

Second-Generation Electron-Poor Platinum(II) Complexes as Efficient Epoxidation Catalysts for Terminal Alkenes with Hydrogen Peroxide

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The preparation and characterization of second-generation electron-poor Pt(II) complexes of general formula [(P–P)Pt(C₆F₅)(H₂O)][X], **1a–h** (P–P = diphosphine, X = BF₄, OTf), bearing a pentafluorophenyl ligand is reported. The complexes are investigated as catalysts in the epoxidation of alkenes with hydrogen peroxide in a chlorinated solvent/H₂O two-phase system. The effects of the P–P ligands and of the Lewis acidity of the metal species are discussed with respect to the catalytic activity in the epoxidation reaction.

Introduction

Epoxides represent important commodities and, at the same time, pivotal building blocks for organic synthesis, from both the industrial and academic points of view.¹ In recent years, their extensive use has prompted the development of a plethora of efficient and selective methods for the epoxidation of alkenes under heterogeneous² and homogeneous³ conditions, the latter being generally characterized by better selectivities.

Among the many terminal oxidants available for this oxidation reaction, hydrogen peroxide has attracted the attention of many research groups due to its many advantages, such as low cost, environmentally friendly character,⁴ being a waste-avoiding oxidant,⁵ and high atom efficiency,⁶ which are all fundamental features for practical applications.⁷

It is noteworthy that most of the known catalytic homogeneous systems making use of “green” oxidants such as hydrogen peroxide are usually applied toward electron-rich olefins such as di- and trisubstituted C=C or di- and trisubstituted electron-poor alkenes.³ On the contrary, simple terminal monosubstituted alkenes, which are much less reactive but more interesting for industry, have been far less successfully investigated and still rely on a few efficient catalysts, the most notable one being TS1.⁸ Styrene derivatives and allylic alcohols are not included in this category of substrates, the former because of their particular reactivity imparted by the aromatic ring, and the latter for the presence of the hydroxyl group, which allows easy coordination to the active site.⁹

Focusing on homogeneous systems employing “green” terminal oxidants such as hydrogen peroxide for alkene epoxidation, examples of organocatalysis¹⁰ can be found, but they require relatively high catalyst loading, while for metal-catalyzed epoxidation noteworthy examples are based on W(VI),^{11–14} Mn(II),¹⁵ Re(V),¹⁶ Fe(III),^{17,18} and V(III). Very recently, bis-(μ -hydroxo)-bridged di-vanadium species implemented in a peroxotungstate framework showed high selective and efficient H₂O₂ epoxidation of alkenes, in particular toward terminal alkenes.¹⁹

Several years ago we described the synthesis of electron-poor Pt(II) diphosphine complexes, characterized by the presence of an electron-withdrawing trifluoromethyl ligand, and found that these complexes were very efficient in the activation of aqueous hydrogen peroxide toward the selective epoxidation of terminal alkenes under mild catalytic condition.²⁰ Kinetic studies indicated that this unusual reactivity was due to the ability of Pt(II) to increase the nucleophilicity of the olefin by

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(1) van Leeuwen, P. W. N. M. *Homogeneous Catalysis*; Kluwer Academic Publishers: Dordrecht, 2004.

(2) For review articles: (a) De Vos, D. E.; Sels, B. F.; Jacobs, P. A. *Adv. Synth. Catal.* **2003**, 345, 457. (b) Lambert, R. M.; Williams, F. J.; Copley, R. L.; Palermo, A. J. *Mol. Catal. A* **2005**, 228, 27.

(3) Lane, B. S.; Burgess, K. *Chem. Rev.* **2003**, 103, 2457.

(4) Strukul, G., Ed. *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*; Kluwer Academic: Dordrecht, The Netherlands, 1992.

(5) Grigoropoulou, G.; Clark, J. H.; Elings, J. A. *Green Chem.* **2003**, 5, 1–7.

(6) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 259–281.

(7) Noyori, R.; Aoki, M.; Sato K. *Chem. Commun.* **2003**, 1977–1986.

(8) Notari, B. *Catal. Today* **1993**, 18, 63, and references therein.

(9) Adam, W.; Wirth, T. *Acc. Chem. Res.* **1999**, 32, 703.

(10) Shu, L.; Shi, Y. *J. Org. Chem.* **2000**, 65, 8807.

(11) (a) Noyori, R.; Aoki, M.; Sato, K. *Chem. Commun.* **2003**, 1977.

(b) Sato, K.; Aoki, M.; Ogawa, M.; Hashimoto, T.; Noyori, R. *J. Org. Chem.* **1996**, 61, 8310.

(12) (a) Venturello, C.; Alneri, E.; Ricci, M. *J. Org. Chem.* **1983**, 48, 3831. (b) Venturello, C.; D'Aloisio, R. *J. Org. Chem.* **1988**, 53, 1553.

(13) (a) Murphy, A.; Pace, A.; Stack, T. D. P. *Org. Lett.* **2004**, 6, 3119.

(b) Murphy, A.; Dubois, G.; Stack, T. D. P. *J. Am. Chem. Soc.* **2003**, 125, 5250. (c) Banfi, S.; Montanari, F.; Quici, S.; Barkanova, S. V.; Lakiya, O. L.; Kopranenkov, V. N.; Luk'yanets, E. A. *Tetrahedron Lett.* **1995**, 36, 2317.

(14) Mizuno, N.; Yamaguchi, K.; Kamata, K. *Coord. Chem. Rev.* **2005**, 249, 1944.

(15) De Vos, D. E.; Sels, B. F.; Reynaers, M.; Subba Rao, Y. V.; Jacobs, P. A. *Tetrahedron Lett.* **1998**, 39, 3221.

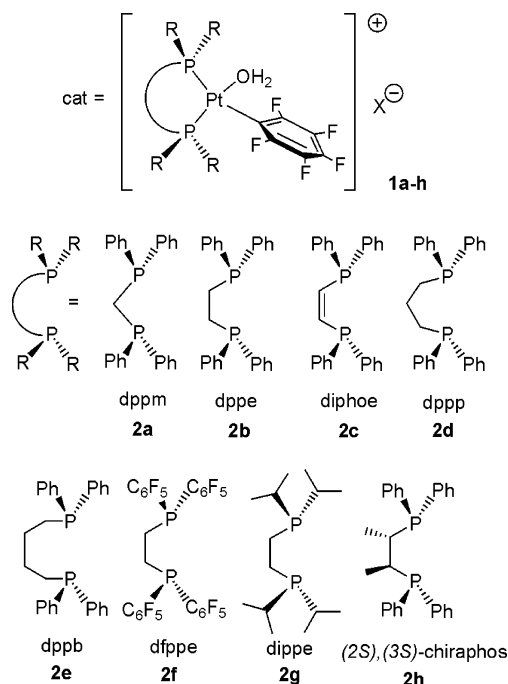
(16) (a) Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, 119, 6189. (b) Copéret, C.; Adolfsson, H.; Sharpless, K. B. *Chem. Commun.* **1997**, 1565.

(17) Dubois, G.; Murphy, A.; Stack, T. D. *Org. Lett.* **2003**, 5, 2469.

(18) White, M. C.; Doyle, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2001**, 123, 7194.

(19) Nakagawa, Y.; Kamata, K.; Kotani, M.; Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2005**, 44, 5136.

(20) (a) Baccin, C.; Gusso, A.; Pinna, F.; Strukul, G. *Organometallics* **1995**, 14, 1161. (b) Strukul, G.; Michelin, R. A. *J. Am. Chem. Soc.* **1985**, 107, 7563. (c) Zanardo, A.; Michelin, R. A.; Pinna, F.; Strukul, G. *Inorg. Chem.* **1989**, 28, 1648.

Scheme 1. New, Second-Generation Monocationic Pt(II) Complexes 1a–h

coordination, thereby changing the traditional electrophile/nucleophile roles in the system.^{20d}

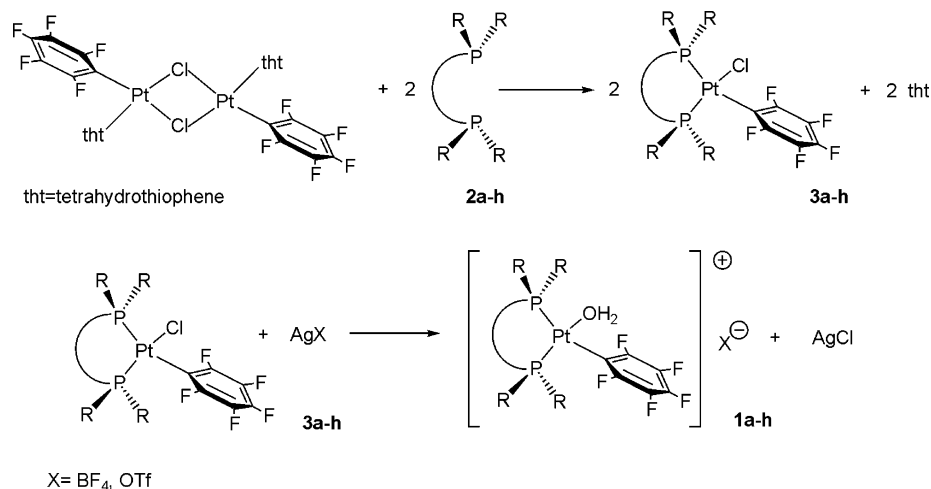
In this work we present the synthesis of second-generation Pt(II) complexes with general structure $[(\text{P}-\text{P})\text{Pt}(\text{C}_6\text{F}_5)(\text{H}_2\text{O})][\text{X}]$, **1a–h** ($\text{P}-\text{P}$ = diphosphine, $\text{X} = \text{BF}_4$, OTf), bearing the more bulky electron-withdrawing perfluorophenyl ligand (Scheme 1), and the employment of these new complexes as catalysts in the epoxidation of alkenes with hydrogen peroxide. This choice allows a more straightforward and versatile preparation method with respect to the old complexes and the possibility to evaluate the influence on the reactivity of a bulky ligand in close proximity of the vacant coordination site.

Results and Discussion

Synthesis of Complexes. The Lewis acid character of metal complexes is a key issue in the activation of oxidants for catalytic oxygen transfer reactions,²¹ and in our studies we observed several times that in oxidation processes high activity correlates well with high Lewis acidity of metal catalysts. This

applies to both epoxidation²⁰ and Baeyer–Villiger oxidation of ketones.^{22,23} Spurred by this general observation we decided to prepare a homologous series of Pt(II) complexes **1a–h** (Scheme 1), bearing a pentafluorophenyl group and different diphosphine ligands **2a–h**, aiming at elucidating the effect of both the activity and selectivity toward alkene epoxidation. Recently, similar complexes bearing alkyl diphosphines were reported in the literature,²⁴ and now we have extended the procedure to a wide range of diphosphine ligands, following and, in some cases, adapting and improving the previously published procedure (Scheme 2). The latter is a very flexible synthetic pathway that allows the preparation of homologous complexes with a wide variety of diphosphine ligands, at variance with the old complexes, where the introduction of the $-\text{CF}_3$ ligand was quite elaborate, hampering the desired synthetic flexibility.²⁰ The diphosphine ligands employed are commercially available except for **2g**, which was prepared following a procedure reported in the literature.²⁵ The synthesis started with the preparation of the dimeric species $[\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{F}_5)(\text{tht})]_2$ (tht = tetrahydrothiophene) by means of lithium aryl reaction on $[\text{PtCl}_2(\text{tht})]_2$.²⁶ Treatment of the binuclear complex in dichloromethane with 2 equiv of the corresponding diaryl diphosphine **2a–h** led in all cases to the formation of the neutral complexes $[(\text{P}-\text{P})\text{Pt}(\text{C}_6\text{F}_5)\text{Cl}]$ **3a–h** in good to high yields (70–99%). In the reaction with ligand **2a** we observed the formation of a byproduct, whose $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) spectrum showed a singlet at 10.53 ppm flanked by ^{195}Pt satellites ($^1J_{\text{P-Pt}} = 2594$ Hz). This impurity can be readily removed by treating the mixture with chloroform, followed by filtration of the solution containing the pure product.

Subsequent abstraction of the halide ligand from **3a–h** in dichloromethane using a wet acetone solution of AgX ($\text{X} = \text{BF}_4$ or OTf) produced the corresponding aquo complexes of general formula $[(\text{P}-\text{P})\text{Pt}(\text{C}_6\text{F}_5)(\text{H}_2\text{O})][\text{X}]$, **1a–h**, in good to high yields (70–98%). After filtration of AgCl , they were isolated as white solids upon addition of *n*-pentane. It is worth noting that we did not observe any disproportionation reaction to form the diaryl complex $[(\text{P}-\text{P})\text{Pt}(\text{C}_6\text{F}_5)_2]$, as reported in the case of $[(\text{dmpe})\text{Pt}(\text{C}_6\text{F}_5)\text{Cl}]$ (dmpe = 1,2-bis(dimethylphosphino)ethane) upon treatment with AgOTf .²⁴ $^{31}\text{P}\{^1\text{H}\}$ NMR data support the chelate structure of the monomeric complex **1a** due to the observation of only one set of signals, in contrast with previous findings related to the analogous reaction involving the CF_3 complex $[(\text{dppm})\text{Pt}(\text{CF}_3)(\text{OH})](\text{OTf})$, where, along with the monomeric species, two more dinuclear species were present

Scheme 2. Synthesis of the Pt(II) Monocationic Catalysts 1a–h Bearing a Perfluorophenyl Residue

differing in the relative orientation of trifluoro methyl and hydroxy residues in the dimer.^{20c}

The complexes [(P-P)Pt(C₆F₅)Cl] (**3a–h**) and [(P-P)Pt(C₆F₅)(H₂O)][X] (X = BF₄, OTf) (**1a–h**) with P–P = dpmm (**2a**), dppe (**2b**), diphoe (**2c**), dppp (**2d**), dppb (**2e**), dfppe (**2f**), dippe (**2g**), and (2*S*),(3*S*)-chiraphos (**2h**) are all new compounds and were characterized by elemental analysis and multinuclear ¹H, ³¹P{¹H}, and ¹⁹F{¹H} NMR spectroscopy, as reported in the Experimental Section.

³¹P{¹H} NMR spectra of chloride complexes **3a–h** show, as expected, two different P resonances. The P atom *trans* to chlorine appears as a singlet or a doublet (due to P–P coupling) depending on the type of the diphosphine, with ¹J_{P–Pt} values in the range 3300–3800 Hz. In the case of the P atom *trans* to the pentafluorophenyl group the corresponding resonances showed more complex multiplicity due to coupling with the fluorine atoms of the C₆F₅ ligand. The observed P–Pt coupling constants are found in the range 1800–2200 Hz (significantly lower than those *trans* to chlorine), owing to the higher *trans* influence of the aryl ligand.²⁷

The aquo complexes **1a–h** showed clearly, in the ¹H NMR spectra, the presence of bound water that fall in the range 2.7–2.8 ppm. In the ³¹P NMR spectra we observed similar multiplicity of the P resonances compared to the previously described chloride derivatives **3a–h**, but significant changes of the ¹J_{P–Pt} values for the P atom *trans* to H₂O were observed, which now fall in the range 3800–4700 Hz, the lowest value belonging to complex **1a**, while the highest to **1f**. The observed increase in the coupling constants can be explained with the lower *trans* influence of the aquo ligand compared to chloride. Again different ¹J_{P–Pt} values were observed for the various diphosphines, reflecting a different electron-withdrawing character of the ligands.²⁸

Catalytic Epoxidation. The scope of the reaction with respect to substrate properties was briefly investigated with triflate catalyst **1b**, exploring its reactivity toward different C=C double bonds.

As can be seen from Table 1, only the terminal alkene 1-hexene is a suitable substrate (89% epoxide yield), while with styrene the reaction is sluggish, and even at higher temperature low conversion is observed. Disubstituted alkenes such as cyclohexene or methylenecyclohexane, being more electron-rich substrates, are both not oxidized. This substrate specificity is in agreement with what was observed with first-generation Pt(II) epoxidation complexes bearing a –CF₃ residue instead of –C₆F₅.²⁹ In our previous paper using –CF₃ derivatives³⁰ we suggested olefin coordination as the key feature toward oxidation. Given the electronic analogies with the present catalysts,

Table 1. Catalytic Epoxidation of Different Categories of Alkenes with Hydrogen Peroxide Mediated by **1b**^a

Substrate	Time (h)	Epoxide yield (%)	TON
	24	4	2
	24	0	0
	24	0	0
	5	89	44

^a Experimental conditions: [substrate]₀ = 0.83 mmol, [H₂O₂]₀ = 0.83 mmol, [**1b**]₀ = 0.0166 mmol (2%), solvent 1 mL of DCE at RT.

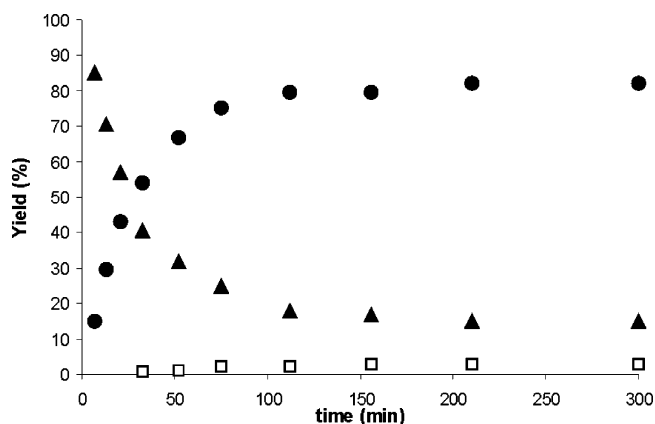


Figure 1. Epoxidation of 1-octene with 35% hydrogen peroxide mediated by **1b**: 1-octene (▲), 1,2-epoxyoctane (●), heptanal (□). Experimental conditions: [1-octene]₀ = 0.83 mmol, [H₂O₂]₀ = 0.83 mmol, [**1b**]₀ = 0.0166 mmol (2%), solvent 1 mL of DCE at RT.

we tend to assume that, in the present case, the reaction occurs with similar features. However, these results may also suggest the existence of a strong steric effect in this kind of oxidation reaction, conceivably due to the narrow space available between the aryl groups of the diphosphine ligand and the perfluoro aromatic ligand to activate the substrate by displacement of the water molecule. As a consequence, only terminal alkenes are able to easily sneak in and reach the Pt(II) active species.

Further investigations were carried out on 1-octene comparing the activity of all the aquo complexes (**1a–h**) prepared. A typical reaction profile is shown in Figure 1, while a summary of the catalytic properties of the different complexes is collected in Table 2.

Weakly coordinating counteranions do not influence the catalytic activity (entries 2, 3), while only hydrogen peroxide emerges as the best oxidant (entries 3, 5, 6). The diphosphine ligand plays a major role, with the best results observed with **1b**, while the more electron-deficient ligand **2f** as well as the sterically crowded ligand **2g** suppress the activity (**1f** and **1g** are both sparingly soluble in 1,2-dichloroethane; therefore addition of 4% methanol for complete solubilization was required). Indeed, the presence of methanol might alter the catalytic properties of the complexes. For this reason we also carried out a test with **1b** as catalyst using the same 4% methanol in dichloroethane reaction medium. The results (entry 4 in Table 2) clearly indicate that such a change in the solvent polarity does not significantly alter either the activity or the productivity of the catalyst,

(21) (a) Corma, A.; Garcia, H. *Chem. Rev.* **2003**, *103*, 4307–4366. (b) Corma, A.; Garcia, H. *Chem. Rev.* **2002**, *102*, 3837–3892. (c) Strukul, G. *Top. Catal.* **2002**, *19*, 33.

(22) Michelin, R. A.; Pizzo, E.; Scarso, A.; Sgarbossa, P.; Strukul, G.; Tassan, A. *Organometallics* **2005**, *24*, 1012–1017.

(23) Brunetta, A.; Strukul, G. *Eur. J. Inorg. Chem.* **2004**, *5*, 1030–1038.

(24) Hughes, R. P.; Ward, A. J.; Golen, J. A.; Incarvito, C. D.; Rheingold, A. L.; Zakharov, L. N. *J. Chem. Soc., Dalton Trans.* **2004**, 2720.

(25) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185.

(26) (a) Uson, R.; Fornies, J.; Espinet, P.; Alfranca, G. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 597. (b) Uson, R.; Fornies, J.; Martinez, F.; Tomas, M. J. *J. Chem. Soc., Dalton Trans.* **1980**, 888.

(27) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

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

(29) Strukul, G.; Michelin, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1538.

(30) Zanardo, A.; Pinna, F.; Michelin, R. A.; Strukul, G. *Inorg. Chem.* **1988**, *27*, 1966–1973.

Table 2. Catalytic Epoxidation of 1-Octene with Hydrogen Peroxide Mediated by Pt(II) Complexes 1a–h^a

entry	catalyst	oxidant	time (h)	yield (%)	TON	initial rate $\times 10^6$ (M·s ⁻¹)
1	1a ·CF ₃ SO ₃	H ₂ O ₂	6	39	20	25
2	1b ·BF ₄	H ₂ O ₂	4	81	40	280
3	1b ·CF ₃ SO ₃	H ₂ O ₂	4	80	40	315
4	1b ·CF ₃ SO ₃ ^d	H ₂ O ₂	6	74	37	305
5	1b ·CF ₃ SO ₃	UHP ^b	24	2	1	
6	1b ·CF ₃ SO ₃	<i>t</i> -BuOOH	24	0	0	
7	1c ·CF ₃ SO ₃	H ₂ O ₂	5	70	35	191
8	1d ·CF ₃ SO ₃	H ₂ O ₂	24	6	3	22
9	1e ·CF ₃ SO ₃ ^c	H ₂ O ₂	3	14 ^c	7	61
10	1f ·CF ₃ SO ₃ ^d	H ₂ O ₂	24	1	0.5	
11	1g ·CF ₃ SO ₃ ^d	H ₂ O ₂	24	2	1	
12	1h ·CF ₃ SO ₃ ^e	H ₂ O ₂	4	73	36	180

^a Experimental conditions: [1-octene]₀ = 0.83 mmol, [oxidant]₀ = 0.83 mmol [cat]₀ = 0.0166 mmol (2%), solvent 1 mL of DCE at RT. ^b Urea hydrogen peroxide adduct; ^c 24% of alkene isomerization to *cis*- and *trans*-2-octene; ^d DCE/MeOH, 96:4. ^e ee 64% determined by ¹H NMR integration in the presence of the chiral shift reagent europium tris[3-(heptafluoropropyl)hydroxymethylene]-(+)-camphorate] at RT.

suggesting that the low conversions observed for **1f** and **1g** are due to their intrinsic electronic and/or steric properties.

The spacer between the P atoms in the diphosphines influences the catalytic activity (Table 2) with a marked decrease in conversion both with the small diphosphine **2a** and with large diphosphines **2d** and **2e**. Surprisingly in the latter case, a concurrent isomerization to internal *cis*- and *trans*-2-octene takes place. The latter products are not reactive under the experimental conditions used, being disubstituted alkenes (Table 1). The parasitic alkene isomerization reaction is activated by the catalysts (no reaction occurs in their absence under the same conditions); in particular with complex **1e** this side reaction reaches 24% of 1-octene conversion, while with the other complexes it never exceeds 1–3%. Increasing the rigidity of the catalyst from **1b** to **1c** decreases the catalytic activity, at variance with what was observed in the past with similar catalysts, where diphoe **2c** ensured the highest activity and productivity.^{20c} With the most active complexes **1b** a byproduct due to overoxidation of the oxirane ring starts being observed only at high epoxide concentrations. At the end of the reaction 3% heptanal (confirmed by NMR and GC-MS analysis) was observed. It is worth noting that with ligand **2h** a chiral complex **1h** is obtained, only slightly lower in activity and productivity compared to **1b**. This chiral complex affords 1-octene epoxide with 64% ee at RT. This value is particularly interesting in view of the few enantioselective epoxidation catalysts known for terminal alkenes.³¹

With ligands **2b**, **2d**, and **2e** the activity for first- and second-generation complexes parallels well,^{20c} with a similar decrease in activity, even though the former complexes bearing –CF₃ residues are intrinsically more reactive probably because of a lower steric hindrance with respect to the –C₆F₅ counterparts.

Determination of the Lewis Acidity of 1a–h and Correlation with Their Catalytic Activity. The electron-withdrawing ability of the pentafluorophenyl ligand and the concomitant effect of the diphosphine ligands should influence the Lewis acidity of complexes **1a–h**. To assess whether there is a qualitative correlation between the catalytic activity and their Lewis acid character, 2,6-dimethyl phenylisocyanide was used as a molecular probe. In fact, the value of the wavenumber shift ($\Delta\bar{\nu}$ = $\bar{\nu}(\text{C}\equiv\text{N})_{\text{coord}} - \bar{\nu}(\text{C}\equiv\text{N})_{\text{free}}$) for the C≡N stretching of 2,6-

Table 3. ¹J_{P–Pt} Coupling Constants for Complexes [(P–P)Pt(C₆F₅)(H₂O)](OTf), $\Delta\bar{\nu}$ (cm⁻¹) of 2,6-Dimethyl Phenylisocyanide Derivatives Prepared in Situ by Water Exchange, and $\Delta\delta$ (ppm) for Ligands 2a–h

ligand	¹ J _{P–Pt} (<i>trans</i> to H ₂ O) (Hz)	$\Delta\bar{\nu}$ (cm ⁻¹)	$\Delta\delta$ (ppm)
2a	3821	82.72	–26.02
2b	4353	78.91	45.47
2c	4440	80.95	55.74
2d	4148	78.20	6.61
2e	4530	77.10	32.16
2f	4712	93.22	33.29
2g	4284	71.68	49.12
2h	4272	78.67	40.18

dimethyl phenylisocyanide provides valuable information about the electrophilicity of the isocyanide carbon atom, which is known to correlate well to the Lewis acidity of the metal complex.³² This approach was recently employed successfully on other Pt(II) complexes bearing partially fluorinated aryl diphosphine used as catalysts in the Baeyer–Villiger oxidation of cyclic ketones to the corresponding lactones with hydrogen peroxide.²²

On this basis, we prepared in situ a homologous series of isocyanide complexes of general formula [Pt(C₆F₅)(CN-2,6-(CH₃)₂C₆H₃)(P–P)](OTf) (P–P = **2a–h**) by simple addition of a stoichiometric amount of 2,6-dimethyl phenylisocyanide to a solution of the aquo complexes **1a–h**.

In Table 3 the $\Delta\bar{\nu}$ for the different complexes are reported, from which, at first sight, it is evident that the fluorinated complex **1f** is characterized by the highest Lewis acidity, while **1g** is the least acidic because of the presence of more electron-donating alkyl residues on the P atoms. All the other complexes fall in a narrow $\Delta\bar{\nu}$ range, suggesting similar Lewis acidity. However, some moderate differences are present, presumably due to the bite angle and steric properties of the different ligands. More in detail, upon increasing the size of the metal–diphosphine ring, $\Delta\bar{\nu}$ moderately decreases, suggesting a decrease in the Lewis acidic character of the metal center. Chiral ligand **2h** produces effects similar to those of **2b**, while the presence of a double bond as in **2c** slightly increases the Lewis acidity of the complex.

In an attempt to compare the catalytic activity (initial rate of epoxidation) with the Lewis acidity determined as above, the lack of direct correlation is quite evident (Figure 2). Unreactive complexes such as **1g** and **1f** are respectively the least and the most acidic of the series. It must be remembered that, because of solubility problems, the conditions in which these complexes were tested cannot directly compare to the other ones. However, we have also demonstrated that the different solvent should not significantly change their catalytic properties. Complex **1b**, which is the most active and productive, is characterized by an intermediate $\Delta\bar{\nu}$ value. Even though **1b** shows similar Lewis acidity compared to many other complexes, the reactivity of the latter is very different and probably dependent on the different ring size, bite angle, and substituents of the complexes under investigation. Moreover, **1d** and **1h**, which are very similar in acidity with respect to **1b**, are much less active. On this basis, the Lewis acidic character gives only very rough indications and does not appear to be a sufficient parameter to rationalize the reactivity within this class of complexes. Other properties, in particular steric requirements, may have a strong influence. Clearly, simple Lewis acidity determination by means of 2,6-dimethyl phenylisocyanide cannot take them into account.

(31) (a) Sinigaglia, R.; Michelin, R. A.; Pinna, F.; Strukul, G. *Organometallics* **1987**, *6*, 728. (b) Collman, J. P.; Wang, Z.; Straumanis, A.; Quelquejeu, M. J. *Am. Chem. Soc.* **1999**, *121*, 460. (c) Matsumoto, K.; Sawada, Y.; Saito, B.; Sakai, K.; Katsuki, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 4935. (d) Valodkar, V. B.; Tembe, G. L.; Ram, R. N.; Rama, H. S. *Catal. Lett.* **2003**, *90*, 91.

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

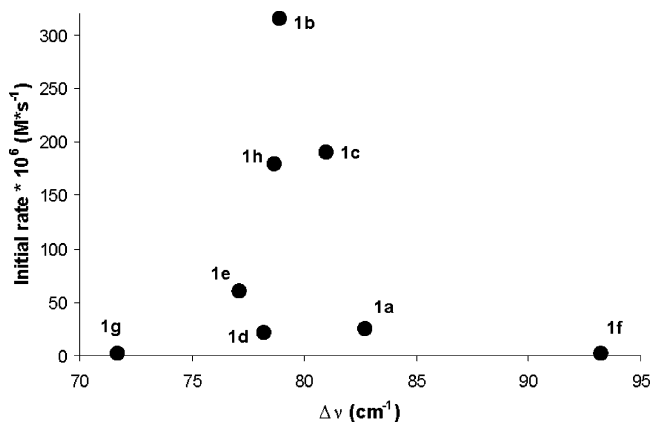


Figure 2. Plot of the initial rates of epoxidation of 1-octene catalyzed by complexes **1a–h** vs the $\Delta\nu$ values (cm⁻¹) of 2,6-dimethyl phenylisocyanide coordinated to the complexes **1a–h**. Experimental conditions as in Table 2.

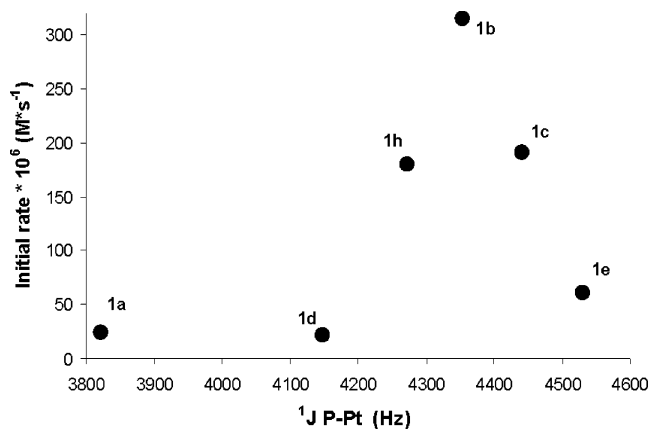


Figure 3. Plot of the initial rates of epoxidation of 1-octene catalyzed by complexes **1a–h** vs the $^1J_{P-Pt}$ (Hz) *trans* to the water ligand of the complexes. Experimental conditions as in Table 2.

We searched for another qualitative correlation between activity and spectroscopic properties of the complexes. Analysis of $^1J_{P-Pt}$ coupling constants for the P atom *trans* to the solvent molecule (Table 3) provides an indication of the lability of the latter and can be assumed as an indication of the availability of the metal for binding the reaction substrates.²⁷ Complex **1a** shows the smallest $^1J_{P-Pt}$, indicative of strong binding of the water molecule, which results in a sluggish epoxidation reaction. Considering complexes with increasing values of $^1J_{P-Pt}$ (decreasing water binding affinity), a gradual increase of reactivity up to complex **1b** is observed, followed by a decrease, giving a plot (Figure 3) with a maximum centered on **1b**. This behavior reflects the fact that if the complex coordinates the water molecule too strongly (small $^1J_{P-Pt}$), the latter is hardly available for exchange with the substrate, and analogously if the water molecule binds too weakly (large $^1J_{P-Pt}$), it is conceivable that also the substrate will bind weakly. An intermediate value of $^1J_{P-Pt}$ is the optimum, as observed by the profile reported in Figure 3. This plot strongly resembles the volcano curves relating chemisorption to catalytic activity in heterogeneous-catalysis.³³ Of course, $^1J_{P-Pt}$ values refer to water coordination and not alkene, which is much more sterically demanding.

³¹P NMR investigation of $\Delta\delta$ ($\delta_{\text{coord}} - \delta_{\text{free}}$) for the P atom *trans* to water in **1a–h** compared to P resonances of the free **2a–h** ligands provided more arguments to address the problem.

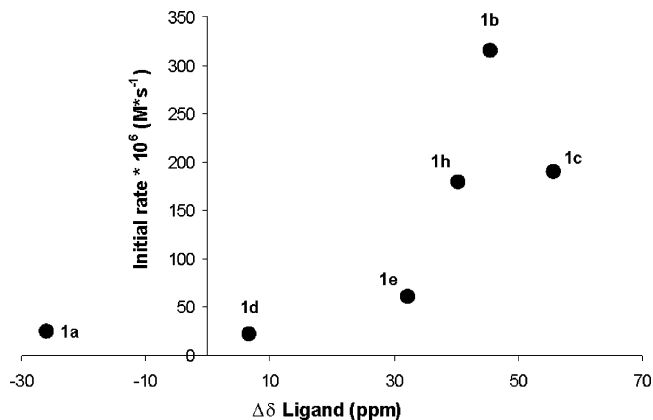


Figure 4. Plot of the initial rates of epoxidation of 1-octene catalyzed by complexes **1a–h** vs the $\Delta\delta$ values for free and coordinated ligands **2a–h**. Experimental conditions as in Table 2.

This difference can be ascribed basically to the shielding effect on P due to the metal and the C₆F₅ ligand upon coordination, significantly reflecting both conformational changes and steric interactions. Ligand **2a** upon complexation experiences an unexpected increase in shielding, probably due to the formation of the strained four-membered ring with the metal center. All other complexes are characterized by a deshielding at P (positive $\Delta\delta$); in particular $\Delta\delta$ increases strongly in **1b** and **1c**, which form five-membered rings with Pt,³⁴ it increases only slightly in the six-membered ring complex **1d**, and it increases further with the seven-membered ring complex **1e**. This clearly indicates that the size of the formed ring, the bite angle, and other conformational and steric features have an effect on the ³¹P chemical shift of the ligand. Figure 4 shows the correlation between the initial rates of epoxidation of 1-octene with the $\Delta\delta$ values for the investigated complexes. Starting from complex **1a**, which is a weak Lewis acid, there is a clear increase in activity on going from **1d** to **1h** to **1b**. On the contrary, **1c**, which is characterized by the highest $\Delta\delta$, is less active than **1b** probably because of the increased rigidity imparted by the alkene spacer between the P atoms, but, over long reaction times, it showed a productivity similar to **1b**. This results again in a plot with a maximum for **1b** (Figure 4).

The general picture that arises from these considerations clearly speaks for an epoxidation reaction catalyzed by Pt(II) complexes where both the steric hindrance of the ligand as well as the ability to exchange water play a key role, with five-membered ring complexes as the most active catalysts. Among others, complex **1b** emerges as the most active one and the chiral version **1h** only slightly less productive.

No clear parallel is observed with the results reported in the past with the first-generation electron-poor Pt(II) complexes bearing the -CF₃ ligand of general formula [(P-Pt)(CF₃)(CH₂-Cl₂)]ClO₄.^{20c} In the latter complexes the order of activity observed as function of the ligand was **2c** > **2h** > **2b** > **2a** > **2d** > **2e**, while for -C₆F₅ complexes it is **2b** > **2c** ≈ **2h** > **2e** > **2a** > **2d**. In both cases, the most reactive complexes are those characterized by five-membered rings, while the ring size effect is not similar. This is not surprising because of the observed steric influence on reactivity. Clearly, the -CF₃ ligand is much less sterically demanding than -C₆F₅. Nevertheless, rates of epoxidation are similar between the two classes, while the overall turnover numbers are slightly better for the new class of complexes.^{20c}

(33) See for example: Bond, G. C. *Heterogeneous Catalysis: Principles and Applications*, 2nd ed.; Clarendon Press: Oxford, 1987.

(34) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

Conclusion

Herein we reported the synthesis and characterization of second-generation Pt(II) complexes **1a–h** containing a perfluorinated aryl ligand that proved to be highly active epoxidation catalysts with hydrogen peroxide as terminal oxidant. Remarkable features of the present catalytic system are the complete selectivity toward terminal alkenes and the high activity with low catalyst loading (2% mol) under very mild conditions, which allows reaction times of a few hours with no need of over-stoichiometric amounts of oxidant. The preliminary results obtained are highly encouraging and stimulate a more extensive investigation of the regio- and diastereoselectivity of the epoxidation process, as well as the need to get insight into the mechanistic aspects of catalysis. This new set of catalysts are characterized by a more straightforward preparation procedure compared to the first generation,²⁰ and this feature allows the extension of the system to the investigation of the chiral complex **1h** and similar congeners in the asymmetric epoxidation of terminal alkenes. These issues are currently under investigation.

Experimental Section

General Procedures and Materials. All synthetic steps were carried out under a dinitrogen atmosphere using standard Schlenck 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. The diphosphines 1,2-bis(dichlorophosphino)ethane, 1,1'-bis(diphenylphosphino)methane (**2a**; dppm), 1,2-bis(diphenylphosphino)ethane (**2b**; dppe), 1,2-bis(diphenylphosphino)ethylene (**2c**; diphoe), 1,3-bis(diphenylphosphino)propane (**2d**; dppp), 1,4-bis(diphenylphosphino)butane (**2e**; dppb), and 1,2-bis(dipentafluorophenylphosphino)ethane (**2f**; dfppe) were commercially available and were used as purchased. The diphosphine 1,2-bis(di-isopropylphosphino)ethane³⁵ (**2g**; dippe) and $[\text{Pt}(\text{C}_6\text{F}_5)(\mu\text{-Cl})(\text{tht})]_2$ ²⁵ were synthesized following procedures reported in the literature. Hydrogen peroxide (35% Fluka), $\text{MgCl}_2\cdot\text{Pr}$, AgBF_4 , and AgOTf were commercial products and used without purification.

IR spectra were taken in CH_2Cl_2 solution using CaF_2 windows using a FT-IR AVATAR 320 spectrophotometer from Nicolet Instrument Corporation; wavenumbers are given in cm^{-1} . Measurements were carried out in dichloromethane solutions of the aquo complexes treated with an excess of 2,6-dimethyl phenylisocyanide. ^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR, and ^{19}F NMR spectra were run on a Bruker AC200 spectrometer operating at 200.13, 81.015, and 188.25 MHz, respectively, at 298 K, unless otherwise stated; δ values in ppm are relative to $\text{Si}(\text{CH}_3)_4$, 85% H_3PO_4 , and CFCl_3 . GLC measurements were taken on a Hewlett-Packard 5890A gas chromatograph equipped with a FID detector (carrier gas He). Quenching of reaction samples was performed by addition of triphenyl phosphine. Identification of products was made with GLC and NMR by comparison with authentic samples. Elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of Università di Padova.

Synthesis. $[\text{PtCl}(\text{C}_6\text{F}_5)(\text{dppm})]$ (3a**).** To a solution of $[\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{F}_5)(\text{tht})]_2$ (0.11 g, 0.12 mmol) in acetone (20 mL) at room temperature was added 0.09 g (0.24 mmol) of dppm. The solution was stirred for 2 h, then was concentrated and treated with *n*-pentane, giving a white solid, which was filtered off and dried under vacuum. Yield: 0.132 g, 69%. Anal. Calc for $\text{C}_{31}\text{H}_{22}\text{ClF}_5\text{P}_2\text{Pt}$: C, 47.61; H, 2.84. Found: C, 47.87; H, 3.02. ^1H NMR (δ , CDCl_3): 7.26–7.80 (m, Ar), 4.43 (t, PCH_2 , $^2J_{\text{P-H}} = 8.5$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , CDCl_3): –51.07 (d, $\text{P}_{\text{Cl-trans}}$, $^1J_{\text{Pt-P}} = 3330$ Hz, $^2J_{\text{P-P}} = 58.9$ Hz); –51.48 (d, $\text{P}_{\text{C-trans}}$, $^1J_{\text{Pt-P}} = 1865$ Hz, $^2J_{\text{P-P}} =$

58.9 Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , CDCl_3): –120.19 (t, *o*-F, $^3J_{\text{Pt-F}} = 275$ Hz, $^3J_{\text{F-F}} = 40.7$ Hz), –162.60 (t, *p*-F, $^3J_{\text{F-F}} = 39.5$ Hz), –165.11 (m, *m*-F).

$[\text{PtCl}(\text{C}_6\text{F}_5)(\text{dppe})]$ (3b**).** This compound was prepared using a procedure similar to that described above for complex **3a** starting from $[\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{F}_5)(\text{tht})]_2$ (0.30 g, 0.31 mmol) in chloroform (30 mL) and 0.26 g (0.65 mmol) of dppe. Yield: 0.492 g, 100%. Anal. Calc for $\text{C}_{32}\text{H}_{24}\text{ClF}_5\text{P}_2\text{Pt}$: C, 48.28; H, 3.04. Found: C, 47.97; H, 2.91. ^1H NMR (δ , CDCl_3): 7.33–8.00 (m, Ar), 2.10–2.55 (m, PCH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , CDCl_3): 39.55 (d, $\text{P}_{\text{Cl-trans}}$, $^1J_{\text{Pt-P}} = 3722$ Hz, $^2J_{\text{P-P}} = 6.2$ Hz); 40.70 (d, $\text{P}_{\text{C-trans}}$, $^1J_{\text{Pt-P}} = 2256$ Hz, $^2J_{\text{P-P}} = 6.2$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , CDCl_3): –120.27 (t, *o*-F, $^3J_{\text{Pt-F}} = 268$ Hz, $^3J_{\text{F-F}} = 19.0$ Hz), –163.29 (t, *p*-F, $^3J_{\text{F-F}} = 20.7$ Hz), –165.16 (m, *m*-F).

$[\text{PtCl}(\text{C}_6\text{F}_5)(\text{diphoe})]$ (3c**).** This compound was prepared using a procedure similar to that described above for complex **3a** starting from $[\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{F}_5)(\text{tht})]_2$ (0.15 g, 0.16 mmol), dissolved in acetone (20 mL), and diphoe (0.13 g, 0.32 mmol). Yield: 0.154 g, 59%. Anal. Calc for $\text{C}_{32}\text{H}_{22}\text{ClF}_5\text{P}_2\text{Pt}$: C, 48.41; H, 2.79. Found: C, 47.98; H, 2.89. ^1H NMR (δ , CDCl_3): 7.37–7.87 (m, Ar), 5.30 (m, PCH). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , CDCl_3): 55.42 (m, $\text{P}_{\text{C-trans}}$, $^1J_{\text{Pt-P}} = 2289$ Hz); 46.49 (s, $\text{P}_{\text{Cl-trans}}$, $^1J_{\text{Pt-P}} = 3778$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , CDCl_3): –120.30 (m, *o*-F), –162.51 (m, *p*-F), –165.18 (m, *m*-F).

$[\text{PtCl}(\text{C}_6\text{F}_5)(\text{dppp})]$ (3d**).** This compound was prepared using a procedure similar to that described above for complex **3a** starting from $[\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{F}_5)(\text{tht})]_2$ (0.201 g, 0.21 mmol), dissolved in acetone (20 mL), and dppp (0.174 g, 0.42 mmol). Anal. Calc for $\text{C}_{33}\text{H}_{26}\text{ClF}_5\text{P}_2\text{Pt}$: C, 48.93; H, 3.24. Found: C, 48.81; H, 3.36. ^1H NMR (δ , CDCl_3): 7.13–7.80 (Ar); 2.02–2.89 (CH_2). ^{31}P NMR (δ , CDCl_3): –4.33 ($\text{P}_{\text{trans-Cl}}$, $J_{\text{Pt-P}} = 3605$ Hz, $J_{\text{P-P}} = 27$ Hz); –4.39 ($\text{P}_{\text{trans-C}}$, $J_{\text{Pt-P}} = 2081$ Hz). ^{19}F NMR (δ , CDCl_3): –120.29 (*o*-F), –164.10 (*p*-F), –165.34 (*m*-F).

$[\text{PtCl}(\text{C}_6\text{F}_5)(\text{dppb})]$ (3e**).** This compound was prepared using a procedure similar to that described above for complex **3a** starting from $[\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{F}_5)(\text{tht})]_2$ (0.15 g, 0.15 mmol) and dppb (0.14 g, 0.32 mmol). Yield: 0.24 g, 93.5%. Anal. Calc for $\text{C}_{34}\text{H}_{28}\text{ClF}_5\text{P}_2\text{Pt}$: C, 49.56; H, 3.42. Found: C, 49.87; H, 3.24. ^1H NMR (δ , $(\text{CD}_3)_2\text{SO}$): 7.24–7.74 (m, Ar), 1.37–2.99 (m, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , $(\text{CD}_3)_2\text{SO}$): 20.14 (d, $\text{P}_{\text{Cl-trans}}$, $^1J_{\text{Pt-P}} = 3776$ Hz, $^2J_{\text{P-P}} = 21.9$ Hz); 1.18 (m, $\text{P}_{\text{C-trans}}$, $^1J_{\text{Pt-P}} = 2149$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , $(\text{CD}_3)_2\text{SO}$): –118.71 (t, *o*-F, $^3J_{\text{Pt-F}} = 297$ Hz, $^3J_{\text{F-F}} = 19.6$ Hz), –164.42 (t, *p*-F, $^3J_{\text{F-F}} = 19.3$ Hz), –164.98 (m, *m*-F).

$[\text{PtCl}(\text{C}_6\text{F}_5)(\text{dfppe})]$ (3f**).** This compound was prepared using a procedure similar to that described above for complex **3a** starting from $[\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{F}_5)(\text{tht})]_2$ (0.20 g, 0.21 mmol) and dfppe (0.33 g, 0.43 mmol). Yield: 0.41 g, 86.3%. Anal. Calc for $\text{C}_{32}\text{H}_4\text{ClF}_{25}\text{P}_2\text{Pt}$: C, 33.25; H, 0.35. Found: C, 33.45; H, 0.54. ^1H NMR (δ , $(\text{CD}_3)_2\text{CO}$): 3.36–3.60 (m, PCH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , $(\text{CD}_3)_2\text{CO}$): 3.78 (s, $\text{P}_{\text{Cl-trans}}$, $^1J_{\text{Pt-P}} = 3799$ Hz); 23.29 (s, $\text{P}_{\text{C-trans}}$, $^1J_{\text{Pt-P}} = 2192$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , $(\text{CD}_3)_2\text{CO}$): –121.11 (t, $\text{Pt-C}_6\text{F}_5$, *o*-F, $^3J_{\text{Pt-F}} = 130$ Hz), –127.34, –129.38 (m, $\text{P-C}_6\text{F}_5$, *o*-F), –127.31 (m, $\text{P-C}_6\text{F}_5$, *p*-F), –164.42 (t, $\text{Pt-C}_6\text{F}_5$, *p*-F, $^3J_{\text{F-F}} = 19.3$ Hz), –161.31 (m, $\text{P-C}_6\text{F}_5$, *m*-F), –164.98 (m, $\text{Pt-C}_6\text{F}_5$, *m*-F).

$[\text{PtCl}(\text{C}_6\text{F}_5)(\text{dippe})]$ (3g**).** This compound was prepared using a procedure similar to that described above for complex **3a** starting from $[\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{F}_5)(\text{tht})]_2$ (0.35 g, 0.36 mmol) and dippe (0.20 g, 0.75 mmol). Yield: 0.30 g, 63.2%. Anal. Calc for $\text{C}_{20}\text{H}_{32}\text{ClF}_5\text{P}_2\text{Pt}$: C, 36.40; H, 4.89. Found: C, 36.23; H, 4.78. ^1H NMR (δ , CDCl_3): 2.20–2.72 (m, CH), 1.61–1.96 (m, PCH_2), 0.98–1.48 (m, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , CDCl_3): 66.94 (s, $\text{P}_{\text{Cl-trans}}$, $^1J_{\text{Pt-P}} = 3708$ Hz); 72.22 (m, $\text{P}_{\text{C-trans}}$, $^1J_{\text{Pt-P}} = 2292$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , CDCl_3): –119.01 (m, *o*-F), –162.92 (m, *p*-F), –164.69 (m, *m*-F).

$[\text{PtCl}(\text{C}_6\text{F}_5)((2\text{S}),(3\text{S})\text{-Chiraphos})]$ (3h**).** This compound was prepared using a procedure similar to that described above for complex **3a** starting from $[\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{F}_5)(\text{tht})]_2$ (0.204 g, 0.21 mmol) and (2S),(3S)-chiraphos (0.182 g, 0.43 mmol). Yield: 0.243 g, 70%. ^1H NMR (δ , CDCl_3): 7.08–7.98 (m, Ar), 2.01–2.58 (m,

(35) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, 3, 185.

PCH), 1.06–1.15 (m, CH₃). ³¹P{¹H} NMR (δ, CDCl₃): 39.45 (d, P_{Cl-trans}, ¹J_{Pt-P} = 3654 Hz, ²J_{P-P} = 16.1 Hz); 39.54 (m, P_{C-trans}, ¹J_{Pt-P} = 2194 Hz). ¹⁹F{¹H} NMR (δ, CDCl₃): -120.62, -121.39 (m, o-F), -163.77 (t, p-F, ³J_{F-F} = 19.9 Hz), -164.91, -165.54 (m, m-F).

[Pt(C₆F₅)(H₂O)(dppm)][OTf] (1a). To a solution of [PtCl(C₆F₅)(dppm)] (0.13 g, 0.16 mmol) in wet dichloromethane (20 mL) was added 0.50 mL of an acetone solution of AgOTf (0.17 mmol). The suspension was stirred for 3 h, then the solid AgCl was filtered off and the solution was concentrated. Upon treatment with *n*-pentane, a white solid was obtained, filtered off, and dried under vacuum. Yield: 0.15 g, 98.1%. Anal. Calc for C₃₂H₂₄F₈O₄P₂PtS: C, 42.07; H, 2.65. Found: C, 41.89; H, 2.89. ¹H NMR (δ, CDCl₃): 7.40–7.82 (m, Ar), 5.35 (m, PCH₂), 2.75 (s, OH₂). ³¹P{¹H} NMR (δ, CDCl₃): -49.73 (d, P_{O-trans}, ¹J_{Pt-P} = 3821 Hz, ²J_{P-P} = 59.4 Hz); -37.80 (m, P_{C-trans}, ¹J_{Pt-P} = 1872 Hz). ¹⁹F{¹H} NMR (δ, CDCl₃): -79.3 (s, OTf), -121.49 (t, o-F, ³J_{Pt-F} = 268 Hz), -160.18 (t, p-F), -164.29 (m, m-F).

[Pt(C₆F₅)(H₂O)(dppe)][BF₄] (1b-BF₄). To a solution of [PtCl(C₆F₅)(dppe)] (0.30 g, 0.38 mmol) in wet dichloromethane (20 mL) was added 0.94 mL of an acetone solution of AgBF₄ (0.40 mmol). The suspension was stirred for an hour, then the solid AgCl was filtered off and the solution was concentrated. Upon treatment with *n*-pentane, a pale yellow solid was obtained, filtered off, and dried under vacuum. Yield: 0.263 g, 76%. Anal. Calc for C₃₂H₂₆BF₉OP₂Pt: C, 44.41; H, 3.03. Found: C, 44.65; H, 2.75. ¹H NMR (δ, CDCl₃): 7.26–7.80 (m, Ar), 2.81 (s, OH₂), 2.13–2.62 (m, PCH₂). ³¹P{¹H} NMR (δ, CDCl₃): 32.07 (d, P_{O-trans}, ¹J_{Pt-P} = 4189 Hz, ²J_{P-P} = 6.3 Hz); 46.38 (m, P_{C-trans}, ¹J_{Pt-P} = 2312 Hz). ¹⁹F{¹H} NMR (δ, CDCl₃): -120.52 (m, o-F), -153.21 (s, BF₄), -159.44 (s, p-F), -163.46 (s, m-F).

[Pt(C₆F₅)(H₂O)(dppe)][OTf] (1b-OTf). This compound was prepared using a procedure similar to that described above for complex **1a** starting from [PtCl(C₆F₅)(dppe)] (0.30 g, 0.38 mmol). Yield: 0.313 g, 83.1%. Anal. Calc for C₃₃H₂₆F₈O₄P₂PtS: C, 42.73; H, 2.83. Found: C, 42.97; H, 2.59. ¹H NMR (δ, CDCl₃): 7.36–7.52 (m, Ar), 2.78 (s, OH₂), 2.05–2.66 (m, PCH₂). ³¹P{¹H} NMR (δ, CDCl₃): 31.63 (d, P_{O-trans}, ¹J_{Pt-P} = 4353 Hz, ²J_{P-P} = 6.6 Hz); 46.33 (m, P_{C-trans}, ¹J_{Pt-P} = 2309 Hz). ¹⁹F{¹H} NMR (δ, CDCl₃): -79.27 (s, OTf), -120.73 (m, o-F), -160.86 (m, p-F), -164.68 (m, m-F).

[Pt(C₆F₅)(H₂O)(diphoe)][OTf] (1c). This compound was prepared using a procedure similar to that described above for complex **1a** starting from [PtCl(C₆F₅)(diphoe)] (0.13 g, 0.16 mmol) in dichloromethane (20 mL). Yield: 0.143 g, 95%. Anal. Calc for C₃₃H₂₄F₈O₄P₂PtS: C, 42.82; H, 2.61. Found: C, 42.44; H, 2.86. ¹H NMR (δ, CDCl₃): 7.33–7.85 (m, Ar), 3.47 (m, PCH), 2.75 (s, OH₂). ³¹P{¹H} NMR (δ, CDCl₃): 59.03 (m, P_{C-trans}, ¹J_{Pt-P} = 2318 Hz); 33.19 (s, P_{O-trans}, ¹J_{Pt-P} = 4441 Hz). ¹⁹F{¹H} NMR (δ, CDCl₃): -79.25 (s, OTf), -119.57 (m, o-F), -160.68 (m, p-F), -164.57 (m, m-F).

[Pt(C₆F₅)(H₂O)(dppp)][OTf] (1d). This compound was prepared using a procedure similar to that described above for complex **1a** starting from [PtCl(C₆F₅)(dppp)] (0.211 g, 0.26 mmol). Yield: 0.223 g, 91%. Anal. Calc for C₃₄H₂₈F₈O₄P₂PtS: C, 43.37; H, 3.00. Found: C, 43.27; H, 3.12. ¹H NMR (δ, CDCl₃): 7.18–7.75 (m, Ar), 2.73 (s, OH₂), 2.08–2.87 (m, CH₂). ³¹P{¹H} NMR (δ, CDCl₃): -9.36 (d, P_{O-trans}, ¹J_{Pt-P} = 4148 Hz, ²J_{P-P} = 26.9 Hz); 0.91 (m, P_{C-trans}, ¹J_{Pt-P} = 2128 Hz). ¹⁹F NMR (δ, CDCl₃): -79.76 (OTf), -120.75 (o-F), -161.38 (p-F), -164.79 (m-F).

[Pt(C₆F₅)(H₂O)(dppb)][OTf] (1e). This compound was prepared using a procedure similar to that described above for complex **1a** starting from [PtCl(C₆F₅)(dppb)] (0.15 g, 0.18 mmol). Yield: 0.147 g, 79%. Anal. Calc for C₃₅H₃₀F₈O₄P₂PtS: C, 43.99; H, 3.16. Found: C, 43.87; H, 2.88. ¹H NMR (δ, CDCl₃): 7.18–7.61 (m, Ar), 1.58–2.87 (m, CH₂ and s, OH₂). ³¹P{¹H} NMR (δ, CDCl₃): 14.76 (d, P_{O-trans}, ¹J_{Pt-P} = 4530 Hz, ²J_{P-P} = 21.6 Hz); 7.34 (m,

P_{C-trans}, ¹J_{Pt-P} = 2136 Hz). ¹⁹F{¹H} NMR (δ, CDCl₃): -79.53 (s, OTf), -120.80 (t, o-F, ³J_{Pt-F} = 267.1 Hz, ³J_{F-F} = 18.4 Hz), -161.52 (t, p-F, ³J_{F-F} = 19.1 Hz), -164.89 (m, m-F).

[Pt(C₆F₅)(H₂O)(dfppe)][OTf] (1f). This compound was prepared using a procedure similar to that described above for complex **1a** starting from [PtCl(C₆F₅)(dfppe)] (0.31 g, 0.27 mmol) in acetone (20 mL) and dichloromethane (20 mL). Yield: 0.344 g, 94%. Anal. Calc for C₃₃H₆F₂₈O₄P₂PtS: C, 30.79; H, 0.47. Found: C, 30.45; H, 0.56. ¹H NMR (δ, CDCl₃): 3.26–3.72 (m, PCH₂), 2.72 (s, OH₂). ³¹P{¹H} NMR (δ, CDCl₃): -9.20 (m, P_{O-trans}, ¹J_{Pt-P} = 4712 Hz); 21.24 (m, P_{C-trans}, ¹J_{Pt-P} = 2176 Hz). ¹⁹F{¹H} NMR (δ, CDCl₃): -121.49 (m, Pt-C₆F₅, o-F), -128.50, -128.91 (m, P-C₆F₅, o-F), -145.53, -146.37 (m, P-C₆F₅, p-F), -159.42 (m, Pt-C₆F₅, p-F), -161.45 (m, P-C₆F₅, m-F) -164.01 (m, Pt-C₆F₅, m-F).

[Pt(C₆F₅)(H₂O)(dippe)][OTf] (1g). This compound was prepared using a procedure similar to that described above for complex **1a** starting from [PtCl(C₆F₅)(dippe)] (0.25 g, 0.38 mmol). Yield: 0.243 g, 77%. Anal. Calc for C₂₁H₃₄F₈O₄P₂PtS: C, 31.86; H, 4.33. Found: C, 31.45; H, 4.54. ¹H NMR (δ, CDCl₃): 2.11–2.59 (m, CH), 2.72 (s, OH₂), 1.65–2.05 (m, PCH₂), 1.00–1.45 (m, CH₃). ³¹P{¹H} NMR (δ, CD₂Cl₂): 61.39 (s, P_{O-trans}, ¹J_{Pt-P} = 3930 Hz); 78.65 (m, P_{C-trans}, ¹J_{Pt-P} = 2456 Hz). ¹⁹F{¹H} NMR (δ, CD₂Cl₂): -79.31 (s, OTf), -119.57 (m, o-F), -160.68 (m, p-F), -164.57 (m, m-F).

[Pt(C₆F₅)(H₂O)((2S),(3S)-Chiraphos)][OTf] (1h). This compound was prepared using a procedure similar to that described above for complex **1a** starting from [PtCl(C₆F₅)((2S),(3S)-chiraphos)] (0.152 g, 0.18 mmol). Yield: 0.142 g, 74%. ¹H NMR (δ, CDCl₃): 7.15–8.03 (m, Ar), 2.79 (s, OH₂), 2.02–2.64 (m, PCH), 1.02–1.13 (m, CH₃). ³¹P{¹H} NMR (δ, CDCl₃): 32.60 (d, P_{O-trans}, ¹J_{Pt-P} = 4272 Hz, ²J_{P-P} = 16.8 Hz); 45.51 (m, P_{C-trans}, ¹J_{Pt-P} = 2222 Hz). ¹⁹F{¹H} NMR (δ, CDCl₃): -79.34 (s, OTf), -120.91, -121.77 (m, o-F), -161.30 (m, p-F), -164.41, -165.02 (m, m-F).

Catalytic Studies. These were carried out in a 2 mL vial 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 °C) was maintained by water circulation through an external jacket connected with a thermostat. The concentration of the commercial 35% H₂O₂ solution was checked iodometrically prior to use.

The required amount of catalyst (0.0166 mmol, 2% with respect to substrate and oxidant) was placed in solid form in the reactor. To this was added 1 mL of 1,2-dichloroethane, followed by the proper amount of substrate (0.83 mmol). After thermostating at the required temperature for a few minutes, a 35% H₂O₂ solution in the appropriate amount (0.83 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; *n*-decane was used as internal standard. 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.

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