$C$_6$H$_3$)(P–P)]$^+$ (P–P = 2Fdppe (**5**), 3Fdppe (**6**), 4Fdppe (**7**), dfppe (**8**), dppe (**9**)), which differ only in the diphosphine ligand. They have been obtained from the corresponding [PtCl$_2$(P–P)] derivatives by initial halide abstraction with an equivalent amount of AgBF$_4$ in CH$_2$Cl$_2$ and subsequent treatment with a stoichiometric amount of the isocyanide ligand (**8** and **9**; Scheme 3, route a) or by halide abstraction with the isocyanide ligand and NaBF$_4$ (**5**–**7**; Scheme 3, route b).

Complexes **5**–**9** display the $\bar{\nu}$(C≡N) absorption in the range 2207–2221 cm^{-1} and $\Delta\bar{\nu}$ values in the range 99–85 cm^{-1} in CH$_2$Cl$_2$ (Table 2). Table 2 shows that upon increasing the number of fluorine atoms in the phenyl groups of the diphosphine, $\Delta\bar{\nu}$ increases and hence the acidity of the metal center increases. Complex **8**, having coordinated dfppe, shows the highest wavenumber shift ($\Delta\bar{\nu}$ = 99 cm^{-1}), and consequently it should possess the highest Lewis acidity among the five complexes. This is also in agreement with its highest catalytic activity in the oxidation of cyclic ketones (see below).

Catalytic Studies. Catalytic studies were performed in the oxidation of 2-methylcyclohexanone with commercial 35% hydrogen peroxide using **1**–**4** and [Pt(μ-OH)(dppe)]$_2$[BF$_4$]$_2$ as catalysts (Pt, 0.017 mmol; ketone, 1.7 mmol; H$_2$O$_2$, 1.7 mmol). The reactions were carried out in two-phase solvent systems (CH$_2$Cl$_2$/H$_2$O or DCE/H$_2$O) at two different temperatures (25 and 70 °C). Some typical reaction profiles (percent conversion vs time) are reported in Figure 1.

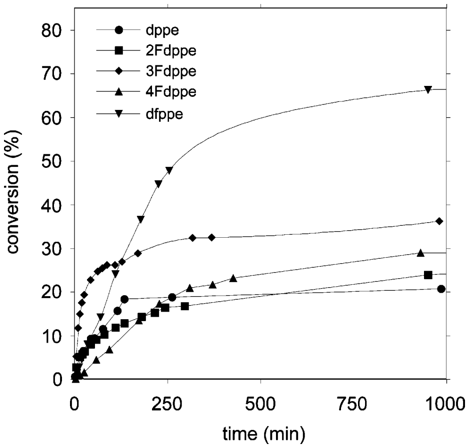


Figure 1. Oxidation of 2-methylcyclohexanone catalyzed by [Pt(μ-OH)(xFdppe)]$_2^{2+}$ (**1**–**4**) and [Pt(μ-OH)(dppe)]$_2^{2+}$. Reaction conditions: Pt, 0.017 mmol; ketone, 1.7 mmol; H$_2$O$_2$, 1.7 mmol; DCM as solvent; T, 25 °C.

As can be observed, the reactions generally begin with relatively fast rates but tend to level off rather quickly. After about 300 min catalytic conversion ceased in all reactions. At 25 °C the selectivity to lactone is >98%. Increasing the reaction temperature obviously results not only in a significant increase in both the initial rate and the maximum conversion but also in a decrease in selectivity since, by the end of the reaction, the formation of 5-methyl-6-hydroxyhexanoic acid arising from hydrolysis of the lactone main product becomes evident.

It has to be pointed out that, while the reaction conditions reported above and in Figure 2 allow relatively high conversions and reaction rates, they do not allow a complete solubilization of all the complexes in the reaction medium. It was observed that the solubility of the catalyst decreases as the degree of fluorine substitution increases. Therefore, an analysis of the effects of the diphosphine on the catalytic properties of the catalysts was not possible.

To solve this problem, a new set of conditions was chosen (Pt, 4.6 μmol; ketone, 1.5 mmol; H$_2$O$_2$, 1.8 mmol; DCE, 3 mL; T, 50 °C). Results are shown in Figure 2 and Table 3. In the latter, the selectivity reported refers to heptalactone, while the only byproduct is 5-methyl-6-hydroxyhexanoic acid. Typical turnover numbers are in the 20–120 range. As can be seen, the trends observed for both the initial rate and the conversion as a function of the degree of fluorine substitution parallel those reported in Table 2 for the $\Delta\nu$ value of the coordinated isocyanide and in Table 1 for the P–Pt coupling constants. In other words, it can be concluded that the Lewis acidity of the catalyst increases both the

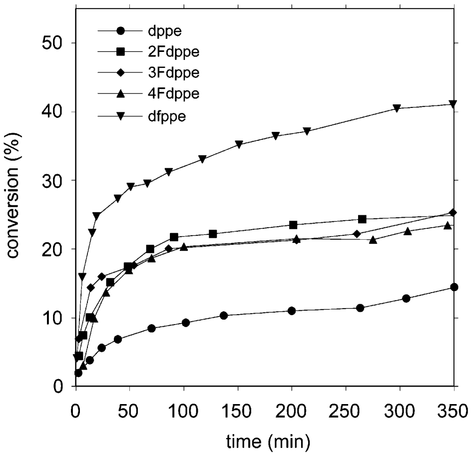


Figure 2. Oxidation of 2-methylcyclohexanone catalyzed by $[Pt(\mu\text{-}OH)(x\text{Fdppe})]_2^{2+}$ (**1**–**4**) and $[Pt(\mu\text{-}OH)(dppe)]_2^{2+}$. Reaction conditions: Pt, 4.6 μmol; ketone, 1.5 mmol; H_2O_2, 1.8 mmol; DCE as solvent; *T*, 50 °C.

Table 3. Summary of the Catalytic Data for the Oxidation of 2-Methylcyclohexanone with Hydrogen Peroxide Catalyzed by $[Pt(\mu\text{-}OH)(x\text{Fdppe})]_2[BF_4]_2$ (1–4) and $[Pt(\mu\text{-}OH)(dppe)]_2[BF_4]_2$ at 50 °C[a]

complex	diphosphine	10^5(init rate) (M/s)	conversn (%) (3 h)	selectivity (%) (3 h)
	dppe	1.4	11	86
1	2Fdppe	4.1	22	99
2	3Fdppe	5.0	21	98
3	4Fdppe	5.2	21	98
4	dfppe	14	37	95

[a] Experimental conditions: Pt, 4.6 μmol; ketone, 1.5 mmol; H_2O_2, 1.8 mmol; DCE, 3 mL; *T*, 50 °C.

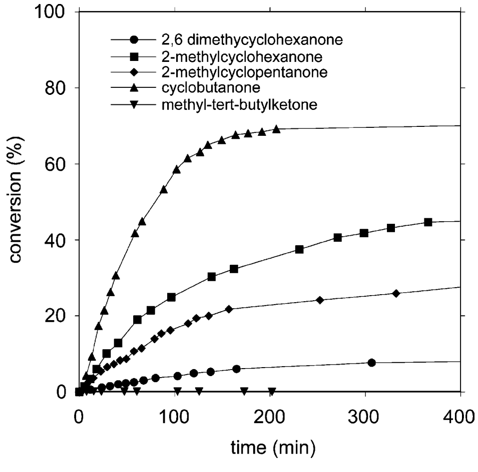


Figure 3. Oxidation of ketones catalyzed by $[Pt(\mu\text{-}OH)(dfppe)]_2^{2+}$ (**4**). Reaction conditions: Pt, 0.017 mmol; ketone, 1.7 mmol; H_2O_2, 1.7 mmol; DCM as solvent; *T*, 25 °C.

activity and the conversion in the BV oxidation of 2-methylcyclohexanone.

The complex $[Pt(\mu\text{-}OH)(dfppe)]_2[BF_4]_2$ (**4**) is the most active, and we tested its catalytic activity in the oxidation of a series of cyclic and acyclic ketones with hydrogen peroxide. The reactions were carried out in two-phase solvent systems (CH_2Cl_2/H_2O and DCE/H_2O) at two different temperatures (25 and 70 °C). Some typical reaction profiles (percent conversion vs time) are reported in Figure 3, while initial rates and conversions are collected in Table 4.

Table 4. Summary of the Catalytic Data for the Oxidation of Different Ketones with Hydrogen Peroxide Catalyzed by $[Pt(\mu\text{-}OH)(dfppe)]_2[BF_4]_2$ (4)[a]

entry	ketone	temp (°C)	time (h)	10^5(init rate) (M/s)	conversn (%)	selectivity (%)
1	2,6-dimethylcyclo-	25	24	0.33	13	100
2	hexanone	70	1	6.2	20	95
3	2-methylcyclo-	25	24	2.8	60	98
4	hexanone	70	1	28^b	85	97
5	2-methylcyclo-	25	24	1.7	33	100
6	pentanone	70	1	27^b	65	100
7	cyclobutanone	25	24	6.7	85	100
8		0	1	0.33	56	100
9	methyl *tert*-butyl	25	24	0	0	0
10	ketone	70	1	0	3	100

[a] Experimental conditions: Pt, 0.017 mmol; ketone, 1.7 mmol; H_2O_2, 1.7 mmol; DCE, 3.0 mL. [b] Diffusion controlled.

Figure 3 shows that the reactions generally begin with relatively fast rates but tend to level off rather quickly. Reactions are generally finished in about 500 min. Methyl *tert*-butyl ketone (the only acyclic ketone) is not oxidized. Figure 3 shows that the leveling off in conversion is practically complete after about 400 min at 25 °C. Increasing the reaction temperature obviously results in a significant increase in both the initial rates and the maximum conversions (the leveling off occurs at about 200 min). At 70 °C reactions may be controlled by the diffusion of H_2O_2 from the aqueous to the organic phase,[10] as was found, for example, in the case of 2-methylcyclohexanone and 2-methylcyclopentanone (Table 4, entries 4 and 6). Cyclobutanone always yields very high conversions and rates, but this is not surprising, as ring strain makes it by far the most reactive substrate.

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 and not depletion of the oxidant.

To investigate this point, the catalysts were checked in randomly selected reactions carried out with **1**–**4** at 25 and 70 °C. ^{31}P NMR spectra showed the disappearance of the signals characteristic of **1**–**4** and the presence of resonances typical for the oxides of the ligands (δ 25.7, 23.6, 22.8, and 34.9 ppm, respectively), thus demonstrating the decomposition of the catalysts. Chemical shifts for authentic samples of the different diphosphine dioxides were obtained by direct oxidation of the free diphosphines with hydrogen peroxide.

3. Conclusions

In this work we have systematically changed the electrophilicity of a homologous series of cationic Pt(II) centers (and hence their Lewis acidity) by varying the degree of fluorine substitution of a series of tetraaryl diphosphine ligands that were employed for the synthesis of μ-hydroxo complexes. The systematic change in Lewis acidity of the different complexes is shown by

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[10] Zanardo, A.; Pinna, F.; Michelin, R. A.; Strukul, G. *Inorg. Chem.* **1988**, *27*, 1966.

spectroscopic evidence, the most convincing of which is the increase in frequency of the C≡N stretching mode of coordinated 2,6-dimethylphenyl isocyanide used as a probe molecule.

In agreement with previous observations,[4a] we have found 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, which represents a key issue for the development of "green" catalysts with high activity for this synthetically useful reaction.[13]

Unfortunately, while the activity of the catalysts can be very high (reactions are even diffusion controlled under certain conditions), their lifetime (and hence their productivity) can be severely limited. Studies are underway to systematically investigate the role of the electron-withdrawing substituents on the stability of the complexes under oxidizing conditions and possibly find catalysts able to conjugate activity and stability under suitably mild conditions.

4. Experimental Section

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), dfppe (Aldrich), and 54% HBF_4 in ether (Aldrich) were commercial products and were used without purification. $[PtCl_2(COD)]$,[11] $[PtCl_2(dfppe)]$,[12] $[Pt(\mu\text{-}OH)(dppe)]_2[BF_4]_2$,[8c] and 1,2-bis(bis($x$-fluorophenyl)phosphino)ethane (x = 2,4 and 2,4,5) and their platinum dichloro complexes[6] were synthesized by following procedures reported in the literature. IR spectra were taken on a Nicolet Instrument Corp. AVATAR 320 FT-IR spectrophotometer in CH_2Cl_2 solution using CaF_2 windows; the wavenumbers are given in cm^{-1}. ^1H NMR, ^{19}F NMR, and $^{31}P\{^1H\}$ NMR spectra were run at 298 K, unless otherwise stated, on a Bruker AC200 spectrometer operating at 200.13, 81.015, and 188.25 MHz, respectively; δ values in ppm are relative to $SiMe_4$, 85% H_3PO_4, and $CFCl_3$. GLC measurements were taken on a Hewlett-Packard 5890A gas chromatograph equipped with an 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 University of Padua.

Synthesis. (a) Synthesis of 1,2-Bis(bis(2,3,4,5-tetrafluorophenyl)phosphino)ethane (4Fdppe). In a 500 mL Schlenk flask equipped with a dropping funnel, 1-bromo-2,3,4,5-tetrafluorobenzene (2.7 mL, 21.8 mmol) was dissolved in dry diethyl ether (40 mL) and the solution was cooled to −78 °C by employing a liquid N_2/2-propanol bath. Over a period of 20 min, a solution of *n*-buthyllitium in *n*-hexane (13.5 mL, 1.6 M) was added by means of the same dropping funnel. Following this addition, stirring was continued for 30 min. The second funnel was charged with a solution of *P,P′*-(1,2-ethanediyl)-bis(dichlorophosphine) (0.92 g, 3.97 mmol) in diethyl ether (15 mL), which was added dropwise at low temperature. The solution was then warmed to room temperature. After hydrolysis with degassed water, the ethereal phase was separated, washed with water and brine, and then dried with anhydrous magnesium sulfate. The solvent was evaporated in vacuo to yield a white product. Recrystallization from ethanol/acetone afforded 4Fddpe as a white crystalline solid. Yield: 1.80 g, 65.9%. Anal. Calcd for $C_{26}H_8F_{16}P_2$: C, 45.50; H, 1.17. Found: C, 45.70; H, 1.18. ^1H NMR (δ, $(CD_3)_2CO$): 7.27 (m, Ar), 2.49 (m, PCH_2). ^{19}F NMR (δ, $(CD_3)_2CO$): −132.27 (m, *o*-F), −140.41 (m, *p*-F), −155.38 (m, *m*-F), −157.20 (m, *m*-F).; $^{31}P\{^1H\}$ NMR (δ, $(CD_3)_2CO$): −32.75 (m, P).

(b) Synthesis of $[PtCl_2(4Fdppe)]$. To a solution of $[PtCl_2(COD)]$ (0.405 g, 1.082 mmol) in dichloromethane (40 mL) at room temperature was added 0.802 g (1.168 mmol) of 1,2-bis(bis(2,3,4,5-tetrafluorophenyl)phosphino)ethane. The reaction mixture was stirred under nitrogen overnight, and then, after concentration, the suspension was treated with Et_2O to give a white solid, which was filtered off and dried under vacuum. Yield: 0.956 g, 92.8%. Anal. Calcd for $C_{26}H_8Cl_2F_{16}P_2Pt$: C, 32.79; H, 0.85. Found: C, 32.44; H, 0.84. IR ($\tilde{\nu}$, PE): 335, 325 (s, Pt−Cl). ^1H NMR (δ, $(CD_3)_2CO$): 7.86 (m, Ar), 3.11 (m, PCH_2). ^{19}F NMR (δ, $(CD_3)_2CO$): −126.72 (m, *o*-F), −138.64 (m, *p*-F), −149.05 (m, *m*-F), −154.85 (m, *m*-F). $^{31}P\{^1H\}$ NMR (δ, $(CD_3)_2CO$): 42.67 (s, $^1J_{Pt-P}$ = 3650 Hz).

(c) Synthesis of $[Pt(\mu\text{-}OH)(2Fdppe)]_2[BF_4]_2$ (1). To a solution of $[PtCl_2(2Fdppe)]$ (0.81 g, 1.00 mmol) in acetone (50 mL) and methanol (25 mL) at room temperature was added 2.10 mL (2.10 mmol) of a 1.0 M acetone solution of $AgBF_4$. The reaction mixture was stirred under nitrogen for 2 h, and then the solid AgCl that formed was filtered off. After concentration, the solution was treated with Et_2O to give a white solid, which was filtered off and dried under vacuum. Yield: 0.84 g, 99.6%. Anal. Calcd for $C_{52}H_{34}B_2F_{24}O_2P_4Pt_2$: C, 37.12; H, 2.04. Found: C, 37.28; H, 2.04. IR ($\tilde{\nu}$, Nujol): 3480 (s, OH). ^1H NMR (δ, CD_3CN): 7.75 (m, Ar), 7.15 (m, Ar), 2.64 (m, PCH_2). ^1H NMR (δ, CD_3CN, 270 K): 2.82 (s, OH). ^{19}F NMR (δ, CD_3CN): −96.85 (m, *o*-F), −102.34 (m, *p*-F), −152.27 (s, BF_4^-). $^{31}P\{^1H\}$ NMR (δ, CD_3CN): 28.75 (s, $^1J_{Pt-P}$ = 3685 Hz).

(d) Synthesis of $[Pt(\mu\text{-}OH)(3Fdppe)]_2[BF_4]_2$ (2). This compound was prepared by using a procedure similar to that described above for complex **1**, starting from $[PtCl_2(3Fdppe)]$ (0.21 g, 0.24 mmol). Yield 0.20 g, 90.7%. Anal. Calcd for $C_{52}H_{26}B_2F_{32}O_2P_4Pt_2$: C, 34.20; H, 1.43. Found: C, 34.31; H, 1.35. IR ($\tilde{\nu}$, Nujol): 3398 (s, OH). ^1H NMR (δ, $(CD_3)_2CO$): 7.80 (m, Ar), 7.46 (m, Ar), 2.79 (m, PCH_2). ^1H NMR (δ, CD_3CN, 260 K): 2.80 (s, OH). ^{19}F NMR (δ, CD_3CN): −101.53 (m, *o*-F), −125.33 (m, *p*-F), −142.35 (m, *m*-F), −152.43 (s, BF_4^-). $^{31}P\{^1H\}$ NMR (δ, CD_3CN): 29.78 (s, $^1J_{Pt-P}$ = 3694 Hz).

(e) Synthesis of $[Pt(\mu\text{-}OH)(4Fdppe)]_2[BF_4]_2$ (3). This compound was prepared by using a procedure similar to that described above for complex **1**, starting from $[PtCl_2(4Fdppe)]$ (0.46 g, 0.49 mmol). Yield: 0.36 g, 75.6%. Anal. Calcd for $C_{52}H_{18}B_2F_{40}O_2P_4Pt_2$: C, 31.70; H, 0.92. Found: C, 31.91; H, 0.95. IR ($\tilde{\nu}$, Nujol): 3400 (s, OH). ^1H NMR (δ, CD_3CN): 7.55 (m, Ar), 2.78 (m, PCH_2). ^1H NMR (δ, CD_3CN, 250 K): 2.89 (s, OH). ^{19}F NMR (δ, CD_3CN): −125.73 (m, *o*-F), −138.18 (m, *p*-F), −147.11 (m, *m*-F), −153.90 (m, *m*-F), −152.52 (s, BF_4^-). $^{31}P\{^1H\}$ NMR (δ, CD_3CN): 31.72 (s, $^1J_{Pt-P}$ = 3721 Hz).

(f) Synthesis of $[Pt(\mu\text{-}OH)(dfppe)]_2[BF_4]_2$ (4). To a suspension of $[PtCl_2(dfppe)]$ (0.50 g, 0.49 mmol) in methanol (35 mL) at room temperature was added 1.15 mL (0.98 mmol) of an acetone solution of $AgBF_4$. The reaction mixture was stirred under nitrogen for 2 h, and then the solid AgCl that formed was filtered off. After concentration, the solution was treated with Et_2O to give a white solid, which was filtered and dried under vacuum. Yield: 0.48 g, 93.0%. Anal. Calcd for $C_{52}H_{10}B_2F_{48}O_2P_4Pt_2$: C, 29.54; H, 0.48. Found: C, 30.05; H, 0.32. IR ($\tilde{\nu}$, Nujol): 3369 (s, OH), 1061 (s, BF_4). ^1H NMR (δ, $(CD_3)_2CO$, 270 K): 4.22 (s, OH, $^2J_{Pt-H}$ = 3.00 Hz), 3.44 (m, CH_2). $^{31}P\{^1H\}$ NMR (δ, $(CD_3)_2CO$): 5.40 (s, $^1J_{Pt-P}$ = 3754 Hz). ^{19}F NMR (δ, $(CD_3)_2CO$, room temperature): −128.8 (d, *o*-C_6F_5, $^3J_{F-F}$ = 14.3 Hz), −145.9 (t, *p*-C_6F_5, $^3J_{F-F}$ = 19.0 Hz), −160.6 (pseudo t, *m*-C_6F_5, $^3J_{F-F}$ = 18.3 Hz), −153.5 (s, BF_4^-).

(g) Synthesis of $[PtCl(CN\text{-}2,6\text{-}(CH_3)_2C_6H_3)(2Fdppe)][BF_4]$ (5). To a solution of $[PtCl_2(2Fdppe)]$ (0.14 g, 0.17 mmol)

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in acetone (35 mL) was added, with stirring, 0.10 g (0.91 mmol) of $NaBF_4$. The solution was then treated dropwise with a solution of 0.023 g (0.18 mmol) of 1,6-dimethylphenyl isocyanide in 12 mL of acetone for 20 min. The reaction mixture was stirred under nitrogen for 1 h, and then the solid NaCl that formed was filtered off. After concentration, the solution was treated with Et_2O to give a yellowish solid, which was filtered off, washed with Et_2O, and dried under vacuum. Yield: 0.12 g, 73.7%. IR ($\tilde{\nu}$, CH_2Cl_2): 2211 (s, $C\equiv N$). ^1H NMR (δ, $CDCl_3$): 7.79 (m, Ph), 7.08 (m, Ph), 3.03 (m, PCH_2), 2.22 (s, CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 22.43 (s, $P_{Cl-trans}$, $^1J_{Pt-P} = 3270$ Hz), 41.13 (s, $P_{C-trans}$, $^1J_{Pt-P} = 2917$ Hz). ^{19}F NMR (δ, $(CD_3)_2CO$, room temperature): −95.41, −96.08 (m, *o*-F), −98.94, −99.84 (m, *p*-F), −154.49 (s, BF_4^-).

(h) Synthesis of $[PtCl(CN\text{-}2,6\text{-}(CH_3)_2C_6H_3)(3Fdppe)][BF_4]$ (6). This compound was prepared using a procedure similar to that described above for complex **5**, starting from $[PtCl_2(3Fdppe)]$ (0.10 g, 0.11 mmol). Yield: 0.08 g, 58.4%. IR ($\tilde{\nu}$, CH_2Cl_2): 2213 (s, $C\equiv N$). ^1H NMR (δ, $(CD_3)_2CO$): 7.90 (m, Ph), 7.35 (m, Ph), 3.43 (m, PCH_2), 2.26 (s, CH_3). $^{31}P\{^1H\}$ NMR (δ, $(CD_3)_2CO$): 30.05 (s, $P_{Cl-trans}$, $^1J_{Pt-P} = 3286$ Hz), 44.64 (s, $P_{C-trans}$, $^1J_{Pt-P} = 2912$ Hz). ^{19}F NMR (δ, $(CD_3)_2CO$): −100.24 (m, *o*-F), −124.88, −125.35 (m, *p*-F), −141.27, −142.98 (m, *m*-F), −151.98 (s, BF_4^-).

(i) Synthesis of $[PtCl(CN\text{-}2,6\text{-}(CH_3)_2C_6H_3)(4Fdppe)][BF_4]$ (7). This compound was prepared using a procedure similar to that described above for complex **5**, starting from $[PtCl_2(4Fdppe)]$ (0.13 g, 0.14 mmol). Yield: 0.11 g, 70.4%. IR ($\tilde{\nu}$, CH_2Cl_2): 2215 (s, $C\equiv N$). ^1H NMR (δ, $CDCl_3$): 7.33 (m, Ph), 3.13 (m, PCH_2), 2.35 (s, CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 26.28 (s, $P_{Cl-trans}$, $^1J_{Pt-P} = 3304$ Hz), 45.10 (s, $P_{C-trans}$, $^1J_{Pt-P} = 2925$ Hz). ^{19}F NMR (δ, $CDCl_3$): −125.54, −126.63 (m, *o*-F), −133.52, −134.85 (m, *p*-F), −143.60, −143.71 (m, *m*-F), −151.08 (m, *m*-F), −152.59 (s, BF_4^-).

(j) Synthesis of $[PtCl(CN\text{-}2,6\text{-}(CH_3)_2C_6H_3)(dfppe)][BF_4]$ (8). To a suspension of $[PtCl_2(dfppe)]$ (0.25 g, 0.24 mmol) in acetone (5 mL) and dichloromethane (50 mL) was added, with stirring, 0.28 mL (0.24 mmol) of a 1.0 M acetone solution of $AgBF_4$. The reaction mixture was stirred under nitrogen for 20 min, and the solid AgCl that formed was filtered off. To the solution was added 2,6-dimethylphenyl isocyanide (0.03 g, 0.24 mmol), and this mixture was stirred at room temperature for 2 h. It was then concentrated under vacuum and treated with Et_2O. The white solid that precipitated was filtered off, washed with Et_2O, and dried under vacuum. Yield: 0.11 g, 37.0%. IR ($\tilde{\nu}$, CH_2Cl_2): 2221 (s, $C\equiv N$). $^{31}P\{^1H\}$ NMR (δ, $(CD_3)_2CO$): 8.3 (s, $P_{Cl-trans}$, $^1J_{Pt-P} = 3368$ Hz), 26.3 (s, $P_{C-trans}$, $^1J_{Pt-P} = 2929$ Hz). ^{19}F NMR (δ, $(CD_3)_2CO$): −127.0 (d, *o*-C_6F_5, $^3J_{F-F} = 20.9$ Hz), −128.6 (d, *o*-C_6F_5, $^3J_{F-F} = 10.4$ Hz), −144.5 (t, *p*-C_6F_5, $^3J_{F-F} = 19.8$ Hz), −145.2 (t, *p*-C_6F_5, $^3J_{F-F} = 19.8$ Hz), −160.0 (pseudo t, *m*-C_6F_5, $^3J_{F-F} = 19.6$ Hz), −160.6 (pseudo t, *m*-C_6F_5, $^3J_{F-F} = 19.6$ Hz), −153.5 (s, BF_4^-).

(k) Synthesis of $[PtCl(CN\text{-}2,6\text{-}(CH_3)_2C_6H_3)(dppe)][BF_4]$ (9). This compound was prepared using a procedure similar to that described above for complex **8**, starting from $[PtCl_2(dppe)]$ (0.40 g, 0.60 mmol). Yield: 0.48 g, 94.0%. IR ($\tilde{\nu}$, CH_2Cl_2): 2208 (s, $C\equiv N$). IR ($\tilde{\nu}$, PE): 314 (s, Pt−Cl). ^1H NMR (δ, $CDCl_3$): 7.0−8.0 (m, Ph), 2.5−3.3 (m, CH_2), 2.05 (s, CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 44.0 (d, $P_{Cl-trans}$, $^1J_{Pt-P} = 3166$ Hz, $^2J_{P-P} = 6.6$ Hz), 45.9 (d, $P_{C-trans}$, $^1J_{Pt-P} = 2844$ Hz, $^2J_{P-P} = 6.6$ Hz).

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, 50, 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 vs 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 solid form in the reactor, which was evacuated and filled with N_2. Purified, N_2-saturated substrate was added under N_2 flow, followed by the required amount of 1,2-dichloromethane. After thermostating at the required temperature for a few minutes, the H_2O_2 solution in the appropriate amount was injected through the septum, and the 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.

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