J = 11.3 Hz), 2.98 (t, 2 H, CH$_2$SPh), 2.77 (t, 2 H, =CCH$_2$), 2.16 (s, 3 H, CH$_3$).

Cp(CO){P(OMe)$_3$}Mo{CH=C(CH$_2$CH$_2$NHPh)C(O)OMe} (15d). A mixture of 3a (52.1 mg, 0.124 mmol) and PhNH$_2$ (0.20 mL, 2.19 mmol) in Et$_2$O was applied to a column of alumina and left to stand at 298 K. After approximately 9 h the column was flushed with 4:1 Et$_2$O/CH$_3$CN and a pale orange solution collected. Removal of the solvent and excess PhNH$_2$ afforded 15d as an orange solid in 33% yield: ^{1}H NMR (CDCl$_3$) δ 11.18 (s, 1 H, CH), 7.13 (t, 2 H, Ph), 6.64 (t, 1 H, Ph), 6.57 (d, 2 H, Ph), 5.10 (d, Cp, $^2J_{HP}$ = 0.9 Hz), 3.82 (s, 3 H, OMe), 3.45 (d, 9 H, P(OMe)$_3$, J = 11.4 Hz), 3.02–3.21 (m, 2 H, CH$_2$NHPh), 2.52–2.67 (m, 2 H, =CCH$_2$), 2.12 (s, 3 H, CH$_3$); ^{31}P NMR (C$_6$D$_6$) δ 203.6; IR (THF) 1843 cm^{-1} (ν_{MoCO}); HRMS (FAB), m/z calc for M$^+$ (C$_{17}$H$_{25}$NO$_6$P^{98}Mo) 519.0708, found 519.0696.

Cp(CO){P(OMe)$_3$}Mo{CH=C(CH$_2$CH$_2$OH)C(O)R} [R = Me (17a), c-C$_3$H$_5$ (17b), Ph (17c)]. A yellow solution of 3a (57.2 mg, 0.14 mmol) in Et$_2$O was applied to a column of alumina to which approximately 1.3% H$_2$O had been added. The resultant orange band was eluted at regular intervals for 72 h with 20:1 THF/EtOH and 17a obtained as a red solid (30.7 mg, 51%) upon removal of solvent. The cyclopropyl and phenyl complexes were prepared in similar fashion from 3b and 3c in 74% and 46% yield, respectively. **17a:** ^{1}H NMR (CDCl$_3$) δ 11.67 (s, 1 H, CH), 5.15 (s, 5 H, Cp), 3.60–3.65 (m, 2 H, CH$_2$OH), 3.38 (d, 9 H, P(OMe)$_3$, J = 11.1 Hz), 2.62–2.74 (m, 2 H, =CCH$_2$), 2.35 (s, 3 H, CH$_3$); ^{13}C NMR (C$_6$D$_6$) δ 253.5 (d, CH=C, $^2J_{CP}$ = 4.3 Hz), 251.5 (d, $^2J_{CP}$ = 29.4 Hz, MoCO), 191.1 (s, C=O), 133.6 (s, CH=C), 91.4 (Cp), 63.7 (CH$_2$OH), 51.7 [(P(OMe)$_3$)], 36.7 (=CCH$_2$), 22.7 (CH$_3$); ^{31}P NMR (C$_6$D$_6$) δ 195.2; IR (CH$_2$Cl$_2$) 1845 cm^{-1} (ν_{MoCO}); HRMS (FAB), m/z calc for M$^+$ (C$_{15}$H$_{23}$O$_6$P^{98}Mo) 428.0286, found 428.0261. **17b:** ^{1}H NMR (C$_6$D$_6$) δ 11.88 (s, 1 H, CH), 4.87 (s, 5 H, Cp), 3.65 (m, 2 H, CH$_2$OH), 3.22 (d, 9 H, P(OMe)$_3$, J = 11.6 Hz), 2.76–2.89 (m, 2 H, =CCH$_2$), 1.91 (m, 1 H, c-C$_3$H$_5$), 1.05 (m, 2 H, c-C$_3$H$_5$), 0.57 (m, 2 H, c-C$_3$H$_5$); ^{31}P NMR (C$_6$D$_6$) δ 196.7; IR (CH$_2$Cl$_2$) 1844 cm^{-1} (ν_{MoCO}); HRMS (FAB), m/z calc for M$^+$ (C$_{17}$H$_{25}$O$_6$P^{98}Mo) 490.0433, found 490.0440. **17c:** ^{1}H NMR (C$_6$D$_6$) δ 12.13 (d, 1 H, CH, $^3J_{HP}$ = 1.4 Hz), 7.82 (d, 2 H, Ph), 7.21 (t, 2 H, Ph), 7.10 (t, 1 H, Ph), 4.95 (s, 5 H, Cp), 3.70 (m, 2 H, CH$_2$OH), 3.27 (d, 9 H, P(OMe)$_3$, J = 11.2 Hz), 2.94–3.10 (m, 2 H, =CCH$_2$); ^{31}P NMR (C$_6$D$_6$) δ 192.1; IR (CH$_2$Cl$_2$) 1862 cm^{-1} (ν_{MoCO}); HRMS

(FAB), m/z calc for M$^+$ (C$_{20}$H$_{25}$O$_6$P^{98}Mo) 490.0443, found 490.0417.

Crystal Structure of 4a. X-ray data collection was performed on a crystal sealed in a 0.5 mm capillary under nitrogen. The diffractometer used was a Siemens P2$_1$ equipped with Mo radiation. Data reduction was done on a DEC micro VAX computer running the SDP programs.[19] The observed data were corrected for decay, Lorentz, and polarization factors, and for absorption. The structure was solved using the Patterson heavy atom method and refined with full-matrix least squares. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not refined due to an error in the data which resulted from a fluctuation in the power supply while collecting.

Crystal Data for 4a: empirical formula C$_{15}$H$_{22}$ClO$_5$PMo; color, habit, dark red blocks; crystal size, 0.20 × 0.35 × 0.20 mm^3; crystal system, P2$_1$/c; a (Å), 9.9718 (23); b (Å), 19.0260 (53); c (Å), 9.8171 (29); β (deg), 92.765 (22); V (Å^3), 1860.4 (9); Z, 4; FW, 444.707; D_{calc} (g/cm^3), 1.588; abs coeff, 9.360; diffractometer, Syntex P2$_1$; radiation, graphite-monochromated Mo Kα (0.710 73 Å); 2θ range (deg), 3–50; scan type, θ–2θ; scan speed, variable 4–29; std reflections, 3 std/47 refl; refl collected, 5068; independent refl, 4356; obsd refl F_o > 3σ(F_o), 2280; data/parameter, 10.9; final R(F), R(wF), 7.3%, 8.8%; weighting scheme, 1/w = σ^2(I)/4F^2 + 0.000225F^2; final GOF, 3.22; D/s (mean), 0.000; highest peak in diff map, 2.686 (peaks over 1.3 were Mo ghosts).

Supplementary Material Available: Tables of bond distances, bond angles, positional parameters, and anisotropic displacement parameters (6 pages). Ordering information is given on any current masthead page.

OM920067Y

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Hydroxylation of Aromatics with Hydrogen Peroxide Catalyzed by Cationic Complexes of Platinum(II). Evidence for the Intermolecular Oxidation of Platinum Aryls

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The catalytic hydroxylation of a variety of aromatic substrates is reported using 70% hydrogen peroxide as primary oxidant and a series of (P-P)Pt(CF$_3$)X complexes (P-P = different tetraaryldiphosphines; X = CH$_2$Cl$_2$, -OH, -OPh) as catalysts. The reactivity observed increases with the presence of electron-releasing substituents at the aromatic ring, selectively producing ortho and para products. Good amounts of products are obtained with the most activated substrates phenol, anisole, m-cresol, and 1,3-dimethoxybenzene, and in all cases an interesting ortho selectivity (up to 95%) is observed. A mechanistic study carried out on the last substrate suggests the involvement of an electrophilic metalation of the aromatic ring to produce platinum-aryl intermediates followed by oxygen transfer from a platinum-hydroperoxy species. This seems to represent a rare example in which a soluble transition-metal complex catalyzes the *direct* hydroxylation of an aromatic ring via *electrophilic metalation* under mild conditions.

Introduction

The hydroxylation of aromatics to produce phenols is a very important industrial reaction that finds applications in a variety of sectors ranging from plastics to agrochem-

icals to pharmaceuticals and is generally accomplished in the industrial practice in multistage processes.[1] For this

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main reason the direct catalytic conversion into products with use of monooxygen donors such as hydrogen peroxide (reaction 1) has long been the subject of both industrial

$$R\text{-}C_6H_5 + H_2O_2 \rightarrow R\text{-}C_6H_4\text{-}OH + H_2O \quad (1)$$
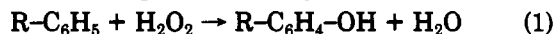
and academic research. The practical interest in the use of hydrogen peroxide relies mainly on the innocuous nature of its byproduct, water, which is important in the context of environmental considerations, and on its high "active oxygen" content that, compared to other low-cost oxidants such as t-BuOOH, NaClO, $KHSO_5$, etc., minimizes the quantity of byproducts formed.

Direct hydroxylation of aromatics with H_2O_2 can be accomplished by increasing the electrophilicity of the oxidant through the use of such Lewis acids as, for instance, $AlCl_3$[2] and $BF_3 \cdot OEt_2$[3] or by carrying out the reaction in superacidic media.[4] These systems are not catalytic, often requiring a large excess of activating agent. Moreover, in order to be effective, the amount of water present has to be minimized; best results are in fact obtained using H_2O_2 in concentrations >90%. However, experimental conditions of this type are hard to meet technically, since for instance detonation problems arise with hydrogen peroxide in concentrations higher than 86%.[5]

This reaction has recently become an industrial reality[6] with the use as catalysts of an interesting class of inorganic materials, Ti silicalites, which allow the conversion of phenol, using H_2O_2, into 1 1/1 mixture of catechol and hydroquinone with high efficiency.[7] Unfortunately, the mechanism of action of these interesting catalysts is still unclear.[6,8] Other selective oxidants for the stoichiometric hydroxylation of aromatics are some (picolinato)vanadium(V) peroxo complexes that are easily formed from H_2O_2.[9] With these reagents very little side-chain oxidation is observed with alkylbenzenes, and mechanistic studies[9,10] have suggested the involvement of homolytic splitting of the peroxo moiety followed by radical attack at the aromatic ring, although some controversy has arisen concerning the nature of the reactive intermediates.[9,10]

Recently, we have reported the use of a wide class of platinum(II) complexes of the type (P-P)Pt(CF$_3$)X (P-P = chelating diphosphine, X = solvent, OH) as catalysts in the selective epoxidation of a variety of simple olefins using H_2O_2 as primary oxidant.[11] A mechanistic study of this

Table I. Hydroxylation of Phenol with H_2O_2 Catalyzed by Platinum(II) Complexes[a]

catalyst	time, h	amt of products, 10^{-2} mmol		
		hydro-quinone	catechol	others
(diphoe)Pt(CF$_3$)(CH$_2$Cl$_2$)$^+$	2.5	10	38	4
	5	90	136	15
(o-dppb)Pt(CF$_3$)(CH$_2$Cl$_2$)$^+$	2		22	3
	6	28	62	11
(dppe)Pt(CF$_3$)(CH$_2$Cl$_2$)$^+$	2	2	20	
	6	7	34	4
(dppe)Pt(CF$_3$)(OH)	5		20	
	7	3	27	
(diphoe)Pt(CF$_3$)(OPh)	0.5	2	38	
	3.5	7	55	4
(dppe)Pt(CF$_3$)(OPh)	4.5		16	
	6.5	2	30	

[a] Reaction conditions: phenol, 60 mmol; 70% H_2O_2, 6 mmol; i-PrOH, 0.65 mL; Pt, 6 × 10^{-2} mmol; N_2, 1 atm; T, 85 °C.

catalytic system has revealed as the key step the nucleophilic attack of a coordinated hydroperoxy anion at the olefin coordinated on a second Pt center (reaction 2).[12]

$$Pt(ol)^+ + HOO\text{-}Pt \rightarrow epoxide + Pt\text{-}OH + Pt^+ \quad (2)$$

This peculiar behavior indicates that these systems are able to activate independently at different metal centers not only the oxidant but also the substrate and is an example of bifunctional catalysis.[13] In principle, the ability to activate the substrate toward nucleophilic attack is not limited to olefins and can be extended to aromatics. It is in fact known that Pd(II) salts can promote the addition of nucleophiles such as AcO$^-$ to both olefins and aromatics via mechanisms that have been suggested to be essentially similar.[14]

We have tested the above Pt(II) catalysts for the direct hydroxylation of aromatics by hydrogen peroxide with the aim of finding a selective, non-radical route to these oxygenated compounds, and the results of this study are reported here.

Results and Discussion

Oxidation of Phenol and Selection of the Reaction Conditions. The reaction was initially tested in the case of phenol in order to determine the most appropriate experimental conditions. The use of solvents such as alcohols, THF, and dichloroethane (DCE) or reaction temperatures below 65 °C resulted in very poor product formation. The best reaction conditions appeared to be temperatures in the range 80–90 °C and the use of 70% H_2O_2 as oxidant and of virtually neat substrate as the solvent, although small amounts of i-PrOH were found to be necessary to dissolve the catalyst in the reaction medium. A summary of the results obtained under the appropriate experimental conditions in the hydroxylation of phenol using a variety of (P-P)Pt(CF$_3$)X catalysts (X = CH$_2$Cl$_2$, –OH, –OPh) is reported in Table I (diphoe = cis-1,2-bis(diphenylphosphino)ethylene; o-dppb = o-bis-

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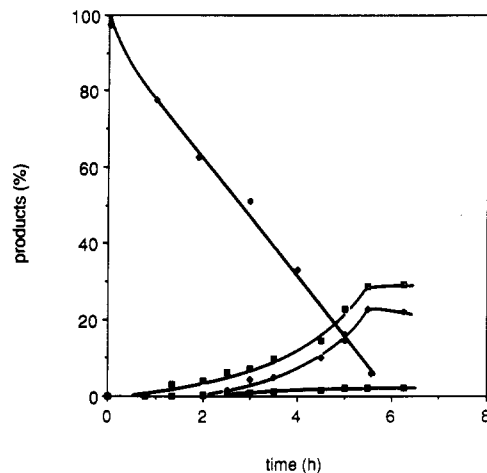
Figure 1. Reaction profile for the hydroxylation of phenol using [(diphoe)Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$ as catalyst. Reaction conditions are as given in Table I. Products (%) is in reference to the H$_2$O$_2$ introduced. Symbols: (◊) H$_2$O$_2$; (♦) hydroquinone; (□) catechol; (■) other products.

Figure 2. Comparison of the activity of [(dppe)Pt(CF$_3$)-(CH$_2$Cl$_2$)]ClO$_4$ (□), (dppe)Pt(CF$_3$)(OH) (♦), and (dppe)Pt-(CF$_3$)(OPh) (■) in the hydroxylation of phenol. Reaction conditions are as given in Table I. Products (%) is in reference to the H$_2$O$_2$ introduced.

(diphenylphosphino)benzene; dppe = 1,2-bis(diphenyl-phosphino)ethane). The use of different diphosphines appears to produce moderate differences in the catalytic activity, at variance with the epoxidation of olefins, where a strong influence was observed depending on the shape and size of the chelating diphosphine–metal ring.[11d] As shown in Table I, moderate amounts of catechol (which represents the preferred product in all cases) and hydroquinone are obtained together with minor amounts of other higher molecular weight oxidation products:
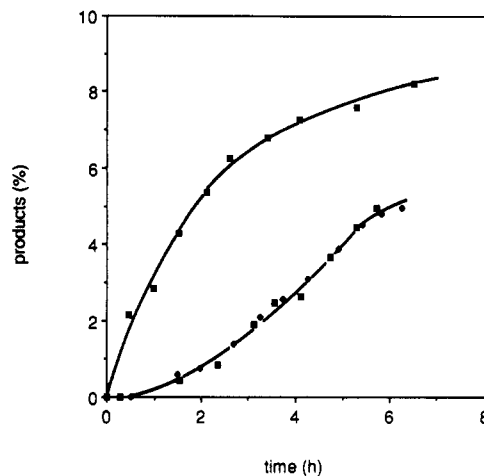

(3)

9/2/1
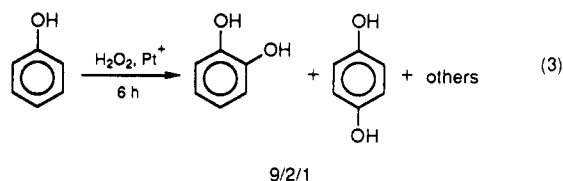
These are analyzed with GC–MS techniques and were identified as products of further reaction of catechol and hydroquinone. The major side products are
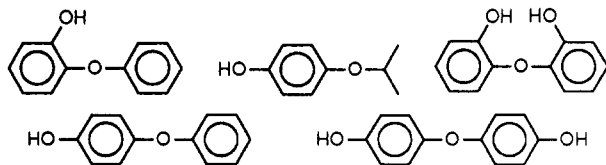
These could well be (at least in part) the "tars" that are very commonly observed in most hydroxylations of aromatic hydrocarbons.[1] In fact, also in this case the reaction mixture darkens rapidly after about 0.5 h in all the cases reported in Table I, even in those in which the above products are not detected by GLC. Apparently, the above products seem to arise from "condensation" of phenol, 2-propanol and the primary oxidation products. Attempts to carry out these condensations starting from the appropriate reactants and [(diphoe)Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$ as catalyst in the absence of H$_2$O$_2$ were unsuccessful, no reaction being observed after 24 h at 90 °C.

A lower activity was observed with (P-P)Pt(CF$_3$)(OH) complexes (in Table I the case of (dppe)Pt(CF$_3$)(OH) is reported for comparison), this behavior being similar to what was already observed in the epoxidation of olefins, where the PtOH complexes were found to be significantly less active. Here, the "condensation" products shown
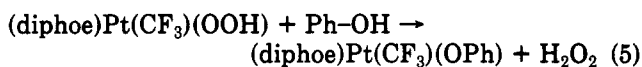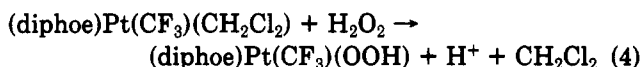
above are not observed, although the reaction mixture darkens, and a marked increase in selectivity toward the formation of catechol is observed.

More information on the hydroxylation of phenol can be gained by the analysis of the reaction profile, including H$_2$O$_2$ consumption, and a typical case is reported in Figure 1 for the complex (diphoe)Pt(CF$_3$)(CH$_2$Cl$_2$)$^+$. This shows clearly that no more than 50–55% of the H$_2$O$_2$ introduced is converted into products and this behavior is quite general, since random analyses for the H$_2$O$_2$ content indicated that ~85–90% of the H$_2$O$_2$ introduced is consumed within 5–6 h in all cases reported in Table I, much more than the total amount of products formed in the individual cases.

A reaction between phenol and (diphoe)Pt(CF$_3$)(OOH),[15] which can easily form by hydrolysis with H$_2$O$_2$[12] (reaction 4) from (diphoe)Pt(CF$_3$)(CH$_2$Cl$_2$)$^+$, yielded the corresponding phenoxy derivative (reaction 5). The compound

$$(diphoe)Pt(CF_3)(CH_2Cl_2) + H_2O_2 \rightarrow$$
$$(diphoe)Pt(CF_3)(OOH) + H^+ + CH_2Cl_2 \quad (4)$$

$$(diphoe)Pt(CF_3)(OOH) + Ph-OH \rightarrow$$
$$(diphoe)Pt(CF_3)(OPh) + H_2O_2 \quad (5)$$

(diphoe)Pt(CF$_3$)(OPh) was characterized by IR (1575 cm^{-1} (Ph); 1280, 1290 cm^{-1} (C-O)) and ^{19}F NMR (-26.48 ppm (dd); $^3J_{F-P_{cis}}$ = 10.1 Hz, $^3J_{F-P_{trans}}$ = 60.9 Hz, $^2J_{F-Pt}$ = 572 Hz) spectroscopy, and IR data appear to be in agreement with similar aryloxy complexes prepared from P$_2$MMe$_2$ complexes (P = PEt$_3$, PPh$_2$Et; M = Ni, Pd) by reaction with substituted phenols.[16] A material showing similar IR features was isolated from the reaction mixture by addition of Et$_2$O at the end of the catalytic reaction using [(diphoe)Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$ as catalyst. From the persistance of a broad band centered at 1040 cm^{-1} typical of BF$_4^-$ it is inferred this material is most likely a mixture of the starting cationic complex and the Pt-OPh complex.

The involvement of the phenoxy complex in the catalytic reaction was demonstrated by its use as catalyst that resulted in the rapid formation of products with a marked selectivity toward catechol (see Table I). Analogous product distribution was observed using (dppe)Pt(CF$_3$)-(OPh) as catalyst (Table I). This behavior is summarized

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Table II. Hydroxylation of 1,3-Dimethoxybenzene with H₂O₂ Catalyzed by [(P-P)Pt(CF₃)(CH₂Cl₂)]⁺ Complexes[a]

| P-P	time, h	amt of products, 10^{-2} mmol		
		2,4-(MeO)₂PhOH	2,6-(MeO)₂PhOH	unknown
diphoe	0.5	167	27	12
	2	229	33	6
	6	247	35	2
dppe	0.5	176	32	17
	2	239	36	2
	6	249	36	0
dppe[b]	0.5	3	0	0
	2	33	4	0
	6	102	11	0
o-dppb	0.5	107	18	13
	2	194	29	7
	6	203	32	5

[a] Reaction conditions: 1,3-dimethoxybenzene, 60 mmol; 70% H₂O₂, 6 mmol; Pt, 6 × 10^{-2} mmol; N₂, 1 atm; T, 85 °C. [b] Pt-OH complex as catalyst.

in Figure 2, where a comparison among the three homologous complexes [(dppe)Pt(CF₃)(CH₂Cl₂)]ClO₄, (dppe)-Pt(CF₃)(OH), and (dppe)Pt(CF₃)(OPh) as catalysts is shown by plotting the total product formation with time. As can be seen the two curves of (dppe)Pt(CF₃)(OH) and (dppe)Pt(CF₃)OPh) are virtually superimposable even in the product distribution (Table I), suggesting in this case the involvement of reaction 6 as a major pathway leading to catalyst evolution, which makes the Pt–OH- and Pt-OPh-based systems equivalent from a practical point of view.

$$(P\text{-}P)Pt(CF_3)(OH) + Ph\text{-}OH \rightarrow$$
$$(P\text{-}P)Pt(CF_3)(OPh) + H_2O \quad (6)$$
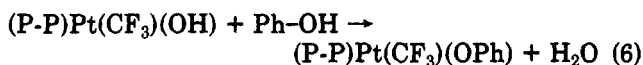
$$P\text{-}P = \text{diphoe, dppe}$$

Oxidation of 1,3-Dimethoxybenzene. The oxidation of 1,3-dimethoxybenzene was carried out under the same experimental conditions as for phenol; however, in the case of 1,3-dimethoxybenzene the catalysts are soluble in the substrate itself, thereby avoiding the use of solvents. Under these conditions there is phase separation between the organic phase and the aqueous phase. A summary of the results obtained in the catalytic hydroxylation of this substrate with a variety of (P-P)Pt(CF₃)(CH₂Cl₂)⁺ complexes is reported in Table II. In this case no tar formation was observed and the reaction mixture remained pale yellow throughout the experiments. Apparently, both the reactivity and the selectivity to phenols seem better than in the previous case, with a marked preference for the less sterically hindered 2,4-dimethoxyphenol:
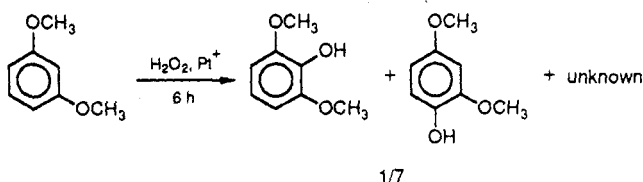
A small amount of an unknown product which tended to disappear with time was observed in the system. This product is not 3,5-dimethoxyphenol.

Similarly to the above described reaction with phenol and the already reported epoxidation of olefins,[11] also in this case a significant difference in activity is observed between the Pt⁺ and the corresponding Pt–OH complexes as catalysts (see in Table II the case of (dppe)Pt(CF₃)-(OH)). Again, the nature of the diphosphine appears to have only moderate influence on the reactivity of the catalysts and the efficiency in the utilization of hydrogen peroxide is similar to the case of phenol (Figure 3).
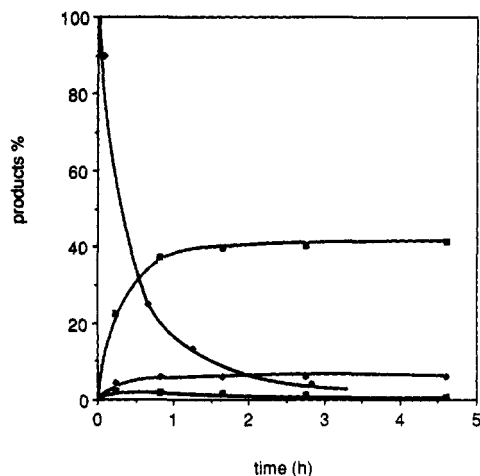
Figure 3. Reaction profile for the hydroxylation of 1,3-dimethoxybenzene using [(dppe)Pt(CF₃)(CH₂Cl₂)]ClO₄ as catalyst. Reaction conditions are as given in Table II. Products (%) is in reference to the H₂O₂ introduced. Symbols: (◊) H₂O₂; (♦) 2,6-dimethoxyphenol; (□) 2,4-dimethoxyphenol; (■) unknown product.

Table III. Hydroxylation of Different Aromatics with H₂O₂ Catalyzed by the [(dppe)Pt(CF₃)(CH₃)(CH₂Cl₂)]ClO₄ Complex[a]

| substrate	time, h	amt of products, 10^{-2} mmol			conversn of H₂O₂, 10^{-2} mmol
		ortho	para	others	
chlorobenzene[b]	4	1			482
benzene[c]	24				570
naphthalene[d]	4	trace	trace	trace	408
toluene[e]	7	4		9[f]	500
N,N-dimethylaniline[g]	3	4	2	27[h]	430
	24	5	3	32[h]	545
phenol[i]	2	20	2		222
	6	34	7	4[j]	600
phenol[i,p]	2	21	2		
	6	36	8	3[j]	
phenol[i,q]	2	3	1		
	6	15	3	2[j]	
m-cresol[i]	0.5	18[k]	16[l]		365
	3	55[k]	19[l]		532
m-cresol[i,m]	2	5			265
	6	13			580
anisole	3	68	15		309
	7	140	25		545
1,3-dimethoxybenzene	0.5	32[n]	176[o]	17[f]	404
	2	36[n]	239[o]	2[f]	546
1,3-dimethoxybenzene[p]	0.5	33[n]	173[o]	11[f]	
	2	37[n]	245[o]	4[f]	
1,3-dimethoxybenzene[q]	0.5	4[n]	22[o]		
	2	6[n]	31[o]		

[a] Reaction conditions: substrate, 60 mmol; 70% H₂O₂, 6 mmol; Pt, 6 × 10^{-2} mmol; N₂, 1 atm; T, 85 °C. [b] Added DCE 1.5 mL, i-PrOH 6.5 mL. [c] Added DCE 2.0 mL. [d] Added DCE 4 mL, i-PrOH 7 mL. [e] Added DCE 2.5 mL, i-PrOH 3.5 mL. [f] Only one unidentified product (see text). [g] Added i-PrOH 1 mL. [h] N-oxide. [i] Added i-PrOH 0.65 mL. [j] See text for the nature of products. [k] 4-Methylcatechol. [l] Methylhydroquinone. [m] (dppe)Pt(CF₃)(OH) as catalyst. [n] 2,6-Dimethoxyphenol. [o] 2,4-dimethoxyphenol. [p] Added DBPC 30 × 10^{-2} mmol. [q] Added AIBN 6 × 10^{-2} mmol.

Oxidation of Other Aromatic Substrates. The catalytic activity of the P₂Pt(CF₃)(CH₂Cl₂)⁺ complexes was tested in the hydroxylation of a series of different aromatic substrates. In most cases, due to the lack of solubility of the catalyst in the neat substrate, minimum amounts of dichloroethane (DCE) and/or i-PrOH were employed in the individual cases. This necessarily resulted in rather different experimental conditions for the various substrates, and hence, a comparison among the different reactivities must be taken only in a broad, qualitative sense.

The results obtained in the case of P-P = dppe are reported in Table III. As shown, either no products or only traces of products were observed in the case of chlorobenzene, benzene, and naphthalene, while with toluene, although more productive, the reaction was still less than catalytic. In addition to o-cresol, an unidentified product was also present, which is not benzyl alcohol, benzaldehyde, benzoic acid, or dibenzyl, indicating the likely absence of alkyl chain oxidation. More significant amounts of products were observed in the case of more activated rings such as N,N-dimethylaniline; however, in this case the major product appeared to be the N-oxide. It is known that tertiary amines can be oxidized by hydroperoxides such as H_2O_2;[17] however, the reaction is generally slow and in fact a blank reaction carried out under the same experimental conditions without catalyst yielded 13×10^{-2} and 15×10^{-2} mmol N-oxide after 3 and 24 h, respectively, indicating a contribution of Pt to the overall N-oxide formation.

In the case of anisole the reaction proceeded quite readily and an marked selectivity toward the formation of the ortho hydroxylation product (guaiacol) was observed (reaction 7). This is particularly interesting, since ortho


6/1
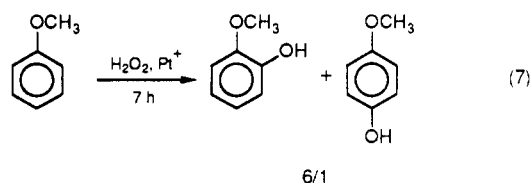
hydroxylation products are generally less favored and, specifically, guaiacol finds therapeutic use as a cough suppressant.[1a] Even in this case, the hydroxy complexes are poorer catalysts compared to the corresponding cationic complexes.

The oxidation of m-cresol is similar to the oxidation of phenol. Tar formation (dark solution) and a selectivity toward the product substituted in the ortho position with respect to the original –OH group were observed (Table III and reaction 8). 4-Methylcatechol became the exclusive product when (dppe)Pt(CF_3)(OH) was used as catalyst.

3/1
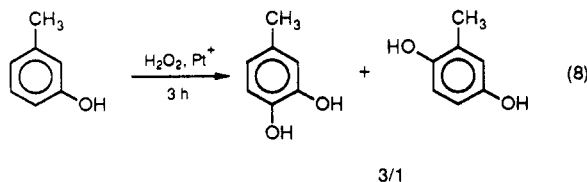
In all cases reported in Table III, the amount of H_2O_2 converted into products was much less the total amount consumed during the reaction, and this appears to be a major limitation in achieving higher amounts of products.

As a general trend, from Table III it appears that activated aromatic rings can be hydroxylated rather efficiently by these catalysts to produce ortho and para substitution products. The overall scale of reactivity reported in Table II seems to parallel that of the electrophilic aromatic substitution. This conclusion seems to be supported also by the observation that when two electron-releasing substituents are present in the ring (m-cresol and 1,3-dimethoxybenzene) these must be mutually in meta position, thereby adding their effects for all the possible substitution positions. Conversely, for ortho- and para-disubstituted substrates it is expected that the activation effects on the aromatic ring will be subtracted. Consist-
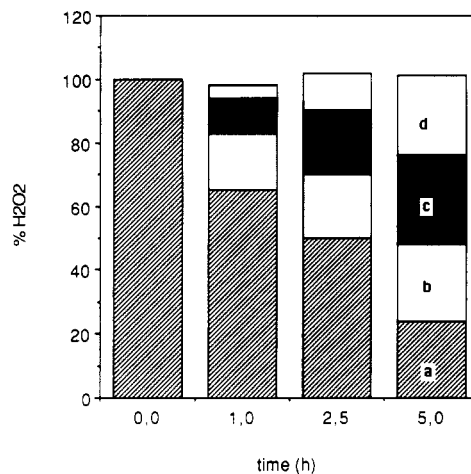
Figure 4. Mass balance at different reaction times of the hydrogen peroxide introduced in the hydroxylation of anisole using $[(dppe)Pt(CF_3)(CH_2Cl_2)]ClO_4$ as catalyst. Reaction conditions are as given in Table III. Symbols: (a) percent residual; (b) percent decomposed by the substrate; (c) percent decomposed by the catalyst; (d) percent converted into products.

ently, no reaction was observed in the case of o-cresol, p-cresol, and 1,4-dimethoxybenzene.

Mass Balance of Hydrogen Peroxide. One of the typical features of this and other[7] hydroxylations of aromatics with hydrogen peroxide catalyzed by transition-metal species is the significant amount of H_2O_2 that is wasted during the reaction. In order to evaluate the factors leading to the partial decomposition of H_2O_2 in the present catalytic system, a series of experiments were carried out with anisole as the substrate. This was chosen because the reaction is particularly clean, no tar formation being observed.

A first experiment involved the hydroxylation of anisole under the standard conditions of Table III, with monitoring of both the formation of products and the amount of residual H_2O_2.

A second experiment was carried out without substrate using THF as solvent in order to evaluate the contribution of the catalyst to the decomposition of H_2O_2.

A third experiment was performed without catalyst in order to evaluate the contribution to decomposition arising from the substrate trace impurities. It has to be pointed out that in this latter case no hydroxylation products were observed even after 24 h.

The results of these experiments are summarized in Figure 4, where the various fractions of H_2O_2, residual (a), decomposed by the substrate (b), decomposed by the catalyst (c), and converted into products (d), at different reaction times are shown. As it appears, the addition of these four contributions always sums up to the total amount introduced. From these experiments it can be inferred that no H_2O_2 is converted into possible nondetected products other than those considered.

Nature of the Hydroxylation Reaction. In order to test the possible involvement of radical intermediates, the reaction was tested in the presence of a radical scavenger such as di-tert-butyl-p-cresol (DBPC) and in the presence of a radical initiator such as azobisisobutyronitrile (AIBN). Phenol and 1,3-dimethoxybenzene were used as prototype substrates.

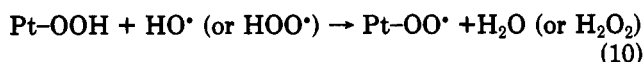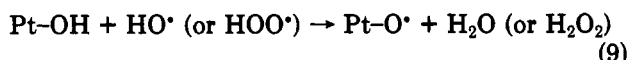In both cases the use of DBPC had no effect on either the reaction rate or the product distribution (Table III), even in the case of phenol, where the nature of the by-products (see above) may suggest free radical contribution to the overall activity. Conversely, the addition of AIBN

(17) Challis, B. C.; Butler, A. R. In *The Chemistry of the Amino Group*; Patai, S., Ed.; Wiley-Interscience: New York, 1968; p 326.

in a 1/1 molar ratio with respect to the catalyst significantly slowed down the catalysis (Table III). A reaction between [(diphoe)Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$, AIBN, and 70% H$_2$O$_2$ (1/5/50 molar ratios) in refluxing THF yielded a white solid showing a sharp IR band at 2190 cm^{-1}. This might be attributed to the presence of a Pt–CN species[18] probably arising from decomposition of AIBN. Partial deactivation of the catalyst through the formation of species of this type might be a plausible explanation for the unexpected effect of AIBN on the catalytic reaction.
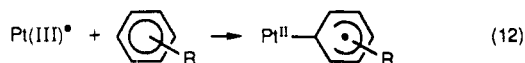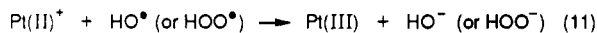
The behavior observed seems to support the idea that a radical-type hydroxylation of the aromatic substrate out of the coordination sphere of the metal (Fenton-type chemistry) has no role in product formation. This is further supported by the product distribution of the present catalytic system (only ortho and para substitution products are formed) compared to that of Fenton-type oxidations, where also extensive amounts of meta isomers and side-chain oxidation products are generally produced.[19] However, this does not rule out the possibility that a radical-type reaction within the coordination sphere of the metal (hardly detectable by DBPC because of steric hindrance) will occur similarly to the behavior of V(V) peroxy complexes.[9,10]

Indeed, the hydroxy and hydroperoxy radicals formed from H$_2$O$_2$ decomposition may react with PtOH or PtOOH to give the corresponding oxy and peroxy radical (reactions 9 and 10). Moreover, the latter species could also be

$$Pt\text{-}OH + HO^\bullet \ (or \ HOO^\bullet) \rightarrow Pt\text{-}O^\bullet + H_2O \ (or \ H_2O_2) \quad (9)$$

$$Pt\text{-}OOH + HO^\bullet \ (or \ HOO^\bullet) \rightarrow Pt\text{-}OO^\bullet + H_2O \ (or \ H_2O_2) \quad (10)$$

produced by spontaneous radical decomposition of the PtOOH intermediate at 85 °C since, as reported above, the catalyst actively participates in the decomposition of hydrogen peroxide. In principle, these radicals might be the intermediates leading to attack at the aromatic ring.

This view contrasts with the observation that the Pt–OH complexes themselves are poorer catalysts for the hydroxylation reaction but does not rule out the possibility that a similar reaction may occur with the Pt$^+$ complexes (reaction 11) to yield a Pt(III) radical species. Subsequent

$$Pt(II)^+ + HO^\bullet \ (or \ HOO^\bullet) \rightarrow Pt(III) + HO^- \ (or \ HOO^-) \quad (11)$$

$$Pt(III)^\bullet + \langle\langle\bigcirc\rangle\rangle_R \rightarrow Pt^{II}\text{-}\langle\langle\bigcirc\rangle\rangle_R \quad (12)$$

attack on the aromatic ring (reaction 12) would account for product formation. Again, the observed product distribution militates against this view; in fact, the only prior example of clear metal-centered radical hydroxylation of aromatics, i.e. the one involving the [(pic)$_2$VO(O$_2$)]$^+$ complex (pic = pyridine-2-carboxylate anion), gave in the case of toluene a product mixture consisting of benzaldehyde and o-, m-, and p-cresol.

As suggested above, an electrophilic substitution at the aromatic ring appears to be the most plausible pathway for the present catalytic process. This is further supported

(18) See for example: Roundhill, D. M. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1985; Vol. 5, p 357 and references therein.

(19) For leading references on this topic see: (a) Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125. (b) Walling, C.; Johnson, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 363. (c) Jefcoate, C. R. E.; Lindsay Smith, J. R.; Norman, R. O. C. *J. Chem. Soc. B* **1969**, 1013. (d) Edwards, J. O.; Curci, R. In *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*; Strukul, G., Ed.; Kluwer: Dordrecht, The Netherlands, in press; Chapter 4, and references therein.
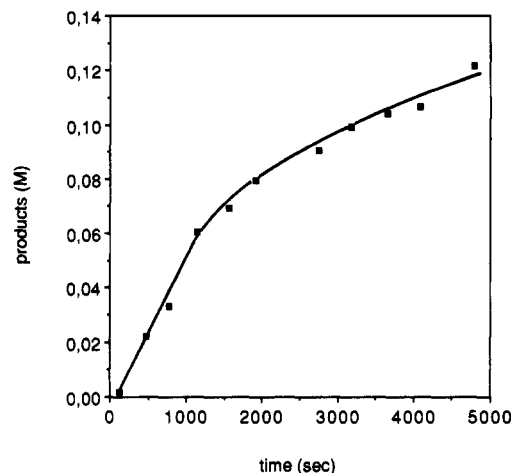
Figure 5. Typical reaction profile for total product formation in the hydroxylation of 1,3-dimethoxybenzene using [(diphoe)-Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$ as catalyst, showing the linear initial rate. Reaction conditions: 1,3-dimethoxybenzene (neat), 60 mmol; 70% H$_2$O$_2$, 6 mmol; [Pt], 4.41 × 10^{-3} M; T, 85 °C; N$_2$, 1 atm.
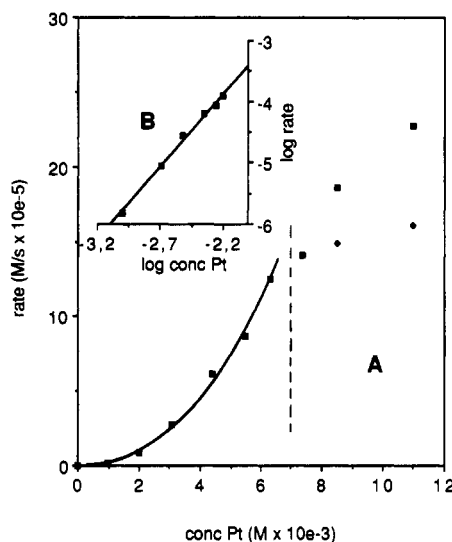
Figure 6. Effect of the concentration of [(diphoe)Pt(CF$_3$)-(CH$_2$Cl$_2$)]BF$_4$ on the initial rate in the catalytic hydroxylation of 1,3-dimethoxybenzene: (a) linear plot; (B) log/log plot. For concentrations higher than the broken line, the rate is controlled by the diffusion of H$_2$O$_2$ from the aqueous to the organic phase. Diamonds represent experiments where the stirring rate was reduced to half. Reaction conditions: 1,3-dimethoxybenzene (neat), 60 mmol; 70% H$_2$O$_2$, 6 mmol; T, 85 °C; N$_2$, 1 atm.

by the electrophilic nature of Pt(II) complexes, as has been recently pointed out by Sen,[20] this character being crucial in determining the dominant pathways for reactions involving the activation of simple C–H bonds.[20]

Effect of Catalyst Concentration. In order to gain more information on the mechanism of the hydroxylation of the more activated substrates, some initial rate analysis experiments were performed. To this purpose 1,3-dimethoxybenzene was chosen as model substrate since product formation is relatively fast and free from tars and the initial rate can be conveniently analyzed as is shown by a typical reaction profile reported in Figure 5. Unfortunately, since the substrate itself is used as solvent and since the decomposition of H$_2$O$_2$ is quite significant, particularly at the beginning of the reaction (see Figure 3), a complete kinetic analysis was not possible. Therefore, we analyzed only the effect of catalyst concentration that,

(20) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421.

on the basis of our previous experience with olefins,[12] is particularly informative on the nature of the oxygen transfer step. This effect is reported in Figure 6A. Notably, for concentrations higher than the broken line, the rate was controlled by the diffusion of H_2O_2 from the aqueous to the organic phase, as is indicated by the experiments duplicated at lower stirring rates. No effect of stirring rate was observed for catalyst concentrations below the broken line. In this range the reaction is second order in catalyst concentration, as is indicated also by the log/log plot (Figure 6B). This indicates that two different Pt-containing species are involved in the rate-determining step, and this behavior is quite similar to that observed in the catalytic epoxidation of olefins,[12] i.e. reaction 2, suggesting similar considerations.

Mechanism of the Reaction. The above kinetic analogies between the present system and the epoxidation of olefins suggest that the actual oxidant in the catalytic hydroxylation reaction might well be the PtOOH species. However, the activation of the substrate to yield the second Pt-containing reactive intermediate can occur in several different, non-radical ways.

The first possibility is that by analogy with olefins the activation of the substrate takes place via formation of (η^2-arene)platinum intermediates. Although not very common, stable complexes of this type[21] with simple arenes have been reported and characterized for Re,[22] Rh,[23] Os,[24] Os–Ru dimers,[25] and Pd[26] or Cu;[27] for Pd and Cu X-ray structural characterization was also reported. Direct nucleophilic attack on species of this type is believed to be the key step in the acetoxylation of benzene catalyzed by Pd(II) salts.[28] However, with toluene the acetoxylation reaction is not specific, giving a mixture of substitution products with the meta isomer as the preferred one,[29] at variance with the present hydroxylation system where only ortho and para products are formed.

Indeed, η^2-arene transition-metal complexes are believed to be the reactive intermediates leading to activation of the aromatic ring to give σ-aryl derivatives. This reaction has been demonstrated to proceed via electrophilic metalation[22] or oxidative-addition[23] processes, either way depending essentially on the electron density at the metal center. The electrophilic metalation with transition metals has been clearly demonstrated for cationic Re(III) complexes by Sweet and Graham,[22] and these authors have also observed that, consistently, it produces mostly ortho and para products. with Pt(II) centers, intramolecular ortho metalation from a variety of aryl-substituted donor ligands to give the corresponding Pt aryls is a well-established reaction.[30] On the other hand, Whitesides et al.[31] have

Scheme I
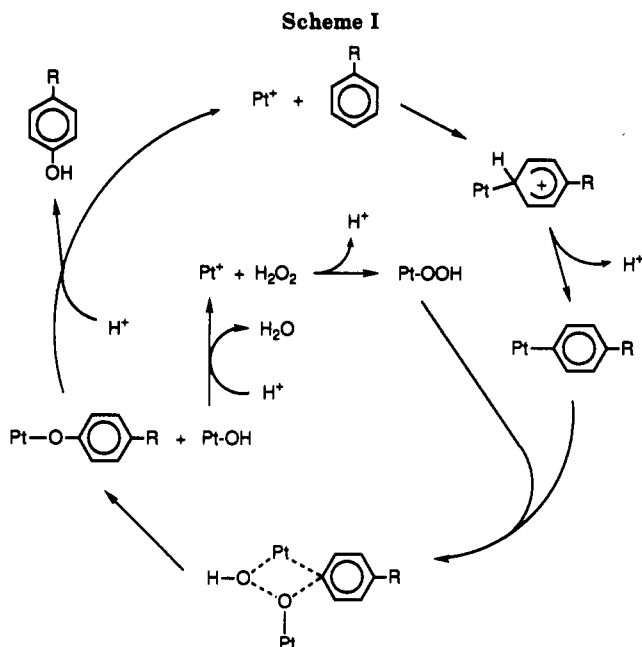
recently accomplished the activation of benzene via oxidative addition on highly unsaturated, electron-rich Pt(0) (dicyclohexylphosphino)ethane intermediates generated in situ from Pt(II) neopentyl hydride complexes.

In the present case, the metal center bearing an electron-withdrawing ligand ($-CF_3$) and a positive charge, the electrophilic metalation appears the most likely pathway for substrate activation, at least for those substrates that are particularly prone to this type of reactivity because of the effect of substituents. This view is not unprecedented, since a similar pathway has been suggested by Shilov and co-workers for the activation of alkanes with Pt(II) species.[32] More recently, Sen and co-workers[33] have reported the indirect conversion of a variety of arenes into the corresponding phenols and of methane to methanol through the formation of the corresponding trifluoroacetato esters catalyzed by Pd(OAc)$_2$ in trifluoroacetic acid. The reaction is believed to proceed via electrophilic metalation of the arene by the Pd(II) centers, followed by nucleophilic attack from the trifluoroacetato anion and two-electron oxidation by the metal. The process is made catalytic by reoxidizing Pd(0) with $K_2S_2O_8$.

The mechanism that we suggest for the overall reaction is shown in Scheme I. This involves two different cycles, i.e. one leading to the formation and regeneration of the oxidizing species PtOOH (inner cycle) and another one leading to activation of the substrate, product formation, and regeneration of the active species (outer cycle). The inner cycle has been already established in the case of the epoxidation of olefins with the same catalysts.[12] The outer cycle involves electrophilic activation of the arene by the Pt$^+$ complex to give a Pt–aryl, probably via a Wheland-type intermediate. Stable carbonium ions of this type coordinated to platinum(II) have already been synthesized by van Koten and co-workers,[34] by addition of MeI to very

(21) For earlier work with substituted arenes see: Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499 and references therein.

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(25) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7555.

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(31) (a) Hackett, M.; Ibers, J. A.; Jernakoff, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 8094. (b) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436.

(32) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Compounds*; Reidel: Dordrecht, The Netherlands, 1984; Chapter 5, and references therein.

(33) (a) Sen, A. *Platinum Met. Rev.* **1991**, *35*, 126. (b) Gretz, E.; Oliver, T. F.; Sen, A. *J. Am. Chem. Soc.* **1987**, *109*, 8109. (c) Sen, A.; Gretz, E.; Oliver, T. F.; Jiang, Z. *New J. Chem.* **1989**, *13*, 755. (d) Kao, L.-C.; Hutson, A. C.; Sen, A. *J. Am. Chem. Soc.* **1991**, *113*, 700.

Table IV. Spectroscopic Characterization of New Complexes[a]

complex	IR	^{1}H NMR	^{19}F NMR
(diphoe)Pt(CF$_3$)(PhOMe)	1600 (Ph); 1250, 1020 (C–O–C)	3.66 s (Me)	−20.76 dd, $^3J_{FP_{cis}}$ 12.9, $^3J_{FP_{trans}}$ 58.9, $^2J_{FPt}$ 577
(diphoe)Pt(CF$_3$)(OPhOMe)	1590 (Ph); 1270, 1280 (C–O–Pt); 1230, 1030 (C–O–C); 520 (Pt–O)	3.57 s (Me)	−26.63 dd, $^3J_{FP_{cis}}$ 10.1, $^3J_{FP_{trans}}$ 60.1, $^2J_{FPt}$ 574
(dppe)Pt(CF$_3$)(Ph)	1560 (Ph)		−20.31 dd, $^3J_{FP_{cis}}$ 15.7, $^3J_{FP_{trans}}$ 53.5, $^2J_{FPt}$ 710
(dppe)Pt(CF$_3$)(OPh)	1590 (Ph); 1260 (C–O–Pt); 520 (Pt–O)		−26.92 dd, $^3J_{FP_{cis}}$ 10.3, $^3J_{FP_{trans}}$ 59.7, $^2J_{FPt}$ 565

[a] IR: units cm^{-1}; Nujol mulls. NMR: δ in ppm, J in Hz; references ^{1}H (TMS), ^{19}F (CFCl$_3$); s = singlet, dd = doublet of doublets.

rigidly held aryl ligands coordinated to Pt. In Scheme I the rate-determining step takes place by attack of the PtOOH species on the Pt–aryl to give, probably via a four-center transition state, a mixture of hydroxy and phenoxy complexes from which, upon acid hydrolysis, the products are liberated and the starting Pt$^+$ active species are regenerated. A nucleophilic attack from an external nucleophile (CF$_3$COO$^-$) on a coordinated aryl (or methyl) is also the basis for the conversion of arenes (methane) into the corresponding trifluoroacetate esters promoted by Pd(II) species.[33] The main advantage of the presence system compared to Sen's[33] is that in our case the aromatics are *directly* converted into the corresponding phenols since the external nucleophile PtOOH is also the oxidant, at variance with the Pd(II) system,[33] where the actual oxidation is carried out by the Pd(II) center through Wacker-type chemistry.

In view of the isolation of the phenoxy derivatives observed with phenol as substrate, Scheme I would predict that some catalyst "poisoning" due to product formation should occur at high conversions. This is evident from Figure 3, where it can be noticed that product formation virtually stops after about 45 min, when about 20% of the initial H$_2$O$_2$ is still present in the system. Experiments carried out by either adding a second 6-mmol amount of H$_2$O$_2$ or doubling from the beginning the amount of H$_2$O$_2$ introduced yielded essentially the same amount of products. A similar behavior has been observed also in the case of anisole.

Scheme I suggests also that the equilibrium of hydrogen peroxide hydrolysis is critical in determining the relative amounts of the actual oxidant (PtOOH) and the electrophile (Pt$^+$) leading to substrate activation. The position of this equilibrium is determined by the amount of H$^+$ present in the system and implies that there will be an optimum H$^+$ concentration for which the maximum initial rate will be observed. This view was supported experimentally (Figure 7) by adding an increasing amount of perchloric acid to the catalytic system. Maximum activity was observed for H$^+$ concentrations corresponding to about 2–3 times the total Pt$^+$ introduced, indicating that the actual concentration of Pt$^+$ must be maximized in order to achieve the activation of the substrate. Further support comes from the observation that the PtOH complexes are poorer catalysts because it is difficult for the substrate to displace the −OH ligand.

The suggested electrophilic activation of the aromatic ring as one of the key steps of the reaction is also in agreement with the observed modest effect of the diphosphine coordinated to platinum on the activity (Tables I and II). Since the process is dominated by electronic factors, the fine variation of steric parameters that was associated with the large differences in activity observed
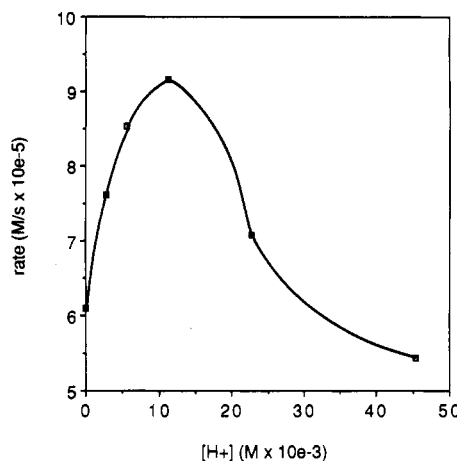
(34) (a) Grove, D. M.; van Koten, G.; Ubbels, H. J. C. *Organometallics* **1982**, *1*, 1366. (b) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609. (c) Terheijden, J.; van Koten, G.; Vinke, I. C.; Spek, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 2891. (d) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681 and references threin.

Figure 7. Effect of the concentration of added H$^+$ (HClO$_4$) on the initial rate in the catalytic hydroxylation of 1,3-dimethoxybenzene using [(diphoe)Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$ as catalyst. Reaction conditions: [Pt], 4.41 × 10^{-3} M; 1,3-dimethoxybenzene (neat), 60 mmol; 70% H$_2$O$_2$, 6 mmol; T, 85 °C; N$_2$ 1 atm.

in the epoxidation of 1-octene with the same complexes[11d] has only minimal influence on the present catalytic process.

Reaction of Platinum Aryls with Hydroperoxy Complexes. In order to substantiate the chemistry reported in Scheme I, we tried to carry out stoichiometrically some of the reactions involved in the catalytic cycle.

We first started with the reaction between [(diphoe)-Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$ and 1,3-dimethoxybenzene (used as solvent) at 60 °C for 2 h. No reaction products were observed.

To test the oxygen transfer step, the complex (diphoe)Pt(CF$_3$)(PhOMe) was prepared from the corresponding solvato complex by reaction with *p*-anisyllithium. The spectroscopic characterization of this complex is reported in Table IV. This compound was reacted with (diphoe)Pt(CF$_3$)(OOH) (1/1 molar ratio) in dry THF at 60 °C. After 2 h the mixture was cooled down, showing no organic oxidation products (GLC). After evaporation of the solvent the residue was dissolved in CD$_2$Cl$_2$ and analyzed by ^{19}F NMR. The spectrum showed the presence of four different species, which were recognized to be (diphoe)Pt(CF$_3$)(PhOMe), (diphoe)Pt(CF$_3$)(OOH), (diphoe)Pt(CF$_3$)(OH), and (diphoe)Pt(CF$_3$)(OPhOMe) (approximate ratio 3/3/1/1) by comparison with authentic samples. An authentic sample of (diphoe) Pt(CF$_3$)-(OPhOMe) was synthesized from (diphoe)Pt(CF$_3$)(OH) and *p*-hydroxyanisole in CH$_2$Cl$_2$, and the full spectroscopic characterization is given in Table IV.

A similar reaction was performed with (dppe)Pt-(CF$_3$)(Ph), which was prepared from the corresponding chloride and phenyllithium (see Table IV for characterization). This complex was reacted with (dppe)Pt(CF$_3$)-(OOH) according to the procedure reported above for (diphoe)Pt(CF$_3$)(PhOMe). The ^{19}F NMR spectrum of the solid residue obtained from this reaction after 2 h showed again the presence of four species recognized as (dppe)-Pt(CF$_3$)(Ph), (dppe)Pt(CF$_3$)(OOH), (dppe)Pt(CF$_3$)(OH),

and (dppe)Pt(CF$_3$)(OPh) (approximate ratio 5/5/2/2) by comparison with authentic samples. Again, an authentic sample of (dppe)Pt(CF$_3$)(OPh) can be easily obtained by reaction of (dppe)Pt(CF$_3$)(OH) with phenol in dry THF (see Table IV for full characterization).

Reactions carried out similarly on the Pt-aryl complexes but with free H$_2$O$_2$ as oxidant gave only evidence of hydrolysis of the complexes. In fact, even at room temperature, the corresponding arenes (benzene or anisole) were detected in the original solutions and the solid residues showed the presence of significant amounts of the corresponding PtOOH complexes.

The results of these experiments provide direct support for the oxygen transfer step hypothesized in Scheme I. Indeed, the experimental data might be consistent also with an evolution of the transition state into a five-coordinate species of the type Pt(aryl)(OOH) giving *intra*molecular oxygen transfer, similar to the case of the Hf(alkyl)(OO-*t*-Bu) complexes described by Bercaw et al.,[35] although in the latter case the reaction is justified by the strong oxophilic character of hafnium. The observation that the oxidation of the phenyl and that of the anisyl derivatives proceeded with similar rates seems to show that the extent of the equilibrium leading to the electrophilic metalation is indeed the most critical part of the catalytic cycle, as is implied also by the reactivity observed in the hydroxylation reaction (Table III).

Origin of Ortho Selectivity. As is evident from Tables I–III, these catalysts have a particular specificity toward the formation of ortho products. The isolation of phenoxy complexes and their direct involvement as intermediates in the catalysis prior to oxygen transfer (see the case of phenol for example) seem to suggest a possible pathway consisting of an ortho metalation leading to the formation of the Pt-aryl intermediate (reaction 13). Analogously, substrates that possess –OR substituents (anisole, 1,3-dimethoxybenzene) could perform the same transformation through coordination of the oxygen atom to the catalyst (reaction 14).

$$\text{(13)}$$
$$\text{(14)}$$
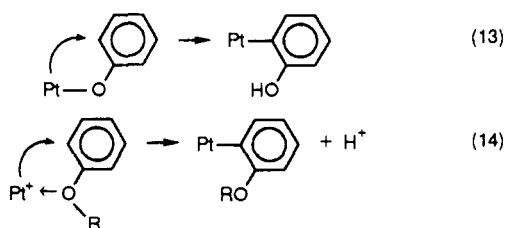
Consistent with this view are several experimental observations: (i) the solubility of the Pt$^+$ catalysts in most of the reactive substrates, which suggests the displacement of the coordinated CH$_2$Cl$_2$ and the consequent formation of the Pt(PhOR)$^+$ intermediates) (ii) the difference in selectivity between PtOH and Pt$^+$ catalysts toward phenol and *m*-cresol, which reflects the different extents of reactions 6 and 4 + 5 toward the formation of the PtOPh intermediate, and (iii) the difference in reactivity between Pt$^+$ and PtOH catalysts, which reflects the different electrophilic characters of the metal in the cationic Pt-(PhOR)$^+$ and the neutral PtOPh intermediates.

Unfortunately, direct proof for reaction 13 could not be obtained, even if an attempt to carry out the molecular rearrangement shown was made thermally by heating a THF solution of (dppe)Pt(CF$_3$)(OPh) at 60 °C for 3 h. Only the starting complex was recovered.

Conclusions

The results reported in this work seem to show that indeed the hydroxylation of aromatics can be accomplished via electrophilic metalation, and to our knowledge this represents the first example in which a soluble transition-metal complex catalyzes the *direct* hydroxylation of an aromatic ring via this route under mild conditions. As already observed above, the present system differs from the one reported by Sen[33] in that metal reduction is not involved, thereby avoiding the necessity to reoxidize the catalyst to close the catalytic cycle.

The coupling reaction leading to the oxygen transfer bears strong similarities with the arene-arene couplings reviwed by Parshall,[14] the main difference being that in the present case the process is *inter*molecular instead of *intra*molecular. This peculiarity allows the use of hydrogen peroxide as the terminal oxidant because of the proven ability of these complexes to bring about separately the activation of H$_2$O$_2$, as was already observed in the oxidation of olefins.[11-13]

Since it is possible, with an appropriate choice of the catalyst, to obtain an interesting regioselectivity toward the formation of the less favored ortho products, given the potential synthetic utility of these catalysts in the case of the more activated aromatic rings, more work is certainly called for in order to broaden the scope of these hydroxylations.

Experimental Section

Apparatus. IR spectra were taken on a Perkin-Elmer 683 spectrophotometer and on a Digilab FTS 40 interferometer either in Nujol mulls using CsI plates or in CH$_2$Cl$_2$ solution using CaF$_2$ windows. ^{1}H and ^{19}F NMR spectra were recorded on a Varian FT 80A spectrometer operating in the FT mode, using as external references TMS and CFCl$_3$, 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. GLC-MS measurements were performed on a Hewlett-Packard 5970 mass selective detector connected to a Hewlett-Packard 5790A gas chromatograph. Identification of products was made with GLC or GLC-MS by comparison with authentic samples.

Materials. Solvents were dried and purified according to standard methods. Aromatic substrates were purified by passing through neutral alumina, prior to use. Hydrogen peroxides (35% from Fluka, 70% from Degussa), diphoe, dppe, and *o*-dppb (all from Strem), DBPC and AIBN (both from Fluka), and most of the hydroxylation reaction products were commercial products and were used without purification.

The following compounds were prepared according to literature procedures: (dppe)Pt(CF$_3$)(OH),[36] [(dppe)Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$,[36] (diphoe)Pt(CF$_3$)(OH),[36] [(diphoe)Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$,[36] (*o*-dppb)Pt(CF$_3$)(OH),[11d] [(*o*-dppb)Pt(CF$_3$)(CH$_2$Cl$_2$)]BF$_4$,[11d] (dppe)Pt(CF$_3$)(OOH),[15] (diphoe)Pt(CF$_3$)(OOH),[15] (*o*-dimethylamino)phenol,[37] 2,4-dimethoxyphenol,[37] and 2,6-dimethoxyphenol.[38]

Preparation of New Complexes. 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.

(diphoe)Pt(CF$_3$)(OPh). The complex (diphoe)Pt(CF$_3$)(OH) (0.20 g, 0.28 mmol), or the equivalent amount of (diphoe)Pt-(CF$_3$)(OOH), was dissolved in 50 mL of dry THF, and to this solution was added phenol (0.20 g, 2.1 mmol). After the mixture was stirred for 1 h under N$_2$, the solvent was partly evaporated in vacuo, and to this solution was added an excess of Et$_2$O. The white solid that precipitated from solution was filtered, washed

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with Et₂O, and dried in vacuo (yield 88%). Anal. Calcd (found) for C₃₃H₂₇F₃OP₂Pt: C, 52.59 (52.73); H, 3.61 (3.82).

(dppe)Pt(CF₃)(Ph). The complex (dppe)Pt(CF₃)Cl (0.30 g, 0.43 mmol) was suspended in dry benzene (10 mL). To the suspension cooled at 5 °C was added slowly with stirring 10 mL of dry benzene containing 0.43 mL of a 2 M solution of phenyllithium in hexane (0.87 mmol). After 30 min the temperature was slowly raised to 25 °C and the mixture stirred for 24 h. The white solid was filtered off and washed several times with benzene, and the pale yellow filtrate was brought to dryness to give a pale yellow solid. This was washed with 10 mL of a 10/1 benzene/Et₂O mixture to leave a cream-colored solid that was filtered, washed several times with Et₂O, and dried in vacuo (yield 30%). Anal. Calcd (found) for C₃₃H₂₉F₃P₂Pt: C, 53.59 (53.31); H, 3.95 (4.13).

(dppe)Pt(CF₃)(OPh). The complex (dppe)Pt(CF₃)(OH) (0.50 g, 0.74 mmol) was dissolved in 30 mL of THF, and phenol (0.10 g, 1.06 mmol) was added. The solution was refluxed with stirring for 4 h. It was then cooled and concentrated in vacuo, and by addition of an excess of Et₂O a white solid precipitated that was filtered, washed with Et₂O, and dried in vacuo. Recrystallization was from benzene/hexane (yield 90%). Anal. Calcd (found) for C₃₃H₂₉F₃OP₂Pt: C, 52.45 (52.63); H, 3.87 (3.99).

(diphoe)Pt(CF₃)(Ph-OMe). The complex [(diphoe)Pt-(CF₃)(CH₂Cl₂)]BF₄ (0.16 g, 0.19 mmol) was dissolved in dry THF (8 mL), and to this solution, cooled to −10 °C, was added 0.95 mL of a 0.4 M solution of *p*-anisyllithium (obtained from *p*-bromoanisole and lithium metal) in hexane (0.38 mmol) slowly with stirring. The temperature was slowly raised to 25 °C and the mixture stirred at that temperature for 1 h. The pale yellow solution was concentrated in vacuo, and an excess of EtOH was added. After this mixture was kept overnight at −20 °C a cream-colored solid was obtained that was rapidly filtered and dried in vacuo (yield 60%). Anal. Calcd (found) for C₃₄H₂₉F₃OP₂Pt: C, 53.20 (52.93); H, 3.81 (3.62).

(diphoe)Pt(CF₃)(O-Ph-OMe). The complex (diphoe)Pt-(CF₃)(OH) (0.10 g, 0.14 mmol) and *p*-hydroxyanisole (0.10 g, 0.85 mmol) were dissolved in dry CH₂Cl₂ (15 mL), and the solution was stirred at room temperature for 1 h. The solution was then concentrated in vacuo to a few milliliters, an excess of Et₂O was added, and finally the mixture was placed at −20 °C overnight. The white microcrystals obtained were rapidly filtered, washed with Et₂O, and dried in vacuo (yield 85%). Anal. Calcd (found) for C₃₄H₂₉F₃O₂P₂Pt: C, 52.11 (52.37); H, 3.73 (3.95).

Oxygen Transfer Reactions. The reactions between (dppe)Pt(CF₃)(Ph) or (diphoe)Pt(CF₃)(Ph-OMe) and (dppe)Pt-(CF₃)(OOH) or (diphoe)Pt(CF₃)(OOH), respectively, were performed according to the following procedure.

Equimolar amounts (0.05 mmol) of the platinum–aryl and the platinum–hydroperoxy complexes were charged in a gastight Schlenk vessel that was evacuated and filled with N₂. Dry, N₂-saturated THF (5 mL) was added, and the resulting solution was heated at 60 °C for 2 h with an external oil bath. Then the solution was cooled down to room temperature and analyzed with GLC to check for the presence of organic products. The solvent was removed in vacuo, and the solid residue was dissolved in CD₂Cl₂ for ¹⁹F NMR analysis.

The reactions between (dppe)Pt(CF₃)(Ph) (0.05 mmol) or (diphoe)Pt(CF₃)(Ph-OMe) (0.05 mmol) and H₂O₂ (0.5 mmol) were carried out according to the above procedure, but at room temperature for 4 h.

Catalytic Reactions. These were carried out in a 25-mL round-bottmed flask equipped with a reflux condenser, a stopcock for vacuum/N₂ operations, and a side arm fitted with a screw-capped silicone septum to allow sampling. Constant temperature (85 ± 0.5 °C) was maintained with an external oil bath equipped with a Vertex thermometer. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer. The absence of diffusional problems below the 14 × 10⁻⁵ M s⁻¹ initial rate was determined by the independence of conversion vs time plots on the stirring rate in kinetic experiments randomly selected from Figure 6A. The concentration of the commercial H₂O₂ solution was checked iodometrically prior to use.

The following general procedure was used. In a typical experiment [(diphoe)Pt(CF₃)(CH₂Cl₂)]BF₄ (0.0496 g, 0.06 mmol) was placed in the reactor, which was evacuated and filled with N₂. Purified, N₂-saturated substrate (60 mmol) was added under an N₂ flow, followed by an appropriate amount of internal standard (chlorobenzene) and, if necessary, by the required amounts of DCE and/or *i*-PrOH to dissolve the catalyst. After the mixture was heated to 85 °C with stirring for a few minutes, a 70% H₂O₂ solution (0.290 mL, 6.0 mmol) was injected through the septum and time was started. The mixture was vigorously stirred to avoid diffusional problems. Where necessary, appropriate amounts of HClO₄ were added to the H₂O₂ solution prior to use.

All reactions were monitored with GLC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Prior quenching of the catalyst with LiCl did not show any differences in randomly selected analyses. Separation of the products was performed on a 25-m HP-5 capillary column using a flame ionization detector. Quantitative data were obtained from calibration curves of the various reactants and products vs the internal standard (chlorobenzene).

Determination of H₂O₂ Concentration. In reaction mixtures where H₂O₂ was separated from the organic phase (all except with phenol and *m*-cresol), the titration of the H₂O₂ present during the course of the reaction was performed according to the procedure described here.

Since the water phase was always much less than the organic phase (typically 8–12 mL) an aliquot (0.25 mL) of the latter was sampled and extracted with a H₂O (10 mL)/CH₂Cl₂ (20 mL) mixture. The water phase was separated and titrated iodometrically to give the amount of free H₂O₂ present in the original organic phase of the reaction mixture. The amount of H₂O₂ present in the water phase of the reaction mixture was determined through the use of partition curves. These were determined for all the water-immiscible substrates similarly to previously described procedures using standard solutions.

Registry No. 1,4-(OH)₂C₆H₄, 123-31-9; *p*-HOC₆H₄OPr-*i*, 7495-77-4; *o*-HOC₆H₄O-*o*-C₆H₄OH, 15764-52-0; *p*-HOC₆H₄OPh, 831-82-3; (diphoe)Pt(CF₃)(PhOMe), 143493-56-5; (diphoe)Pt-(CF₃)(O-Ph-OMe), 143493-55-4; (diphoe)Pt(CF₃)(CH₂Cl₂)⁺, 119325-87-0; (*o*-dppb)Pt(CF₃)(CH₂Cl₂)⁺, 119296-37-6; (dppe)Pt-(CF₃)(CH₂Cl₂)⁺, 119325-80-3; (dppe)Pt(CF₃)(OH), 72953-78-7; (diphoe)Pt(CF₃)(OH), 143493-54-3; (dppe)Pt(CF₃)(OPh), 143493-52-1; (dppe)Pt(CF₃)(Ph), 143493-53-2; (diphoe)Pt-(CF₃)(OOH), 72953-62-9; (dppe)Pt(CF₃)Cl, 125892-87-7; (diphoe)Pt(CF₃)(OH), 70504-87-9; [(diphoe)Pt(CF₃)(CH₂Cl₂)]BF₄, 128680-76-2; (dppe)Pt(CF₃)(OOH), 72953-61-8; [(dppe)Pt-(CF₃)(CH₂Cl₂)]ClO₄, 119325-81-4; phenol, 108-95-2; 1,2-benzenediol, 120-80-9; 4,4'-oxybis(phenol), 1965-09-9; 2-phenoxyphenol, 2417-10-9; chlorobenzene, 108-90-7; benzene, 71-43-2; naphthalene, 91-20-3; toluene, 108-88-3; *N*,*N*-dimethylaniline, 121-69-7; *m*-cresol, 108-39-4; anisole, 100-66-3; 1,3-dimethoxybenzene, 151-10-0; *o*-hydroxytoluene, 95-48-7; *o*-hydroxy-*N*,*N*-dimethylaniline, 3743-22-4; *o*-hydroxy-*m*-cresol, 452-86-8; *o*-hydroxyanisole, 90-05-1; 2,4-dimethoxyphenol, 13330-65-9; *p*-hydroxy-*N*,*N*-dimethylaniline, 619-60-3; *p*-hydroxy-*m*-cresol, 95-71-6; *p*-hydroxyanisole, 150-76-5; 2,6-dimethoxyphenol, 91-10-1; *p*-bromoanisole, 104-92-7.

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