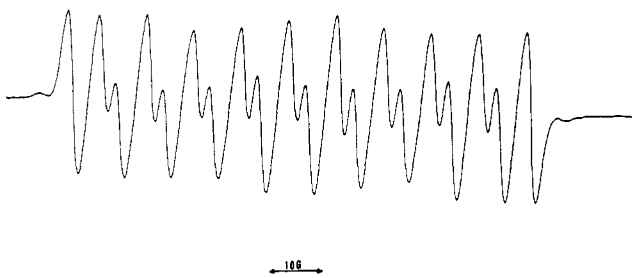


Figure 3. ESR spectrum of (TBSQ)InI_2 in tetrahydrofuran + 4-methylpyridine.

for example, TBQ are (TBSQ$^\bullet$)Tl and (TBCAT)Tl_2, which can be interconverted by appropriate redox reagents. The hyperfine coupling constants for (TBSQ$^\bullet$)Tl are A_{Tl} = 62.0 G and A_H = 3.2 G. It is also useful to compare this value for A_{Tl} with that in the thallium(III) species (TBSQ$^\bullet$)Tl$(C_2H_5)_2$, for which A_{Tl} = 23.9 G. The ratio between A_{Tl} for these two different oxidation states, in admittedly rather different compounds, is $Tl^I:Tl^{III} \sim$ 2.6, while that for the indium reported above is ca. 2.0, depending on the compounds involved. The values for thallium are much larger than those for indium, irrespective of the oxidation state, due to the Fermi contact terms involved.

The coupling of the electron with the semiquinone ring system is obviously less diagnostic insofar as the structures of the complexes are concerned. As noted above, only one coupling, that involving the hydrogen atom on C4, was observed, and no coupling to the *tert*-butyl groups was detected in any of the present systems. Detailed arguments based on similar results in *o*-benzoquinones have been presented by Felix and Sealy.[19] The observation of coupling of the electron with the selenium atoms of the $-SeC_6H_5$ derivative suggests a further use of ESR parameters in structural investigations of these indium compounds.

In general then, the ESR spectra confirm unambiguously that the reaction of indium with TBQ gives the indium(I)–semiquinonate complex, and that this species can be oxidized to give indium(III)–semiquinonate derivatives. These spectroscopic results are entirely congruent with the preparative work and with the vibrational spectra discussed above.

Acknowledgment. This work was supported in part by Operating Grants (to B.R.M. and D.G.T.) from the Natural Sciences and Engineering Research Council of Canada.

---

(19) Felix, C. C.; Sealy, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 1555.

Contribution from the Department of Chemistry, University of Venice, 30123 Venezia, Italy,
and Institute of Industrial Chemistry, University of Padua, 35100 Padova, Italy

Epoxidation of Olefins Catalyzed by Chelating Diphosphine–Platinum(II) Complexes. Ring-Size and Ring-Shape Effects on the Catalytic Activity

Andrea Zanardo,[1a] Rino A. Michelin,[1b] Francesco Pinna,[1a] and Giorgio Strukul*,[1a]

Received March 23, 1988

The epoxidation of 1-octene with H_2O_2 has been examined by using as catalysts a homologous class of 10 (diphosphine)Pt(CF_3)(solv)$^+$ and 10 (diphosphine)Pt(CF_3)(OH) type complexes, where the diphosphine has been systematically varied. All diphosphines contain two $-PPh_2$ groups but differ in the hydrocarbon chain linking together the two phosphorus atoms. The epoxidation reaction experimental conditions have been chosen in order to study the effect of the metal–diphosphine ring size and ring shape on the catalytic activity. It appears that diphosphine complexes with rigid, five-membered chelate rings prove to be the best catalysts.

Introduction

The interest in the direct oxidation of olefins to epoxides with transition-metal complexes has remained very high during the years, since these compounds are key industrial intermediates for the preparation of a wide variety of chemicals such as glycols, alkanolamines, and polymers like polyesters, polyurethanes and epoxy resins.[2]

We have recently described a platinum-based system that is capable of catalyzing very efficiently the selective epoxidation of simple terminal olefins using as primary oxidant diluted (5–35%) H_2O_2.[3,4] The catalysts, of the general type shown in Figure 1, play in the system a bifunctional role[5] since (i) they activate otherwise unreactive olefins toward nucleophilic attack and (ii) they increase H_2O_2 nucleophilicity by forming Pt–OOH species through acid–base reactions. This system is highly chemoselective since epoxides are the only detectable oxidation products. The catalysts, modified with chiral diphosphines, lead to asymmetric epoxidations with enantioselectivity up to 41% in the case of propylene.[6] The reaction rates observed in the latter work seem to suggest an important role of the metal–diphosphine ring size and shape in affecting the overall catalytic activity. we have therefore undertaken a systematic study in order to establish some structure/reactivity correlations and to optimize the catalyst, by synthesizing the homologous class of complexes shown in Figure 1 with a wide variety of diphosphines, which have been tested in the epoxidation of 1-octene.

Results

Some of the complexes shown in Figure 1 have been already described in the literature, i.e., the CF_3 derivatives of dppe,[7] diphoe,[7] prophos,[6] and chiraphos;[6] all of the others have been prepared according to the general synthetic route outlined in the following sequence of reactions:

---

* To whom correspondence should be addressed.

(1) (a) University of Venice. (b) University of Padua.

(2) Weissermel, K.; Arpe, H.-J. *Industrial Organic Chemistry: Important Raw Materials and Intermediates*; Verlag Chemie: Weinheim, FRG, 1978.

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

(4) Strukul, G.; Michelin, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 7563.

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

(6) Sinigalia, R.; Michelin, R. A.; Pinna, F.; Strukul, G. *Organometallics* **1987**, *6*, 728.

(7) Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *174*, 239.

$$(PPh_3)_4Pt + CF_3Br \rightarrow \textit{trans}\text{-}(PPh_3)_2Pt(CF_3)Br + 2PPh_3$$

$$\textit{trans}\text{-}(PPh_3)_2Pt(CF_3)Br \xrightarrow{AgBF_4} \xrightarrow{LiCl} \textit{trans}\text{-}(PPh_3)_2Pt(CF_3)Cl$$

$$\textit{trans}\text{-}(PPh_3)_2Pt(CF_3)Cl + P\text{-}P \rightarrow (P\text{-}P)Pt(CF_3)Cl + 2PPh_3$$

$$(P\text{-}P)Pt(CF_3)Cl + AgBF_4 \rightarrow [(P\text{-}P)Pt(CF_3)(solv)]BF_4 + AgCl$$

$$[(P\text{-}P)Pt(CF_3)(solv)]BF_4 + KOH \rightarrow (P\text{-}P)Pt(CF_3)(OH) + KBF_4$$

For (dppm)Pt(CF_3)(OH) the diphosphine exchange was performed on *trans*-(PPh_3)$_2$Pt(CF_3)(OH), because on addition of KOH on (dppm)Pt(CF_3)(solv)$^+$ extensive decomposition to Pt(0) takes place.

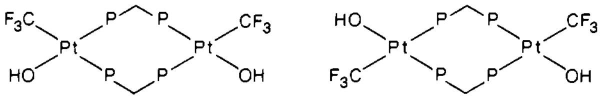
Alternatively, for the $-C_6F_5$ derivatives the following route has been employed:

$$(COD)PtI_2 + LiC_6F_5 \rightarrow (COD)Pt(C_6F_5)I + LiI$$

$$(COD)Pt(C_6F_5)I + P\text{-}P \rightarrow (P\text{-}P)Pt(C_6F_5)I + COD$$

etc.

All new complexes have been characterized by IR, ^{19}F NMR, and, in most cases, ^{31}P NMR spectroscopies. The basic spectroscopic features are reported in Table I. Where available, ^{31}P NMR data can give useful informations concerning the possibility that a diphosphine is coordinated in a chelating or bridging fashion.[8] The chelating nature of the dppm ligand in (dppm)Pt(CF_3)Cl seems to be confirmed by the ^{31}P chemical shifts, which are in good agreement with those found in (dppm)Pt(R)Cl (R = σ-carbon donor) type complexes.[9] In contrast to that for the Cl derivative, for the (dppm)Pt–OH species the ^{31}P NMR spectrum shows a very complicated pattern in the ranges −33 to −36 and −46 to −49 ppm, suggesting also the possible presence of a bridging ligand.[10] This unusual behavior is confirmed in the ^{19}F NMR spectrum, where the observed pattern shows the presence of two apparently nonequivalent $-CF_3$ ligands (1:1 ratio), each seeing one P cis and one P trans, having identical coupling constants and slightly different chemical shifts; this might be consistent with the formation of two isomeric dimers



each having two equivalent CF_3 ligands but differing in the relative position of the two $-CF_3$ and −OH ligands. The tendency of dppm–transition-metal derivatives to dimerization is well-known, and this argument has been recently reviewed.[10] An alternative possibility, again consistent with the ^{19}F NMR spectrum and related to the synthetic procedure (see above), is associated with the occurrence of a species containing three phosphorus ligands like [(dppm)Pt(PPh_3)(CF_3)]OH. Molecular weight determination (MW 481 by osmometry) excludes the former possibility and might agree with the latter (MW 927) assuming ionic dissociation. Molar conductivity data in THF/10% H_2O strongly support this view. The 33 Ω^{-1} mol^{-1} cm^2 value found for a 10^{-3} M solution assuming MW 927 is in good agreement with the value of 35 Ω^{-1} mol^{-1} cm^2 found for the 1/1 electrolyte [(diphoe)Pt(CF_3)(CH_2Cl_2)]BF_4 under the same experimental conditions.[4]

A third minor species (<10%) is present at δ −16.95 that could well be the mononuclear *cis*-(dppm)Pt(CF_3)(OH).

As to the dppp and dppb derivatives, the ^{31}P NMR data are again consistent with a chelating nature of the ligands by analogy with previous data on similar Pt(II) complexes.[11]

All catalysts have been tested in the catalytic epoxidation of 1-octene with H_2O_2, working either in a two-phase CH_2Cl_2/H_2O medium (cationic solvato complexes) or in monophasic THF/H_2O (hydroxo complexes). Analogous to previous reports on this system,[3,4] 1,2-epoxyoctane was the exclusive oxidation product for all of the catalysts tested. All reactions have been carried out at 20 °C and followed by GLC analysis of epoxide formed vs time. A summary of the results of the catalytic experiments (initial rates and turnovers) are reported in Tables II and III (cationic solvato and hydroxo complexes, respectively). As a general trend, from Table II it is clear that all diphosphines capable of making five-membered chelate rings give rise to better catalysts. Among these, the highest efficiency is given by diphoe.

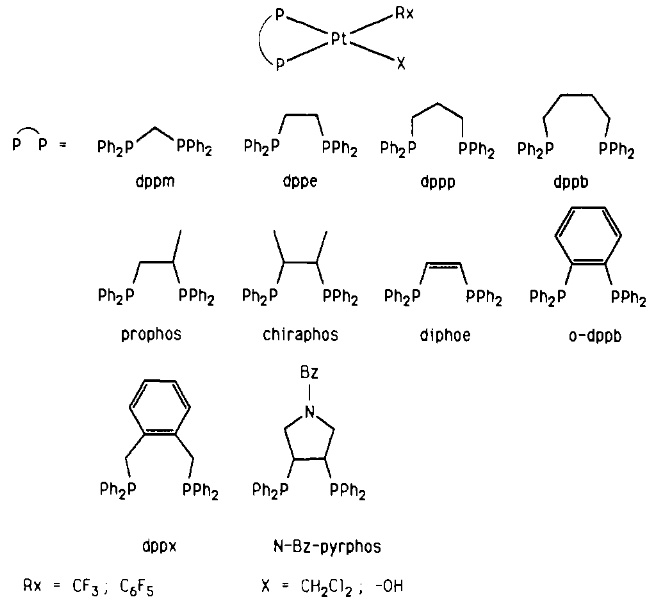


Figure 1. Catalysts employed in the selective epoxidation of 1-octene with hydrogen peroxide. dppm = 1,2-bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,2-bis(diphenylphosphino)propane; dppb = 1,2-bis(diphenylphosphino)butane; prophos = 1,2-bis(diphenylphosphino)propane; chiraphos = 2,3-bis(diphenylphosphino)butane; diphoe = *cis*-1,2-bis(diphenylphosphino)ethylene; *o*-dppb = *o*-bis(diphenylphosphino)benzene; dppx = *o*-bis(diphenylphosphino)methyl)benzene; *N*-Bz-pyrphos = *N*-benzyl-3,4-bis(diphenylphosphino)pyrrolidine.

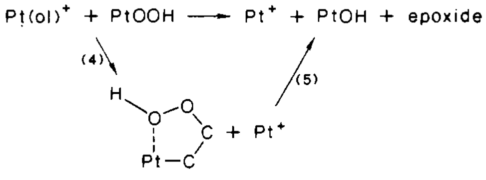
It is useful to recall[5] the basic mechanistic features of this platinum system, which involves the following reaction sequence:

$$Pt^+ + ol \rightleftharpoons Pt(ol)^+ \qquad (1)$$

$$Pt^+ + H_2O_2 \rightleftharpoons PtOOH + H^+ \qquad (2)$$

$$PtOH + H_2O_2 \rightleftharpoons PtOOH + H_2O \qquad (3)$$

where Pt^+ represents a $P_2Pt(CF_3)(solvent)^+$ species. Epoxide formation takes place in the rate-determining step by nucleophilic attack of the hydroperoxide onto the coordinated olefin:



However this reaction is most likely a stepwise process going through the formation of a quasi peroxymetallacycle, which is responsible for the selectivity of the overall process toward the formation of epoxides.[4,5,12] Additional equilibria that are not involved in the catalytic cycle but determine the concentrations of the active species are

$$Pt^+ + H_2O \rightleftharpoons Pt(H_2O)^+$$

$$Pt^+ + H_2O_2 \rightleftharpoons Pt(H_2O_2)^+$$

---

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

(9) Hassan, F. S. M.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1501.

(10) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.

(11) Anderson, G. K.; Lumetta, G. J. *Organometallics* **1985**, *4*, 1542. Slack, D. A.; Baird, M. C. *Inorg. Chim. Acta* **1977**, *24*, 277.

(12) Strukul, G.; Sinigalia, R.; Zanardo, A.; Pinna, F.; Michelin, R. A. *Inorg. Chem.* **1989**, *28*, 554.

(13) Strukul, G.; Ros, R.; Michelin, R. A. *Inorg. Chem.* **1982**, *21*, 495.

Table I. Spectroscopic Features of New Chloro- and Hydroxoplatinum(II) Complexes[a]

complex	IR	^{19}F NMR	^{31}P{^{1}H} NMR
(dppm)Pt(CF_3)Cl	311 (Pt–Cl)	-24.25 dd ($^3J_{\mathrm{FPcis}} = 21.4$, $^3J_{\mathrm{FPtrans}} = 65.7$, $^2J_{\mathrm{FPt}} = 618$)	-54.26 dq (trans CF_3) ($^3J_{\mathrm{PF}} = 65.7$, $^2J_{\mathrm{PP}} = 13.7$, $^1J_{\mathrm{PPt}} = 1445$), -46.94 dq (cis CF_3) ($^3J_{\mathrm{PF}} = 21.4$, $^2J_{\mathrm{PP}} = 13.7$, $^1J_{\mathrm{PPt}} = 3569$)
[(dppm)Pt(PPh_3)(CF_3)](OH)	3598 (O–H)	-9.90 ddd ($^3J_{\mathrm{FPPh3}} = 23.7$, $^3J_{\mathrm{FPtrans}} = 60.7$, $^3J_{\mathrm{FPcis}} = 11.6$ $^2J_{\mathrm{FPt}} = 576$), -16.95 dd ($^3J_{\mathrm{FPcis}} = 21.9$, $^3J_{\mathrm{FPtrans}} = 65.6$, $^2J_{\mathrm{FPt}} = 626$)	-33 to -36,[b] -46 to -49[b]
(dppp)Pt(CF_3)Cl	312 (Pt–Cl)	-24.98 dd ($^3J_{\mathrm{FPcis}} = 14.6$, $^3J_{\mathrm{FPtrans}} = 55.9$, $^2J_{\mathrm{FPt}} = 547$)	-4.76 dq (trans CF_3) ($^3J_{\mathrm{PF}} = 55.9$, $^2J_{\mathrm{PP}} = 27.6$, $^1J_{\mathrm{PPt}} = 1713$), -1.34 dq (cis CF_3) ($^3J_{\mathrm{PF}} = 14.6$, $^2J_{\mathrm{PP}}$ 27.5, $^1J_{\mathrm{PPt}} = 3850$)
(dppp)Pt(CF_3)(OH)	3616 (O–H)	-30.32 dd ($^3J_{\mathrm{FPcis}} = 9.6$, $^3J_{\mathrm{FPtrans}} = 53.8$, $^2J_{\mathrm{FPt}} = 572$)	-3.05 dq (trans CF_3) ($^3J_{\mathrm{PF}} = 53.1$, $^2J_{\mathrm{PP}} = 27.5$, $^1J_{\mathrm{PPt}} = 1918$), -6.87 dq (cis CF_3) ($^3J_{\mathrm{PF}} = 9.9$, $^2J_{\mathrm{PP}} = 27.5$, $^1J_{\mathrm{PPt}} = 3185$)
(dppb)Pt(CF_3)Cl	306 (Pt–Cl)	-24.36 dd ($^3J_{\mathrm{FPcis}} = 14.0$, $^3J_{\mathrm{FPtrans}} = 54.4$, $^2J_{\mathrm{FPt}} = 535$)	*c*
(dppb)Pt(CF_3)(OH)	3612 (O–H)	-29.58 dd ($^3J_{\mathrm{FPcis}} = 7.9$, $^3J_{\mathrm{FPtrans}} = 53.4$, $^2J_{\mathrm{FPt}} = 573$)	13.57 dq (trans CF_3) ($^3J_{\mathrm{PF}} = 53.4$, $^2J_{\mathrm{PP}} = 19.5$, $^1J_{\mathrm{PPt}} = 1989$), 5.3 dq (cis CF_3) ($^3J_{\mathrm{PF}} = 7.9$, $^2J_{\mathrm{PP}} = 19.5$, $^1J_{\mathrm{PPt}} = 3305$)
(dppx)Pt(CF_3)Cl	307 (Pt–Cl)	-25.42 dd ($^3J_{\mathrm{FPcis}} = 13.7$, $^3J_{\mathrm{FPtrans}} = 56.9$, $^2J_{\mathrm{FPt}} = 527$)	-1.92 dq (trans CF_3); ($^3J_{\mathrm{PF}} = 56.9$, $^2J_{\mathrm{PP}} = 20.6$, $^1J_{\mathrm{PPt}} = 1779$), 2.77 dq (cis CF_3) ($^3J_{\mathrm{PF}} = 13.7$, $^2J_{\mathrm{PP}} = 20.6$, $^1J_{\mathrm{PPt}} = 4059$)
(dppx)Pt(CF_3)(OH)	3620 (O–H)	-30.16 dd ($^3J_{\mathrm{FPcis}} = 9.0$, $^3J_{\mathrm{FPtrans}} = 53.9$, $^2J_{\mathrm{FPt}} = 569$)	1.04 dq (trans CF_3) ($^3J_{\mathrm{PF}} = 53.9$ $^2J_{\mathrm{PP}} = 20.7$, $^1J_{\mathrm{PPt}} = 1988$), -0.77 dq (cis CF_3) ($^3J_{\mathrm{PF}} = 9.0$, $^2J_{\mathrm{PP}} = 20.7$, $^1J_{\mathrm{PPt}} = 3365$)
(*o*-dppb)Pt(CF_3)Cl	320 (Pt–Cl)	-24.35 dd ($^3J_{\mathrm{FPcis}} = 11.5$, $^3J_{\mathrm{FPtrans}} = 58.3$, $^2J_{\mathrm{FPt}} = 558$)	*c*
(*o*-dppb)Pt(CF_3)(OH)	3628 (O–H)	-28.47 dd ($^3J_{\mathrm{FPcis}} = 8.1$, $^3J_{\mathrm{FPtrans}} = 55.5$, $^2J_{\mathrm{FPt}} = 583$)	39.73 dq (trans CF_3) ($^3J_{\mathrm{PF}}$ 55.5, $^2J_{\mathrm{PP}} = 3.9$, $^1J_{\mathrm{PPt}} = 2083$), 32.78 dq (cis CF_3) ($^3J_{\mathrm{PF}} = 8.1$, $^2J_{\mathrm{PP}} = 3.9$, $^1J_{\mathrm{PPt}} = 3270$)
(*N*-Bz-pyrphos)Pt(CF_3)Cl	313 (Pt–Cl)	-24.66 dd ($^3J_{\mathrm{FPcis}} = 14.2$, $^3J_{\mathrm{FPtrans}} = 58.6$, $^2J_{\mathrm{FPt}} = 560$)	16.02 dq (trans CF_3) ($^3J_{\mathrm{PF}} = 58.6$, $^2J_{\mathrm{PP}} = 16.8$, $^1J_{\mathrm{PPt}} = 1830$), 18.60 dq (cis CF_3) ($^3J_{\mathrm{PF}} = 14.2$, $^2J_{\mathrm{PP}} = 16.8$, $^1J_{\mathrm{PPt}} = 4004$)
(*N*-Bz-pyrphos)Pt(CF_3)(OH)	3642 (O–H)	-29.09 dd ($^3J_{\mathrm{FPcis}} = 9.7$, $^3J_{\mathrm{FPtrans}} = 55.3$, $^2J_{\mathrm{FPt}} = 591$)	16.36 dq (trans CF_3) ($^3J_{\mathrm{PF}} = 55.3$, $^2J_{\mathrm{PP}} = 18.2$, $^1J_{\mathrm{PPt}} = 2058$), 12.58 dq (cis CF_3) ($^3J_{\mathrm{PF}} = 9.7$, $^2J_{\mathrm{PP}} = 18.2$, $^1J_{\mathrm{PPt}} = 3286$)
(diphoe)Pt(C_6F_5)Cl		-119.24 m (ortho) ($^3J_{\mathrm{FPt}} = 128$),[b] -164.45 m (meta), -161.91 m (para)	
(diphoe)Pt(C_6F_5)(OH)		-117.98 m (ortho) ($^3J_{\mathrm{FPt}} = 145$),[b] -164.28 m (meta), -161.52 m (para)	

[a] IR (Nujol mull) in cm^{-1}. NMR: δ in ppm; J in Hz; external references $CFCl_3$ and 85% H_3PO_4. [b] Extensive overlapping of signals. [c] Poorly soluble for ^{31}P NMR characterization.

Table II. Catalytic Activity of [(P-P)Pt(CF_3)(CH_2Cl_2)]ClO_4 Complexes in the Epoxidation of 1-Octene with 16% H_2O_2[a]

P-P	initial rate × 10^6, M s^{-1}	turnover (2 h)	P-P	initial rate × 10^6, M s^{-1}	turnover (2 h)
dppm	55	13.6	chiraphos	118	37.8
dppe	110	21.1	*N*-Bz-pyrphos	99	28.7
dppp	11	5.8	diphoe[b]	>280	>40
dppb	0.75	0.6	*o*-dppb	88	22.8
prophos	48	9.7	dppx	19	8.1

[a] Rates calculated from epoxide formed vs time plots determined by GLC. Experimental conditions: [Pt] = 10^{-2} M; 1-octene/Pt = 140; H_2O_2/Pt = 40; solvent CH_2Cl_2; T = 20 °C; N_2, 1 atm. [b] Under the experimental conditions employed, this reaction is diffusion controlled.

Table III. Catalytic Activity of (P-P)Pt(CF_3)(OH) in the Epoxidation of 1-Octene with 32% H_2O_2[a]

P-P	initial rate × 10^7, M s^{-1}	turnover (48 h)	P-P	initial rate × 10^7, M s^{-1}	turnover (48 h)
dppe	2.6	1.5	*N*-Bz-pyrphos	11.4	8.2
dppp	4.2	4.8	diphoe	18.7	12.0
dppb	1.0	2.1	*o*-dppb	16.4	13.0
prophos	19.4	15.6	dppx[b]		1.3[c]
chiraphos	12.0	8.2			

[a] Rates calculated from epoxide formed vs time plots determined by GLC. Experimental conditions: [Pt] = 1.4 × 10^{-2} M; 1-octene/Pt = 53; H_2O_2/Pt = 43; solvent THF; T = 20 °C; N_2, 1 atm. [b] Insoluble in the reaction medium. [c] After 10 days.

The initial rates for epoxide formation depend on the relative concentrations of the relevant Pt(ol)$^+$) and PtOOH species, and also on the individual rate constants for reactions 4 and 5.

Table IV. pH Measurements of the Aqueous Phase in Catalytic Reactions Carried Out with [(P-P)Pt(CF_3)(CH_2Cl_2)]ClO_4 Complexes[a]

P-P	pH	P-P	pH
dppm	2.63	chiraphos	2.69
dppe	2.70	*N*-Bz-pyrphos	2.64
dppp	2.68	diphoe	2.64
dppb	2.72	*o*-dppb	2.65
prophos	2.75	dppx	2.66

[a] Experimental conditions were as in Table II. Samples were diluted 1/10 prior to measurements.

The compounds in the homologous class of catalysts differ only in the hydrocarbon chain linking together the two diphenylphosphino groups. It seems reasonable that the electronic factors affecting the formation of the individual hydroperoxo species should be essentially similar. When cationic solvato complexes are used as catalysts, the hydroperoxide formation is determined mostly by equilibrium 2.[5] Since the catalytic experiments were carried out under identical experimental conditions, the amount of PtOOH produced in each case can be inferred by the acidity induced in the catalytic reaction mixture. Hence, we measured the pH of a sample of the aqueous phase for all catalysts after a 15-min reaction time and diluted 1/10. The data are reported in Table IV and indicate that the amount of PtOOH involved in the catalysis is essentially the same in all cases, independent of the diphosphine used.

The same conclusion can be drawn also for the hydroxo complexes as catalysts. In this case the PtOOH formation takes place essentially through equilibrium 3. We have determined the extent of equilibrium 3, for the various hydroxo complexes, by ^{19}F NMR spectroscopy in CD_2Cl_2 using concentrations identical with those

Table V. Spectroscopic Features of New (P-P)Pt(CF_3)(OOH) Complexes[a]

P-P	IR (O–H)	^{19}F NMR
dppp	3546	−30.11 dd ($^3J_{FPcis}$ = 10.5, $^3J_{FPtrans}$ = 58.9, $^2J_{FPt}$ = 548)
dppb	3533	−29.82 dd ($^3J_{FPcis}$ = 8.1, $^3J_{FPtrans}$ = 58.2, $^2J_{FP}$ = 547)
prophos	(3531)	−28.42 dd ($^3J_{FPcis}$ = 11.8, $^3J_{FPtrans}$ = 59.3, $^2J_{FPt}$ = 552), −29.35 dd ($^3J_{FPcis}$ = 9.8, $^3J_{FPtrans}$ = 59.7, $^2J_{FPt}$ = 543)
chiraphos	3538, 3548	−29.87 dd ($^3J_{FPcis}$ = 10.6, $^3J_{FPtrans}$ = 59.5, $^2J_{FPt}$ = 544)
N-Bz-pyrphos	(3522)	−29.07 dd ($^3J_{FPcis}$ = 11.5, $^3J_{FPtrans}$ = 62.4, $^2J_{FPt}$ = 555)
o-dppb	(3538)	−29.62 dd ($^3J_{FPcis}$ = 10.3, $^3J_{FPtrans}$ = 60.7, $^2J_{FPt}$ = 555)
dppx	3549	−30.00 dd ($^3J_{FPcis}$ = 9.4, $^3J_{FPtrans}$ = 59.5, $^2J_{FPt}$ = 535)

[a] IR in cm^{-1}; Nujol mulls or CH_2Cl_2 solutions (in parentheses). NMR: δ in ppm; J in Hz; external reference $CFCl_3$.

employed in Table III. The spectra taken before and after addition of H_2O_2 show that under catalytic experimental conditions the only Pt species that are macroscopically involved are the individual (P-P)Pt(CF_3)(OOH) complexes. These have been identified by comparison with authentic samples, which have been prepared according to the general procedure outlined in ref 9. Of these only the diphoe and dppe derivatives were already known,[12] all of the others are reported for the first time (see Table V and the Experimental Section).

Therefore, under the experimental conditions used in the epoxidation of 1-octene both with Pt(solv)$^+$ catalysts (Table II) and with PtOH catalysts (Table III), the Pt–OOH amount involved is essentially the same for all diphosphine ligands; hence, the two major factors that enter into the determination of the differences observed in the individual reaction rates are (i) the ease with which the Pt(ol)$^+$ species is produced and (ii) the ease with which the crucial quasi-peroxymetallacycle can form.

Discussion

If the data of Table II are reorganized, some qualitative correlations can be drawn. In Figure 2, we have plotted the log [initial rate] taken from Table II vs either the number of carbon atoms in the ring or the number of substituents present in five-membered rings.

The sequence dppe, dppp, and dppb illustrates clearly the above-mentioned decrease in catalytic activity as the ring size increases. In this respect, the results obtained with the dppm derivative must be regarded carefully because of the well-known tendency of the ligand to give bridged species.[10] We believe that the observed ring-size effect can be ascribed mainly to steric reasons, because of a more hindered site for the coordination of the olefin (and hence a more difficult reaction 1) in the case of larger rings, due to the accommodation of the phenyl groups of the adjacent phosphorus atom. In fact, as indicated by molecular models, the chelate bite of $Ph_2P(CH_2)_nPPh_2$ increases with n. Although X-ray crystallographic data on PMP bond angles for homologous series of metal complexes are rare in the literature, this view is supported by previous reports by Palenik and coworkers[14] on square-planar (P-P)PdX_2 complexes (X = CNS, Cl), where P-P = dppm, dppe, and dppp, for which PPdP angles were found to be respectively 73.3, 85.1, and 89.3 Å (X = CNS) and 72.7, 85.8, 90.6 Å (X = Cl). Although less pronounced, the same trend is evident also in unsaturated rings like those of diphoe, *o*-dppb, and dppx. The sensitivity of reaction 1 to steric hindrance seems to be particularly evident in the case of [(diphoe)Pt(C_6F_5)(CH_2Cl_2)]$^+$ where the very likely rotation of the pentafluorophenyl ligand in solution hinders significantly the vacant coordination site. With this complex the catalytic activity is very poor: initial rate < 0.7 × 10^{-6} M s^{-1}; turnover (2 h) < 0.5.

A second observation can be made when the number of substituents at the carbon atoms in five-membered rings is considered, i.e., the sequence dppe, prophos, and chiraphos or even *N*-Bz-pyrphos and *o*-dppb. When a methyl group is added to the basic dppe structure (i.e. in the case of prophos), this can easily slide from the equatorial to the axial position, giving rise to different conformers as we have been able to show[6] by ^{19}F NMR in the case of [(prophos)Pt(CF_3)(CH_2Cl_2)]$^+$ or [(prophos)Pt(CF_3)(olefin)]$^+$ complexes. The axial methyl group makes the formation of the crucial quasi-peroxymetallacycle more difficult (reaction 4), and this in turn reflects in a lower reaction rate. When two methyl substituents are added to the basic five-membered ring structure (i.e. in the case of chiraphos), the catalyst shows practically only the equatorial conformation[6] and therefore the reaction rates increases again. This view is supported by the results obtained with *N*-Bz-pyrphos and *o*-dppb where the substituents to the five-membered ring can exist only in the equatorial position.

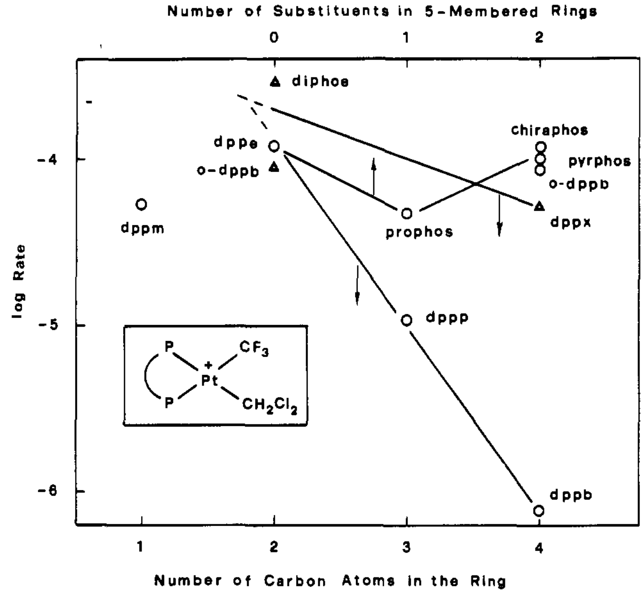


Figure 2. Effect of the chelating diphosphine on the catalytic activity of cationic platinum–solvato complexes. Due to lack of space, *N*-Bz-pyrphos has been shortened to pyrphos.

A further piece of information that can be gained from Figure 2 is the influence of unsaturation in the diphosphine–metal rings on the catalytic activity, i.e., comparing diphoe with dppe and dppx with dppb. It is quite evident that the presence of unsaturation increases significantly the catalytic activity. Qualitatively, we may ascribe this behavior again to steric reasons due to the presumably smaller chelate bite of unsaturated diphosphines compared to saturated ones, although no structural data could be found in the literature for homologous complexes. An alternative but equally likely view is that this behavior might be due to a minor decrease in basicity of the unsaturated ligands, due to the presence of delocalizing groups. Again, no direct measurements of the pK_a of these diphosphines could be found in the literature; however, reliable estimates can be made according to the widely accepted[15] method of Mastryukova and Kabachnik[16] based on the use of Hammett equation and σ^{ph} constants for organophosphorus compounds. According to this method, the estimated pK_a is inversely proportional to the $\Sigma\sigma^{ph}$ of the phosphorus substituents. For one P of diphoe, dppe, dppx, and dppb the $\Sigma\sigma^{ph}$'s were found

---

(14) Palenik, G. J.; Mathew, M.; Steffen, W. L.; Beran, G. *J. Am. Chem. Soc.* **1975**, *97*, 1059. Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432.

(15) McAuliffe, C. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 2, p 1030.

(16) Mastryukova, T. A.; Kabachnik, M. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1969**, *38*, 795 and references therein.

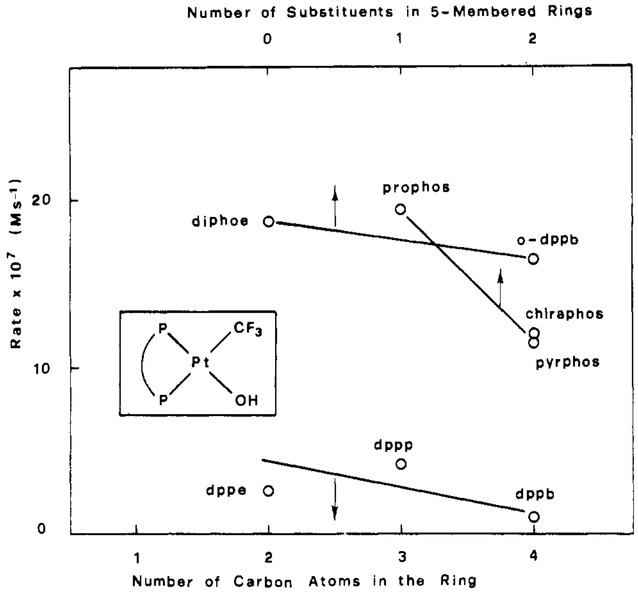


Figure 3. Effect of the chelating diphosphine on the catalytic activity of platinum–hydroxo complexes. Due to lack of space, *N*-Bz-pyrphos has been shortened to pyrphos.

to be −1.85, −2.28, −1.87, and −2.40 respectively. The use of traditional Taft σ^* parameters[17] gave essentially the same trend ($\Sigma\sigma^*$ = 1.83, 1.14, 1.45, and 1.11, respectively). This lower basicity for unsaturated ligands would result in a lower electron density on the metal, which therefore is less available for back-donation in the metal–olefin complex formation, making the olefin more activated for nucleophilic attack.

In Figure 3 the activities of the hydroxo complexes have been considered. In this case we have used a linear plot, since the activity range is less pronounced probably because of the coordinating properties of THF. Although less evident, most of the above observations seem to be confirmed, in particular the effect of unsaturation in five-membered rings: notice the difference between diphoe and dppe and between *o*-dppb and chiraphos or *N*-Bz-pyrphos.

A further observation can be made, again related to steric factors. All of the complexes present in the upper part of the plot are characterized by rigid five-membered rings either because of planarity (diphoe, *o*-dppb) or because of substituents (prophos,[18] chiraphos, *N*-Bz-pyrophos). The three less active complexes possess flexible rings (dppe, dppp, dppb). Now, again, this will reflect in a more hindered coordination site for the coordination of the olefin, which appears to be the most critical factor in determining the catalytic activity of this class of complexes.

Experimental Section

Apparatus. IR spectra were taken on a Perkin-Elmer 683 spectrophotometer either in Nujol mulls using CsI plates or in CH_2Cl_2 solution using CaF_2 windows. ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian FT 80A spectrometer operating in FT mode, using as external references $CFCl_3$ and 85% H_3PO_4, respectively. Negative chemical shifts are upfield from the reference. GLC measurements were taken on a Hewlett-Packard 5790A gas chromatograph equipped with a 3390 automatic integrator. Identification of products was made with GLC by comparison with authentic samples. pH measurements were performed on a Orion 701 digital pH meter. Molecular weight determinations in $C_2H_4Cl_2$ were carried out on a Dampfdrück osmometer. Conductivity measurements were made with a AMEL 123 instrument.

Materials. Solvents were dried and purified according to standard methods. 1-Octene (Fluka) was purified by passing it through neutral alumina and was distilled and stored under N_2 in the dark. Hydrogen peroxide (35% Fluka), diphoe, dppm, dppe, dppp, dppb, dppx, *o*-dppb, chiraphos, and prophos (all from Strem) were commerical products and used without purification. *N*-Bz-pyrphos was a generous gift of Degussa AG.

The following compounds were prepared according to literature procedures: *trans*-$(PPh_3)_2Pt(CF_3)Cl$,[7] *trans*-$(PPh_3)_2Pt(CF_3)(OH)$,[7] [(diphoe)$Pt(CF_3)(CH_2Cl_2)]BF_4$,[7] (diphoe)$Pt(CF_3)(OH)$,[7] (diphoe)$Pt(CF_3)(OOH)$,[13] [(dppe)$Pt(CF_3)(CH_2Cl_2)]BF_4$,[7] (dppe)$Pt(CF_3)(OH)$,[7] (dppe)$Pt(CF_3)(OOH)$,[13] [(prophos)$Pt(CF_3)(CH_2Cl_2)]BF_4$,[6] (prophos)$Pt(CF_3)(OH)$,[6] [(chiraphos)$Pt(CF_3)(CH_2Cl_2)]BF_4$,[6] and (chiraphos)$Pt(CF_3)(OH)$,[6] (COD)PtI_2.[19] The preparation of new complexes was performed under dry N_2 by using conventional Schlenk and syringe techniques, although all of them were found to be air stable once isolated.

Preparation of New Complexes. All trifluoromethyl derivatives were prepared from *trans*-$(PPh_3)_2Pt(CF_3)Cl$ by following the general procedure outlined in ref 7. All complexes gave satisfactory elemental analysis.

(dppm)Pt(CF$_3$)Cl. To a suspension of *trans*-$(PPh_3)_2Pt(CF_3)Cl$ (0.96 g, 1.16 mmol) in benzene (100 mL) was added in one portion a solution of dppm (0.46 g, 1.19 mmol) in benzene (20 mL). The clear solution obtained was stirred at room temperature for 2 days. It was then concentrated to 20 mL, and Et_2O (80 mL) was added. The white solid was filtered off, washed with Et_2O, and dried in vacuo. The compound was first recrystallized from CH_2Cl_2/benzene to eliminate (dppm)$PtCl_2$ (<6%) and then from CH_2Cl_2/MeOH (yield 88%).

(dppm)Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$. (dppm)$Pt(CF_3)Cl$ (0.68 g, 1.00 mmol) was dissolved in dry N_2-saturated CH_2Cl_2 (10 mL). To the solution was added 1.32 mL of a 0.76 M solution of $AgBF_4$ in acetone, and the mixture was stirred for 15 min in the dark. AgCl was removed by filtration, and the resulting solution was centrifugated to eliminate traces of colloidal silver. The clear solution was brought to dryness in vacuo (10^{-2} Torr) to yield a white solid (yield 95%).

[(dppm)Pt(PPh$_3$)(CF$_3$)](OH). *trans*-$(PPh_3)_2Pt(CF_3)(OH)$[7] (0.40 g, 0.50 mmol) was suspended in a 1/1 toluene/hexane mixture (50 mL), and a solution of dppm (0.20 g, 0.52 mmol) in toluene (10 mL) was added in one portion. The suspension was stirred overnight, and the crude product was filtered off, washed with hexane, and dried. Recrystallization with CH_2Cl_2/hexane gave a white product (yield 93%).

(dppp)Pt(CF$_3$)Cl. To a suspension of *trans*-$(PPh_3)_2Pt(CF_3)Cl$ (2.53 g, 3.07 mmol) in benzene (40 mL) under N_2 was added a solution of dppp (1.32 g, 3.22 mmol) in benzene (10 mL) and the reaction mixture stirred at room temperature for 3 days. Et_2O (100 mL) was added to complete precipitation. The white solid was filtered off, washed with Et_2O, dried in vacuo, and recrystallized from CH_2Cl_2/MeOH (yield 87%).

[(dppp)Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$. (dppp)$Pt(CF_3)Cl$ (0.71 g, 1.00 mmol) was dissolved in dry N_2-saturated CH_2Cl_2 (20 mL). To the solution was added 1.32 mL of a 0.76 M solution of $AgBF_4$ in acetone, and the mixture was stirred for 30 min in the dark. AgCl was filtered off, and the resulting solution was centrifugated to eliminate traces of colloidal silver. The clear solution was brought to dryness in vacuo (10^{-2} Torr) to yield a white solid (yield 98%).

(dppp)Pt(CF$_3$)(OH). [(dppp)$Pt(CF_3)(CH_2Cl_2)]BF_4$ (0.83 g, 0.98 mmol) was suspended in MeOH (15 mL) and treated with 2.0 mL of a 1 M solution of KOH in H_2O for 1 h. The solution was evaporated to dryness in vacuo to yield an off-white solid. This was extracted with benzene (80 mL), and the residual solid was filtered off. The clear solution was evaporated in vacuo to a few milliliters, and the precipitation was completed with Et_2O. The solid was filtered, washed with Et_2O, dried in vacuo, and recrystallized from CH_2Cl_2/Et_2O (yield 90%).

(dppp)Pt(CF$_3$)(OOH). To a solution of (dppp)$Pt(CF_3)(OH)$ (0.35 g, 0.5 mmol) in CH_2Cl_2 (10 mL) was added an excess of 34% H_2O_2 (0.1 mL). The mixture was stirred for 1 h, and then 10 mL of water was added. The two phases were separated, the organic phase was concentrated to a few milliliters, and Et_2O (10 mL) was added. The white solid obtained was filtered off, washed with Et_2O, and dried. The product was recrystallized from CH_2Cl_2/Et_2O (yield 93%).

(dppb)Pt(CF$_3$)Cl. To a suspension of *trans*-$(PPh_3)_2Pt(CF_3)Cl$ (1.24 g, 1.50 mmol) in toluene (80 mL) was added in one portion a solution of dppb (0.65 g, 1.53 mmol) in toluene (20 mL). The mixture was stirred for 2 days at room temperature. The white solid formed was filtered off, washed with Et_2O, dried in vacuo, and recrystallized from CH_2Cl_2/MeOH (yield 75%).

[(dppb)Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$. This complex was prepared as [(dppp)$Pt(CF_3)(CH_2Cl_2)]BF_4$, starting from (dppb)$Pt(CF_3)Cl$ (0.72 g, 1.00 mmol) (yield 98%).

(dppb)Pt(CF$_3$)(OH). This complex was prepared as (dppp)$Pt(CF_3)(OH)$, starting from [(dppb)$Pt(CF_3)(CH_2Cl_2)]BF_4$ (0.84 g, 0.98 mmol). The white product was recrystallized from CH_2Cl_2/Et_2O (yield 85%).

(dppb)Pt(CF$_3$)(OOH). This complex was prepared as (dppp)$Pt(CF_3)(OOH)$, starting from (dppb)$Pt(CF_3)(OH)$ (0.35 g, 0.50 mmol). The white product was recrystallized from CH_2Cl_2/Et_2O (yield 89%).

---

(17) Henderson, W. A.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791.

(18) Equatorial–axial equilibrium has not been observed in (prophos)$Pt(CF_3)(OH)$.

(19) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

(*o*-dppb)Pt(CF_3)Cl. To a suspension of *trans*-(PPh_3)$_2$Pt(CF_3)Cl (1.65 g, 2.00 mmol) in toluene (100 mL) was added in one portion a solution of *o*-dppb (0.94 g, 2.10 mmol) in toluene (25 mL). The mixture was stirred overnight at room temperature. The white solid formed was filtered off, washed with Et_2O, dried in vacuo, and recrystallized from CH_2Cl_2/benzene (yield 87%). The compound is only sparingly soluble in CH_2Cl_2.

[(*o*-dppb)Pt(CF_3)(CH_2Cl_2)]BF_4. This complex was prepared as [(dppp)Pt(CF_3)(CH_2Cl_2)]BF_4, starting from (*o*-dpppb)Pt(CF_3)Cl (0.75 g, 1.00 mmol) (yield 97%).

(*o*-dppb)Pt(CF_3)(OH). This complex was prepared as (dppp)Pt(CF_3)(OH), starting from [(*o*-dppb)Pt(CF_3)(CH_2Cl_2)]BF_4 (0.85 g, 0.97 mmol). The white product was recrystallized from CH_2Cl_2/toluene (yield 89%).

(*o*-dppb)Pt(CF_3)(OOH). This complex was prepared as (dppp)Pt(CF_3)(OOH), starting from (*o*-dppb)Pt(CF_3)(OH) (0.36 g, 0.50 mmol). The white product was recyrstallized from CH_2Cl_2/toluene (yield 89%).

(dppx)Pt(CF_3)Cl. To a suspension of *trans*-(PPh_3)$_2$Pt(CF_3)Cl (2.06 g, 2.50 mmol) in benzene (80 mL) was added in one portion a solution of dppx (1.20 g, 2.53 mmol) in benzene (20 mL). The reaction mixture was stirred overnight at room temperature. Et_2O (100 mL) was added to complete precipitation, and the white solid was filtered off, washed with Et_2O, and recrystallized from CH_2Cl_2/MeOH (yield 88%).

[(dppx)Pt(CF_3)(CH_2Cl_2)]BF_4. This complex was prepared as [(dppp)Pt(CF_3)(CH_2Cl_2)]BF_4, starting from (dppx)Pt(CF_3)Cl (0.77 g, 1.00 mmol) (yield 95%).

(dppx)Pt(CF_3)(OH). This complex was prepared as (dppp)Pt(CF_3)(OH), starting from [(dppx)Pt(CF_3)(CH_2Cl_2)]BF_4 (0.87 g, 0.95 mmol). The white product was recrystallized from CH_2Cl_2/toluene (yield 93%).

(dppx)Pt(CF_3)(OOH). This complex was prepared as (dppp)Pt(CF_3)(OOH), starting from (dppx)Pt(CF_3)(OH) (0.38 g, 0.50 mmol). The white product was recrystallized from CH_2Cl_2/Et_2O (yield 88%).

(*N*-Bz-pyrphos)Pt(CF_3)Cl. To a suspension of trans-(PPh_3)$_2$Pt(CF_3)Cl (2.10 g, 2.50 mmol) in a 1/1 toluene/hexane mixture (100 mL) was added in one portion a solution of *N*-Bz-pyrphos (1.36 g, 2.60 mmol) in toluene (30 mL). The reaction mixture was stirred overnight at room temperature. The white solid was filtered off, washed with hexane, and dried in vacuo. The compound was recrystallized from CH_2Cl_2/MeOH (yield 90%).

[(*N*-Bz-pyrphos)Pt(CF_3)(CH_2Cl_2)]BF_4. This complex was prepared as [(dppp)Pt(CF_3)(CH_2Cl_2)]BF_4 starting from (*N*-Bz-pyrphos)Pt(CF_3)Cl (0.80 g, 1.00 mmol) (yield 98%).

(*N*-Bz-pyrphos)Pt(CF_3)(OH). This complex was prepared as (dppp)Pt(CF_3)(OH), starting from [(*N*-Bz-pyrphos)Pt(CF_3)(CH_2Cl_2)]BF_4 (0.95 g, 0.98 mmol). The white product was recrystallized from CH_2Cl_2/hexane (yield 93%).

(*N*-Bz-pyrphos)Pt(CF_3)(OOH). This complex was prepared as (dppp)Pt(CF_3)(OOH), starting from (*N*-Bz-pyrphos)Pt(CF_3)(OH) (0.40 g, 0.50 mmol). The white product was recrystallized from CH_2Cl_2/hexane (yield 93%).

(prophos)Pt(CF_3)(OOH). This complex was prepared as (dppp)Pt(CF_3)(OOH), starting from (prophos)Pt(CF_3)(OH) (0.35 g, 0.50 mmol). The white product was recrystallized from CH_2Cl_2/hexane (yield 90%).

(chiraphos)Pt(CF_3)(OOH). This complex was prepared as (dppp)Pt(CF_3)(OOH), starting from (chiraphos)Pt(CF_3)(OH) (0.36 g, 0.50 mmol). The white product was recrystallized from CH_2Cl_2/Et_2O (yield 91%).

(COD)Pt(C_6F_5)I. Pentafluorophenyl bromide (0.50 g, 2.0 mmol) in anhydrous Et_2O (20 mL) was treated at −60 °C with a hexane solution (1.6 M, 1.25 mL) of *n*-butyllithium. The mixture was stirred for 10 min, and a solution of (COD)PtI_2 in anhydrous THF (30 mL) was added. After being gently warmed to room temperature (1 h), the mixture was shaken with water and the organic layer evaporated to dryness to give a pale yellow product (yield 34%).

(diphoe)Pt(C_6F_5)I. To a solution of (COD)Pt(C_6F_5)I (0.41 g, 0.6 mmol) in benzene (50 mL) was added solid diphoe (0.28 g, 0.6 mmol), and the mixture was stirred at room temperature overnight. After addition of Et_2O (50 mL), a white product was obtained, which was filtered, washed with Et_2O, and recrystallized from CH_2Cl_2/MeOH (yield 94%).

(diphoe)Pt(C_6F_5)Cl. To a solution of (diphoe)Pt(C_6F_5)I (0.5 g, 0.56 mmol) in CH_2Cl_2 (30 mL) was added 0.63 mL of a 0.9 M solution of $AgClO_4$ in acetone. AgI was filtered off, and the filtrate was reduced to small volume and then treated with 25 mL of acetone and an excess of LiCl (0.1 g). The white precipitate was filtered off and recrystallized from CH_2Cl_2/EtOH (yield 98%).

[(diphoe)Pt(C_6F_5)(CH_2Cl_2)]BF_4. To a solution of (diphoe)Pt(C_6F_5)Cl (0.18 g, 0.22 mmol) in CH_2Cl_2 (15 mL) was added 0.22 mL of a 1 M solution of $AgBF_4$ in acetone. The mixture was reacted for 2 h, AgCl was filtered off, and the solution was evaporated to dryness under reduced pressure. The residual white solid was stored under N_2 (yield 97%).

(diphoe)Pt(C_6F_5)(OH). [(diphoe)Pt(C_6F_5)(CH_2Cl_2)]BF_4 (0.34 g, 0.37 mmol) was suspended in MeOH (10 mL), and 1 mL of a 1 M solution of KOH in H_2O was added with stirring. After addition of 50 mL of H_2O, a white product was recovered by filtration. This was washed with H_2O, dried in vacuo overnight, and recrystallized from CH_2Cl_2/Et_2O.

Catalytic Reactions. These were carried out in a 25-mL round-bottomed flask equipped with a stopcock for vacuum/N_2 operations and a side arm fitted with a screw-capped silicone septum to allow sampling. Constant temperature (25 °C) was maintained by water circulation through an external jacket connected with a thermostat. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer. Absence of diffusional problems below 2.0×10^{-4} M s^{-1} initial rates was determined by the independence of conversion vs time plots on the stirring rate on experiments randomly selected from Tables II and III.

The general procedure here reported was followed in all cases. In a typical experiment, the appropriate amount of catalyst was placed solid in the reactor, which was evacuated and placed under N_2 atmosphere. Dry, N_2-saturated CH_2Cl_2 (or THF) was added, followed by 1-octene. After the mixture was stirred for a few minutes, the appropriate H_2O_2 solution was injected and the time was started. The conversion was monitored by sampling periodically the reaction mixture with a microsyringe.

Acknowledgment. This work was supported jointly by the European Economic Community (Brussels) and Degussa AG (Frankfurt, FRG) through the special program BRITE. Degussa AG also provided a free sample of *N*-Bz-pyrphos. Special thanks are expressed to Drs. G. Prescher and M. Schmidt (Degussa AG), to Professor W. Drenth (University of Utrecht), and to Professor J. W. Buchler (University of Darmstadt) for stimulating discussions.

Registry No. dppm, 2071-20-7; dppp, 6737-42-4; dppb, 7688-25-7; *o*-dppb, 13991-08-7; dppx, 62144-65-4; *N*-Bz-pyrphos, 119296-22-9; diphoe, 983-80-2; *trans*-(PPh_3)$_2$Pt(CF_3)Cl, 71581-10-7; (dppm)Pt(CF_3)Cl, 119296-30-9; [(dppm)Pt(CF_3)(CH_2Cl_2)]BF_4, 119296-32-1; *trans*-(PPh_3)$_2$Pt(CF_3)(OH), 71588-93-7; [(dppm)Pt(PPh_3)(CF_3)](OH), 119296-26-3; (dppp)Pt(CF_3)Cl, 119296-33-2; [(dppp)Pt(CF_3)(CH_2Cl_2)]BF_4, 119296-28-5; (dppp)Pt(CF_3)(OH), 119296-25-2; (dppp)Pt(CF_3)(OOH), 119296-24-1; (dppb)Pt(CF_3)Cl, 119296-29-6; [(dppb)Pt(CF_3)(CH_2Cl_2)]BF_4, 119296-35-4; (dppb)Pt(CF_3)(OH), 119296-23-0; (dppb)Pt(CF_3)(OOH), 119325-74-5; (*o*-dppb)Pt(CF_3)Cl, 119296-36-5; [(*o*-dppb)Pt(CF_3)(CH_2Cl_2)]BF_4, 119296-38-7; (*o*-dppb)Pt(CF_3)(OH), 119296-39-8; (*o*-dppb)Pt(CF_3)(OOH), 119296-40-1; (dppx)Pt(CF_3)Cl, 119296-46-7; [(dppx)Pt(CF_3)(CH_2Cl_2)]BF_4, 119296-48-9; (dppx)Pt(CF_3)(OH), 119296-41-2; (dppx)Pt(CF_3)(OOH), 119296-42-3; (*N*-Bz-pyrphos)Pt(CF_3)Cl, 119296-49-0; [(*N*-Bz-pyrphos)Pt(CF_3)(CH_2Cl_2)]BF_4, 119296-51-4; (*N*-Bz-pyrphos)Pt(CF_3)(OH), 119296-43-4; (*N*-Bz-pyrphos)Pt(CF_3)(OOH), 119296-44-5; (prophos)Pt(CF_3)(OH), 119364-66-8; (prophos)Pt(CF_3)(OOH), 119296-52-5; (chiraphos)Pt(CF_3)(OH), 106864-65-7; (chiraphos)Pt(CF_3)(OOH), 119296-45-6; (COD)PtI_2, 12266-72-7; (COD)Pt(C_6F_5)I, 112100-79-5; (diphoe)Pt(CF_3)OH, 70504-87-9; (diphoe)Pt(C_6F_5)I, 119325-75-6; (diphoe)Pt(C_6F_5)Cl, 119325-76-7; (diphoe)Pt(C_6F_5)(CH_2Cl_2)]BF_4, 119325-78-9; (diphoe)Pt(C_6F_5)(OH), 119325-89-2; [(dppm)Pt(CF_3)(CH_2Cl_2)]ClO_4, 119325-79-0; (dppe)Pt(CF_3)(OH), 72953-78-7; [(dppe)Pt(CF_3)(CH_2Cl_2)]ClO_4, 119325-81-4; [(dppp)Pt(CF_3)(CH_2Cl_2)]ClO_4, 119325-82-5; [(dppb)Pt(CF_3)(CH_2Cl_2)]ClO_4, 119325-83-6; [(prophos)Pt(CF_3)(CH_2Cl_2)]ClO_4, 119365-51-4; [(chiraphos)Pt(CF_3)(CH_2Cl_2)]ClO_4, 119365-52-5; [(*N*-Bz-pyrphos)Pt(CF_3)(CH_2Cl_2)]ClO_4, 119325-84-7; [(diphoe)Pt(CF_3)(CH_2Cl_2)]ClO_4, 119325-88-1; [(*o*-dppb)Pt(CF_3)(CH_2Cl_2)]ClO_4, 119325-85-8; [(dppx)Pt(CF_3)(CH_2Cl_2)]ClO_4, 119325-86-9; pentafluorophenyl bromide, 344-04-7; 1-octene, 111-66-0.