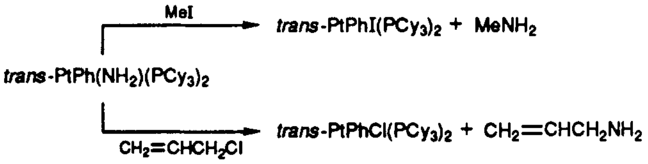
Organometallics 1991, 10, 623-631

We have therefore prepared monomeric phenyl amide complexes of platinum(II) with tricyclohexylphosphine ligands in order to try and direct selectivity toward the Pt–NH_2 bond. Treating *trans*-$PtPhCl(PCy_3)_2$ with $AgClO_4$, followed by ammonia gas, gives *trans*-$[PtPh(NH_3)(PCy_3)_2]ClO_4$ (**18**) ($^{31}P\{^1H\}$ NMR: δ 17.7 (s)). This complex reacts with the amide ion to give *trans*-$PtPh(NH_2)(PCy_3)_2$ (**19**) ($^{31}P\{^1H\}$ NMR: δ 17.0 (s)) (eq 15).

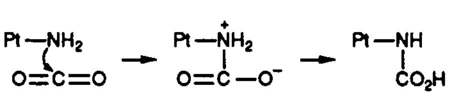
$$\underset{\mathbf{18}}{trans\text{-}[PtPh(NH_3)(PCy_3)_2]ClO_4} + NaNH_2 \rightarrow \underset{\mathbf{19}}{trans\text{-}PtPh(NH_2)(PCy_3)_2} + NaClO_4 + NH_3 \quad (15)$$

Treating *trans*-$PtPh(NH_2)(PCy_3)_2$ with trifluorosulfonic acid or water gives the ammine cation complexes *trans*-$[PtPh(NH_3)(PCy_3)_2]X$ (X = CF_3SO_3, OH). Treating *trans*-$PtPh(NH_2)(PCy_3)_2$ with methyl iodide or allyl chloride gives *trans*-$PtPhX(PCy_3)_2$ (X = I, Cl) (eq 16). The amine products have not been detected.



(16)

Carbon dioxide reacts with *trans*-$PtPh(NH_2)(PCy_3)_2$ in benzene solvent with the precipitation of *trans*-$PtPh(NHCO_2H)(PCy_3)_2$ (**22**) (ν(CO) 1602 cm^{-1}, ν(NH + OH) 3351, 3318 cm^{-1}; ^1H NMR δ 3.35 (br, N*H*; ^2J(PtH = 24 Hz))).[21] This N-bonded carbamato complex is formed by electrophilic attack at the amide nitrogen by the carbon atom of carbon dioxide (eq 17). When this carbamato-*N*



(17)

complex is dissolved in dichloromethane, isomerization to the O-bonded complex *trans*-$PtPh(OCONH_2)(PCy_3)_2$ (ν(CO) 1616 cm^{-1}; ^1H NMR δ 4.01 (s, NH_2); ^{13}C $\{^1H\}$ NMR δ 162.5) occurs.[22] This O-bonded isomer can be obtained in a single step by reacting *trans*-$PtPh(NH_2)(PCy_3)_2$ with carbon dioxide in dichloromethane solvent, when the N-isomer *trans*-$PtPh(NHCO_2H)(PCy_3)_2$ is observed as an intermediate in solution. These transformations are shown in Scheme II.

Acknowledgment. We thank the Louisiana Board of Regents for support through the Louisiana Education Quality Support Fund. We thank the Office of Naval Research for funds to purchase the FTIR spectrometer. We thank Dr. F. Joslin for assistance.

Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates and isotropic thermal parameters (4 pages); a listing of F_o and F_c values (37 pages). Ordering information is given on any current masthead page.

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Synthesis of Platinum(II) Hydroxycarbonyl Complexes and Related Species and Their Reactions with Hydrogen Peroxide: Existence of Organometallic Peroxy Acids

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

Department of Chemistry, University of Venice, 30123 Venice, Italy,
and Institute of Industrial Chemistry, University of Padua, 35100 Padua, Italy

Received March 15, 1990

The synthesis and characterization of a class of complexes of the type $P_2Pt(Rx)(COOH)$ (P_2 = $(PPh_3)_2$, $(PPh_2Me)_2$, dppe, diphoe, dppp; Rx = CF_3, Me, Ph) obtained by insertion of CO into the Pt–OH bond of the corresponding hydroxo complexes is reported, together with their reactivity toward MeOH, $P_2Pt(CF_3)(OH)$, and $P_2Pt(CF_3)(OOH)$ species (P_2 = diphosphine). The reaction between PtCOOH and PtOH complexes leads to the formation of CO_2-bridged dinuclear species. The reactions of all the carboxy compounds with hydrogen peroxide were studied with the aim of finding a synthetic route to organometallic peroxy acids. Spectroscopic studies suggest the existence of transient hydroperoxy species of the type $PtCOO_2H$; however, attempts to exploit their oxidizing properties in the oxidation of olefins resulted only in the catalytic oxidation of carbon monoxide.

Introduction

Hydrogen peroxide is a poor oxidant for organic synthesis, but it is a key starting material for the preparation of organic peroxy acids, which are very versatile reagents in a variety of organic oxidation reactions, including the synthesis of epoxides and glycols from olefins, sulfoxides and sulfones from sulfides, tertiary amine oxides from tertiary amines, and esters or lactones from ketones.[2] Organic peroxy acids are also employed in industry, for example in the Bayer–Degussa[3] and Propylox[4] processes

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

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for the production of propylene oxide, thereby allowing the ultimate use of H_2O_2 as a terminal oxidant in industrial organic chemistry.

However, more direct methods for the activation of hydrogen peroxide are needed. Despite the flourishing of new chemical systems based on d^0 transition-metal centers in alkene oxidation with organic hydroperoxides, the related use of hydrogen peroxide has met with only limited success, mostly because of the unavoidable presence of water.[5]

We have recently reported complexes of the type $P_2Pt(CF_3)X$ (P_2 = diphosphine, X = solvent, -OH) that are totally tolerant of aqueous systems and have been used as catalysts for the selective and enantioselective epoxidation of terminal olefins with diluted (5–35%) H_2O_2.[6,7] These compounds are essentially organometallic bases that form PtOOH species very easily through acid–base reaction with H_2O_2:

$$Pt^+ + H_2O_2 \rightarrow PtOOH + H^+$$

$$PtOH + H_2O_2 \rightarrow PtOOH + H_2O$$

$$Pt = P_2Pt(CF_3)$$

The coordinated hydroperoxide is then transferred to the olefin via activation of the latter on a second platinum center,[7] thereby resulting in a genuine example of bifunctional catalysis. The $P_2Pt(CF_3)(OH)$ complexes are versatile reagents since, by insertion of carbon monoxide into the Pt–OH bond, they allow the synthesis of what may be formally considered as the organometallic carboxylic acids MCOOH (or hydroxycarbonyl complexes).

Although the synthesis and characterization of these hydroxycarbonyl compounds have been accomplished relatively recently,[8] they were believed for many years, and in some cases proved, to be involved as intermediates in a variety of reactions involving carbon monoxide, including the homogeneously catalyzed water-gas shift reaction.[9] In this paper we report the synthesis of a class of $P_2Pt(Rx)(COOR)$ complexes (P_2 = two monophosphines or one diphosphine; Rx = alkyl or aryl; R = H, Me) along with their reactions with H_2O_2 with the aim of finding a synthetic route to organometallic peroxy acids.

Results and Discussion

Table I. IR Data (cm^{-1}) for the Complexes $P_2Pt(Rx)(COOH)^a$

complex	ν(O—H)	ν(C=O)	ν(C—O)/ δ(O—H)
(diphoe)Pt(CF_3)-(COOH)	2690 (3440)	1610 (1655)	1155, 1170
(dppe)Pt(CF_3)-(COOH)	2680 (3440)	1610 (1652)	1155
trans-(PPh_2Me)$_2$Pt-(CF_3)(COOH)	2685 (3440)	1590, 1600	1148, 1163
(dppp)Pt(CF_3)-(COOH)	2685 (3440)	1610 (1655)	1165, 1170
trans-(PPh_3)$_2$Pt-(CF_3)(COOH)	(3440)	1655, 1670 (1655)	1148, 1165
(dppe)Pt(Ph)-(COOH)	(2690)	1655 (1635)	
(diphoe)Pt(CH_3)-(COOH)	2670 (3440)	1600 (1635)	
trans-(PCy_3)$_2$Pt-(CH_3)(COOH)^b	2660	1620 (1658, 1600)	

[a] Spectra recorded in Nujol mulls with use of CsI windows; data in parentheses refer to CH_2Cl_2 solutions, in 0.5-mm CaF_2 cells. Band assignments are according to ref 11. [b] Only slightly soluble in CH_2Cl_2.

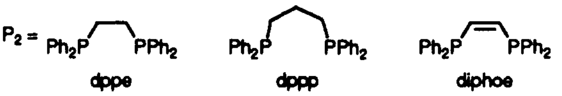
Table II. NMR Spectroscopic Data for the Complexes $P_2Pt(CF_3)(COOH)^a$

complex	^{1}H δ(COOH)	^{19}F δ(CF_3)
(diphoe)Pt(CF_3)(COOH)	10.62 (s)	−14.83 (dd); $^3J_{FP_{cis}} = 14.1$, $^3J_{FP_{trans}} = 54.9$, $^2J_{FPt} = 729$
(dppe)Pt(CF_3)(COOH)	10.45 (s)	−15.3 (dd); $^3J_{FP_{cis}} = 18.3$, $^3J_{FP_{trans}} = 53.3$, $^2J_{FPt} = 718$
trans-(PPh_2Me)$_2$Pt(CF_3)-(COOH)	10.15 (s) 2.19 (t, δ($PMePh_2$); $^2J_{HP} + {}^4J_{HP} = 6.2$, $^3J_{HPt} = 37.4$	−15.00 (t); $^3J_{FP} = 11.4$, $^2J_{FPt} = 413.2$
trans-(PPh_3)$_2$Pt(CF_3)-(COOH)		−14.58 (t); $^3J_{FP} = 12.0$, $^2J_{FPt} = 401$
cis-(PPh_3)$_2$Pt(CF_3)(COOH)		−17.12 (dd); $^3J_{FP_{cis}} = 13.7$, $^3J_{FP_{trans}} = 50.1$, $^2J_{FPt} = 711$

[a] Spectral data taken at room temperature in DMSO-d_6; δ in ppm, J in Hz. References: ^{1}H, TMS; ^{19}F, $CFCl_3$. Abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublets.

Synthesis and Characterization. The platinum(II) complexes of general formula $P_2Pt(Rx)(COOH)$ were prepared by the insertion of carbon monoxide into the Pt–OH bond of the corresponding $P_2Pt(Rx)(OH)$ complexes:

$$P_2Pt(Rx)(OH) + CO \rightarrow P_2Pt(Rx)(COOH) \qquad (1)$$



P = PPh_3, PPh_2Me, PCy_3
Rx = CF_3, Ph, Me

This synthetic procedure, which was developed by some of us[10] and by Bennett and co-workers,[8,11] is peculiar for platinum, while for other metals, the synthesis consists of the addition of HO^- or H_2O to coordinated carbon monoxide.[9a]

Reaction 1 is carried out in toluene at low Pt concentration (<0.007 M) and room temperature and is generally complete in 6 h. Yields are generally good (65–89%) but are considerably lower if the Pt concentration is increased or if THF is used as solvent because of the precipitation

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Table III. NMR Spectroscopic Data for the Complexes $P_2Pt(Ph)(COOH)$ and $P_2Pt(Me)(COOH)$[a]

complex	^1H	$^{31}P\{^1H\}$
(diphoe)Pt(Me)(COOH)	10.03 (s, COOH) 0.67 (t, Me); $^3J_{HP}$ = 14.5, $^2J_{HPt}$ = 71.8	55.13 (d); $^1J_{PPt}$ = 1855, $^2J_{PP}$ = 16.2 51.24 (s); $^1J_{PPt}$ = 1741, $^2J_{PP}$ = 16.2
trans-$(PCy^3)_2Pt(Me)(COOH)$[b]	9.67 (s, COOH) −0.05 (t, Me); $^3J_{HP}$ = 5.0, $^2J_{HPt}$ = 72.0	20.8 (s); $^1J_{PPt}$ = 2820
(dppe)Pt(Ph)(COOH)	9.98 (s)	39.94 (s); $^1J_{PPt}$ = 1792 37.37 (s); $^1J_{PPt}$ = 1736, $^2J_{PP} \approx 0$

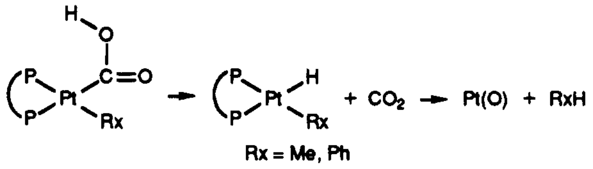
[a] Spectral data taken at room temperature in DMSO-d_6; δ in ppm, J in Hz. References: ^1H, TMS; ^{31}P, 85% H_3PO_4. Abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublets. [b] CD_2Cl_2 as solvent for solubility reasons.

of a side product formed by condensation of the PtCOOH product with the unreacted PtOH starting complex (vide infra). The reaction of CO with *trans*-$(PPh_3)_2Pt(Ph)(OH)$[12] and *trans*-$(PPh_3)_2Pt(Bz)(OH)$[13] failed to give the desired hydroxycarbonyl complexes but instead gave only orange solutions containing Pt(0) species (vide infra).

The hydroxycarbonyl complexes are white microcrystalline solids, insoluble in H_2O and fairly soluble in acetone, tetrahydrofuran (THF), CH_2Cl_2, dimethyl sulfoxide (DMSO), and dimethoxyethane (DME). They have been characterized spectroscopically by IR, ^1H NMR and either ^{19}F or $^{31}P\{^1H\}$ NMR methods and the relevant data are reported in Tables I–III. A comparison of the ν(OH) and ν(CO) values in the IR spectra for the solid and in CH_2Cl_2 solution (Table I) indicates that most of the $-CF_3$ derivatives and (diphoe)Pt(Me)(COOH) are associated in the solid state through hydrogen bonding (2660–2690 cm^{-1} (OH), 1590–1610 cm^{-1} (CO)), while they are monomeric in solution (3440 cm^{-1} (OH), 1635–1655 cm^{-1} (CO)). On the other hand, *trans*-$(PPh_3)_2Pt(CF_3)(COOH)$ appears to be monomeric even in the solid state, *trans*-$(PCy_3)_2Pt(Me)(COOH)$ is partially associated, and (dppe)Pt(Ph)(COOH) is completely associated in CH_2Cl_2 solution. In this respect, the former group of complexes differ strongly from organic carboxylic acids that are partially associated even in the gas phase,[14] while the latter intermediate behavior resembles the observations for *trans*-$(PEt_3)_2Pt(Ph)(COOH)$ reported by Bennett et al.[11c]

The ^1H NMR spectra do not show the carboxylic proton resonance in most common solvents, probably because of both rapid exchange and partial overlapping with the phosphine phenyl signals; however, the use of DMSO-d_6 allowed us to locate the COOH proton (Tables II and III) of all the complexes with the exception of $(PPh_3)_2Pt(CF_3)(COOH)$. The ^{19}F NMR spectrum of this compound reveals the presence of a mixture of cis and trans isomers (approximate ratio 1/2) both in DMSO-d_6 and in CD_2Cl_2, which is in contrast with the solid-state IR spectrum, where no bands are observed at 555 cm^{-1} typical of *cis*-$(PPh_3)_2PtX_2$ species according to Mastin's identification method.[15] This behavior suggests that this complex is most likely trans in the solid state. For all the other complexes either the ^{19}F NMR data or the $^{31}P\{^1H\}$ NMR data are in agreement with the proposed structures (Tables II and III).

Chemical Properties. All the PtCOOH complexes synthesized are stable in the solid state and do not decompose at room temperature with elimination of CO_2. Solutions of the CF_3 derivatives are stable in CH_2Cl_2, while solutions of (dppe)Pt(Ph)(COOH) and (diphoe)Pt(Me)(COOH) evolve CO_2. In fact, the IR spectra (CH_2Cl_2 solution) show in the case of (diphoe)Pt(Me)(COOH) the rapid decay of the original bands at 1625 and 3440 cm^{-1} and the growth of a sharp band at 2320 cm^{-1} typical of free CO_2. The reaction is complete in about 20 min. A similar result was obtained for (dppe)Pt(Ph)(COOH). This behavior might be associated either with the facile hydrolysis of the Pt-alkyl or -aryl σ bond in the latter complexes by traces of HCl present in CH_2Cl_2 followed by carbon dioxide evolution or, more likely, with a β-hydride elimination process according to the reaction



(2)

This type of reaction has been observed for other metals[9a,16] and was reported by Catellani and Halpern for *trans*-$(PPh_3)_2Pt(COOH)Cl$.[17] In both cases the IR spectrum does not give evidence of bands around 2000 cm^{-1} due to ν(PtH) absorptions, but it is known that *cis*-hydrido–alkyl or *cis*-hydrido–aryl species of Pt(II) reductively eliminate RxH even at −50 °C.[18] This behavior is likely to occur also for the species derived by CO insertion in *trans*-$(PPh_3)_2Pt(Ph)(OH)$ and *trans*-$(PPh_3)_2Pt(Bz)(OH)$. The presumed PtCOOH derivatives could not be isolated; instead, the orange solid that was isolated from the reaction of the benzyl complex with CO shows IR bands at 1850 and 1795 cm^{-1} typical of $Pt_3(CO)_3(PPh_3)_4$.[19]

Despite the presence of a carboxylic moiety the PtCOOH complexes described here differ from organic carboxylic acids in that they are very poor acids. Attempts to determine their acidity constant were unsuccessful due to the lack of solubility in aqueous alkali solutions. The hydroxycarbonyl compounds do not protonate 1,8-bis(dimethylamino)naphthalene in polar solvents such as acetone, DMSO, and DME. Instead, the compounds react with strong noncoordinating acids to give the corresponding metal carbonyl complexes according to the reaction

$$Pt\text{-}COOH + H^+ \rightarrow Pt\text{-}CO^+ + H_2O \qquad (3)$$

For example the reaction between (diphoe)$Pt(CF_3)(COOH)$ and a stoichiometric amount of 12.7 M $HClO_4$ leads to the formation of a species showing spectroscopic features

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Table IV. IR Features (cm^{-1}) of the Complexes $P_2Pt(Rx)(COOMe)$[a]

complex	ν(C=O)	ν(C—OC)
(diphoe)Pt(CF_3)(COOMe)	1657, 1643 (1643)	1055[b]
(dppe)Pt(CF_3)(COOMe)	1665, 1643 (1640)	1070[b]
(dppp)Pt(CF_3)(COOMe)	1650 (1642)	1050[b]
(diphoe)Pt(CH_3)(COOMe)	1632 (1628)	1100 (1100)

[a] As Nujol mulls with use of CsI windows. Data in parentheses refer to CH_2Cl_2 solutions in 0.5-mm CaF_2 cells. [b] In solution covered by CF_3 absorptions.

identical with those of [(diphoe)Pt(CF_3)(CO)]ClO_4 (IR Nujol) 2130 cm^{-1} (CO); ^{19}F NMR (CD_2Cl_2, −70 °C) δ −14.51 dd, $^3J_{FP_{cis}}$ = 10.7 Hz, $^3J_{FP_{trans}}$ = 57.8 Hz, $^2J_{FPt}$ = 565 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ(CO) 171.48 m, $^2J_{CP_{cis}}$ = 7 Hz, $^2J_{CP_{trans}}$ = 125 Hz, $^3J_{CF}$ = 7 Hz, $^1J_{CPt}$ = 312 Hz). The ^{19}F NMR data are quite similar to those for previously reported complexes of the same type,[6,7,10] while the ^{13}C parameters are in agreement with the general behavior of Pt carbonyl compounds.[20] The $^2J_{CP_{cis}}$ and $^3J_{CF}$ values are very close, giving rise to an apparent quintet. The IR spectrum is similar to the spectra of previously reported complexes of the same type such as [$(PPh_3)_2Pt(CF_3)$(CO)]PF_6 and [$(PPh_3)_2Pt(CO)Cl$]PF_6 (ν(CO) (THF solution) 2143 and 2121 cm^{-1}, respectively)[21] and indicates the presence of a very weakly bound CO. In fact the complex tends to lose carbon monoxide even in the solid state on storage at room temperature. In solution, CO is easily displaced by the solvent, but the solvato cationic species obtained when treated with CO restores the starting carbonyl complex even at −70 °C (^{19}F NMR evidence).

Despite their very weak acidic character the $P_2Pt(Rx)(COOH)$ complexes readily react with methanol to form esters (reaction 4). The preparation can be carried out more conveniently, either in a one-pot synthesis starting from the hydroxy complex, carbon monoxide, and methanol in the presence of triethylamine or by insertion of CO into the corresponding methoxo complexes.[22] The former procedure yields better synthetic results, and through this route the new complexes (dppe)Pt(CF_3)(COOMe), (dppp)Pt(CF_3)(COOMe), and (diphoe)Pt(Me)(COOMe) have been prepared together with the already known[10] complex (diphoe)Pt(CF_3)(COOMe).

$$\text{Pt-COOH} + \text{MeOH} \xrightarrow{NEt_3} \text{Pt-COOMe} + H_2O \quad (4)$$

The complexes have been characterized by IR, ^1H NMR, ^{19}F NMR, and $^{31}P\{^1H\}$ NMR spectroscopies, and the relevant data are reported in Tables IV and V. Consistent with the structures, the IR spectra do not show the existence of OH stretching and the carboxylate group frequencies do not significantly differ in solution and in the solid state. A typical singlet is observed in the ^1H NMR spectra in the region 2.89–3.40 ppm due to the –OMe group with evidence for ^{195}Pt couplings of about 6 Hz for the CF_3 derivatives and 3.4 Hz for (diphoe)Pt(Me)(COOMe). The ^{19}F and ^{31}P NMR data are in agreement with the proposed structures. It is interesting to note that the values of the $^1J_{PPt}$ coupling constants reflect the strong trans influence of both Pt–C σ bonds.[23] In fact, the magnitudes of the two $^1J_{PPt}$ values are very similar and an assignment of the phosphorus signals is possible only on the basis of the $^3J_{PF}$ value, where present.

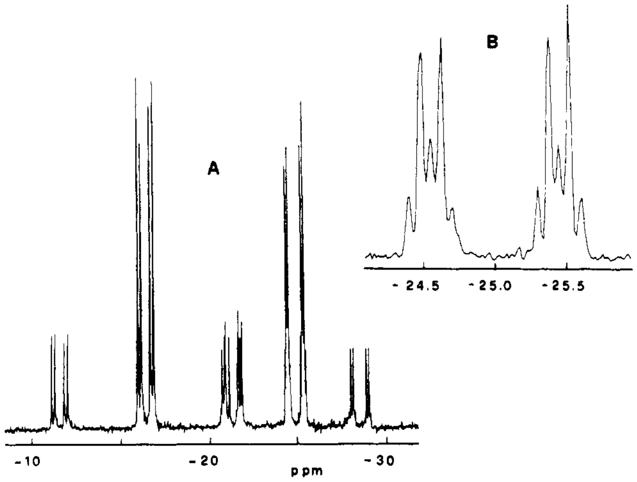
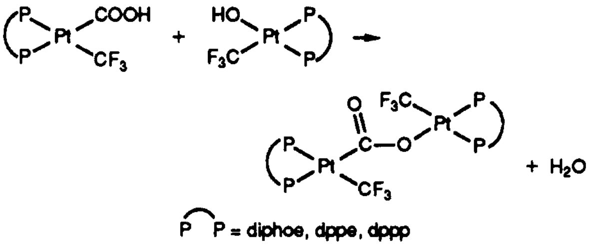


Figure 1. ^{19}F NMR spectrum of [(diphoe)Pt(CF_3)]$_2$(μ-CO_2): (A) full spectrum; (B) expansion of the region around −25 ppm showing the existence of $^5J_{FPt}$.

Dimerization Reactions. In the description of the preparation of the PtCOOH complexes, the condensation of $P_2Pt(Rx)(COOH)$ and $P_2Pt(Rx)(OH)$ in THF solutions has been mentioned. The formation of a well-characterized dinuclear species during the preparation of the PtCOOH complex occurred only in the case of (diphoe)Pt(CF_3)(COOH). To generalize this process, we have carried out the synthesis of other complexes of this kind, varying the diphosphine ligand bound to the metal (reaction 5).



(5)

The compounds (diphoe)Pt(CF_3)(COOH), (dppe)Pt(CF_3)(COOH), and (dppp)Pt(CF_3)(COOH) were reacted with stoichiometric amounts of the corresponding hydroxo complexes in concentrated THF solutions. Quantitative formation of the diphoe μ-CO_2 compound is observed in 3 h, while the dppe derivative requires 24 h. During the same time, the reaction does not occur in the case of the dppp derivative. We have also attempted the preparation of a mixed dinuclear compound by treating (diphoe)Pt(CF_3)(COOH) with (dppp)Pt(CF_3)(OH). The formation of an equilibrium yield of about 60% of product was observed. A ^{19}F NMR analysis of the isolated solid shows the presence of both starting reagents and the presence of a new species, which was identified as the mixed dinuclear compound on the basis of its pattern by analogy with the other homologous complexes. Formulation of the compounds with structure as in reaction 5 was based on IR and ^{19}F NMR spectroscopic data (Table VI). $^{31}P\{^1H\}$ NMR spectra were exceedingly complicated due to extensive overlapping of signals, and no assignments were attempted. As shown in Table VI, the IR spectra are characterized by the absence of OH stretchings and the carboxylate group frequencies are the same both in solid and in solution. Their values become closer to each other than in the corresponding bands of the PtCOOH complexes, and this behavior resembles that of the symmetric and asymmetric CO_2^- stretchings of the organic carboxylate

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Table V. NMR Spectral Data for the Complexes $P_2Pt(Rx)(COOMe)$[a]

complex	^1H $\delta(OCH_3)$	^{19}F $\delta(CF_3)$	$^{31}P\{^1H\}$	
$(diphoe)Pt(CF_3)(COOMe)$	3.31 (s); $^4J_{PtH} = 6.3$	−17.7 (dd); $^3J_{FP_{cis}} = 13.8$, $^3J_{FP_{trans}} = 67.0$, $^2J_{Pt} = 736$	cis CF_3 (dq) 53.23; $^3J_{PF} = 13.8$, $^2J_{PP} = 10.8$, $^1J_{PPt} = 1835$	trans CF_3 (dq) 48.7; $^3J_{PF} = 67.0$, $^2J_{PP} = 10.8$, $^1J_{PPt} = 1736$
$(dppe)Pt(CF_3)(COOMe)$	3.26 (s); $^4J_{PtH} = 6.2$	−18.1 (dd); $^3J_{FP_{cis}} = 13.8$, $^3J_{FP_{trans}} = 54.6$, $^2J_{PtF} = 718$	cis CF_3 (dq) 41.2; $^3J_{PF} = 13.8$, $^2J_{PP} = 3.2$, $^1J_{PPt} = 1833$	trans CF_3 (dq) 54.6; $^3J_{PF} = 54.6$, $^2J_{PP} = 3.2$, $^1J_{PPt} = 1980$
$(dppp)Pt(CF_3)(COOMe)$	2.89 (s); $^4J_{PtH} = 6.0$	−19.5 (dd); $^3J_{FP_{cis}} = 13.4$, $^3J_{FP_{trans}} = 52.1$, $^2J_{PtF} = 716$	cis CF_3 (dq) −5.87; $^3J_{PF} = 13.4$, $^2J_{PP} = 27.5$, $^1J_{PPt} = 1778$	trans CF_3 (dq) −9.48; $^3J_{PF} = 52.1$, $^2J_{PP} = 27.5$, $^1J_{PPt} = 1828$
$(diphoe)Pt(CH_3)(COOMe)$	3.4 (s); $^4J_{PtH} = 3.4$ 0.71 (dd);[b] $^3J_{HP_{cis}} = 6.9$, $^3J_{HP_{trans}} = 7.8$, $^2J_{PtH} = 71.0$		(dq) 52.2; $^2J_{PP} = 12.8$, $^1J_{PPt} = 1876$	(dq) 57.6; $^2J_{PP} = 12.8$, $^1J_{PPt} = 1810$

[a] Spectral data taken at room temperature in CD_2Cl_2; δ in ppm, J in Hz. References: ^1H, TMS; ^{19}F, $CFCl_3$; ^{31}P, 85% H_3PO_4. Abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dq, doublet of quartets. [b] $Pt-CH_3$.

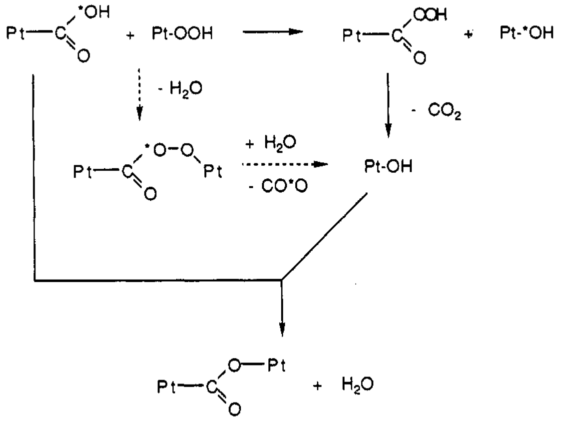
Table VI. Spectral Data for $[P_2Pt(CF_3)]_2(\mu\text{-}CO_2)$ Complexes[a]

		^{19}F NMR ($\delta(CF_3)$)	
complex	IR ($\nu(CO)$)	cis to O	cis to C
$[(diphoe)Pt(CF_3)]_2(\mu\text{-}CO_2)$	1535 (1535), 1205 (1205)	−24.96 (dd); $^3J_{FP_{cis}} = 10.8$, $^3J_{FP_{trans}} = 68.1$, $^2J_{FPt} = 559$, $^5J_{FPt} = 11.6$	−16.32 (dd); $^3J_{FP_{cis}} = 14.9$, $^3J_{FP_{trans}} = 55.6$, $^2J_{FPt} = 757$
$[(dppe)Pt(CF_3)]_2(\mu\text{-}CO_2)$	1545 (1545), 1200 (1185)	−25.59 (dd); $^3J_{FP_{cis}} = 12.1$, $^3J_{FP_{trans}} = 65.7$, $^2J_{FPt} = 551$, $^5J_{FPt} = 11.4$	−17.23 (dd); $^3J_{FP_{cis}} = 15.8$, $^3J_{FP_{trans}} = 54.3$, $^2J_{FPt} = 750$, $^5J_{FPt} = 1.5$
$(diphoe)(CF_3)Pt(\mu\text{-}CO_2)Pt(CF_3)(dppp)$		−25.03 (dd); $^3J_{FP_{cis}} = 13.8$, $^3J_{FP_{trans}} = 58.2$, $^2J_{FPt} = 500$, $^5J_{FPt} = 2.3$	−15.99 (dd); $^3J_{FP_{cis}} = 16.5$, $^3J_{FP_{trans}} = 55.9$, $^2J_{FPt} = 751$

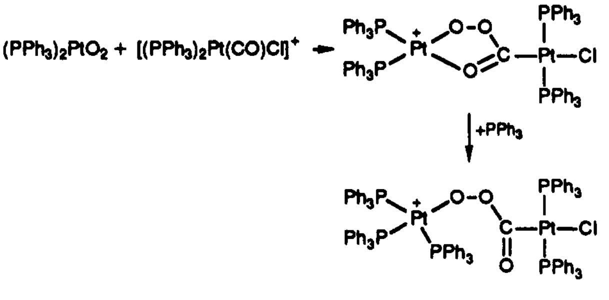
[a] IR: in Nujol mulls with use of CsI windows; data in parentheses refer to CH_2Cl_2 solutions in 0.5-mm CaF_2 cells. ^{19}F NMR: in CD_2Cl_2 at room temperature; δ in ppm referenced to $CFCl_3$, J in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublets.

anion.[24] ^{19}F NMR spectra were more informative since they show two different sets of signals (1/1 ratio), one corresponding to a CF_3 ligand cis to oxygen and the other to a CF_3 cis to carbon. The assignment is based on their very different $^2J_{FPt}$ values, which closely resemble those of the parent PtCOOH and PtOH complexes. Even more important, in all cases at least one of the two CF_3 signals shows a small long-range coupling with the distal ^{195}Pt center in the form of satellites (Figure 1). A similar complex, *trans*-$[(PEt_3)_2Pt(Ph)]_2(\mu\text{-}CO_2)$, has been recently reported by Bennett, and the bridging nature of the CO_2 moiety was determined by ^{13}C NMR spectroscopy on an enriched sample (δ 201.0 ppm in CD_2Cl_2).[11c] Unfortunately, in the present case due to the moderate solubility of the samples, the cis nature of the complexes, and the presence of C–F couplings the $^{13}C\{^1H\}$ NMR signals for the μ-CO_2 complexes appeared as very weak multiplets centered at ~206 ppm, and a parameter analysis was impossible. It has to be pointed out that, while CO_2 complexes in which both carbon and oxygen are bound to the same metal center are rather common,[25] species in which CO_2 bridges two different metal centers are relatively rare.[26] These species can be seen as models for the CO_2 activation at the metal surface of heterogeneous catalysts.[27]

Scheme I



Peroxy Dimerization Reactions. The occurrence of the condensation reaction reported above to give bridging carboxylato complexes suggests that a similar reaction may take place between the hydroxycarbonyl complexes and the corresponding hydroperoxy species PtOOH. In the literature there is only one example of a peroxycarbonyl complex of Pt(II), which was obtained by Kubota and co-workers[28] according to reaction 6. The compound is particularly stable, probably because of the bridging tridentate coordination mode of the peroxycarbonyl ligand. However, further reaction of the tridentate derivative with PPh_3 allowed the same authors the isolation also of the



(6)

(7)

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bridging bidentate peroxycarbonyl (reaction 7).[28]

We have tried to synthesize a similar bridging peroxy compound by condensation of (diphoe)Pt(CF_3)(COOH) and (diphoe)Pt(CF_3)(OOH) in THF at room temperature. After 3 h an analysis of the gas phase reveals the existence of significant amounts of CO_2, while the IR spectrum of the solid that precipitated from solution shows the presence of [(diphoe)Pt(CF_3)]$_2$(μ-CO_2), which was confirmed also by ^{19}F NMR analysis.

The same reaction was monitored with ^{19}F NMR spectroscopy in CD_2Cl_2 at low temperature with the hope of identifying the intermediate species involved. Solutions of the starting complexes (final concentration for both 0.1 M) were mixed at -80 °C, and the temperature was gradually increased. At -20 °C the reaction gave no evidence of any intermediate except [(diphoe)Pt(CF_3)]$_2$(μ-CO_2). A possible explanation might be the occurrence of a rapid partial exchange (Scheme I) between HOO^- and HO^- to form an intermediate hydroperoxycarbonyl species from which carbon dioxide is produced by intramolecular oxidation. The hydroxy complex thus formed reacts with the remaining PtCOOH to give the observed dimeric species.

More evidence for the existence of transient species of the $PtCOO_2H$ complex was found with a labeling experiment. The complex (diphoe)Pt(CF_3)(^{18}OH) was synthesized by exchange in CH_2Cl_2 solution between the corresponding PtOH complex and $H_2{}^{18}O$. As indicated by IR spectroscopy (CH_2Cl_2 solution), the exchange is complete after about 10 h (ν(O-H) in PtOH 3620 cm^{-1}, in Pt^{18}OH 3611 cm^{-1}). CO insertion into the Pt^{18}OH complex afforded (diphoe)Pt(CF_3)(CO^{18}OH) (ν(O-H) 3432 cm^{-1}). The reaction shown in Scheme I was repeated with the labeled hydroxycarbonyl compound, yielding CO_2 containing only 5% of CO^{18}O. This seems to rule out the possible existence of a peroxy dimerization intermediate similar to Kubota's[28] (dashed arrows in Scheme I), since in this case mostly CO^{18}O should be observed in the gas phase.

Reactions with Hydrogen Peroxide. As mentioned in the Introduction, the main goal in the preparation of the present PtCOOH complexes was to test their utility as precursors for the synthesis of metal peracidic species $P_2Pt(Rx)(COO_2H)$ to be employed as oxidants in organic synthesis, which would allow the ultimate use of hydrogen peroxide in a more direct and catalytic fashion. Organic peroxy acids are generally prepared from the corresponding carboxylic acid by reaction with concentrated solutions of H_2O_2 in strongly acidic media.[2] Further operations include separation, purification, and finally use as oxidants in organic synthesis. This series of operations, while tolerable on a laboratory scale, is undesirable for the industrial practice, because the coproduct carboxylic acid must be recovered and recycled.

We tested the reactions of the $P_2Pt(Rx)(COOH)$ complexes with hydrogen peroxide without any added H^+ because of the above-described protonation reaction to give metal carbonyl complexes. The reactions were carried out in THF at 0 °C with use of H_2O_2 in different concentrations. At the end, the presence of CO_2 in the gas phase was determined for each reaction. The product consisted always of a mixture of variable amounts of PtOH and PtOOH complexes. Some Pt hydroxycarbonyl complexes react only with 72% H_2O_2, while for others 34% H_2O_2 is sufficient for the reaction to proceed. A summary of the results is reported in the upper part of Scheme II. It should be pointed out that the same products were obtained some years ago when we tried to insert carbon monoxide into the Pt-O bond of some $P_2Pt(CF_3)(OOH)$ complexes:[29]

$$P_2Pt(CF_3)(OOH) + CO \rightarrow P_2Pt(CF_3)(OH) + CO_2 \quad (8)$$

$$P_2 = \text{diphoe, dppe, 2 } PPh_2Me$$

Scheme II

$$P_2Pt(Rx)(COOH) + H_2O_2 \longrightarrow CO_2 + P_2Pt(Rx)(OH) + P_2Pt(Rx)(OOH)$$

H_2O_2 34% P_2 = dppp Rx = CF_3
P = PPh_3
P_2 = diphoe Rx = Me
P_2 = dppe Rx = Ph

H_2O_2 72% P_2 = diphoe Rx = CF_3
P_2 = dppe
P = PPh_2Me

$$P_2Pt(Rx)(COOMe) + H_2O_2 \longrightarrow Pt\text{-}OH + Pt\text{-}OOH + CO_2$$

H_2O_2 34% P_2 = diphoe Rx = CH_3

H_2O_2 72% P_2 = diphoe Rx = CF_3
P_2 = dppe
P_2 = dppp

$$[P_2Pt(CF_3)]_2(\mu\text{-}CO_2) + H_2O_2 \longrightarrow Pt\text{-}OH + Pt\text{-}OOH + CO_2$$

H_2O_2 72% P_2 = diphoe
P_2 = dppe

The above reaction and the one reported in Scheme II most likely proceed through a common organometallic peroxycarboxylic intermediate. In order to detect the existence of this intermediate, we have studied in detail the case of (diphoe)Pt(CF_3)(COOH). This complex was chosen because of its greater stability and the expected higher acidity of the carboxylic proton compared to those in the other homologous complexes because of the electron-withdrawing effect of the CF_3 ligand. As shown in Scheme II, this complex reacts only with 72% H_2O_2, while with 34% H_2O_2 it is recovered unaltered.

In order to trap the putative hydroperoxycarbonyl intermediate, we carried out some ^{19}F NMR spectroscopy studies at variable temperature (-80 °C to room temperature). Reaction 8 appeared to be better suited for this purpose because of the higher solubility of the starting materials at low temperature. The complex (diphoe)Pt(CF_3)(OOH) was dissolved in CD_2Cl_2 (0.1 M), and the solution was placed in an NMR tube, cooled to -80 °C, degassed, and saturated with CO. The reaction mixture evolution with temperature and time was monitored with ^{19}F NMR spectroscopy. At -80 °C only the signals corresponding to the starting complex are present (δ -27.32 dd, $^3J_{FP_{cis}}$ = 11.0 Hz, $^3J_{FP_{trans}}$ = 62.0 Hz, $^2J_{FPt}$ = 554 Hz),[7] and no evolution was observed after 15 h at -80 °C. Then the temperature was slowly raised; at -20 °C the signals of a new species appeared, the intensity of which increased regularly with time. By its typical pattern this species was recognized to be [(diphoe)Pt(CF_3)]$_2$(μ-CO_2). No other products were detected (spectra were registered every 40 min), and after about 6 h the reaction had gone to completion. CO_2 was present in the gas phase.

Although the expected $PtCOO_2H$ intermediate could not be directly observed, the formation of the dimer requires prior formation of the corresponding PtOH complex, which in turn implies the insertion of CO into PtOOH to give as a transient intermediate the peracidic species from which CO_2 is formed. Partial insertion of CO in the PtOH com-

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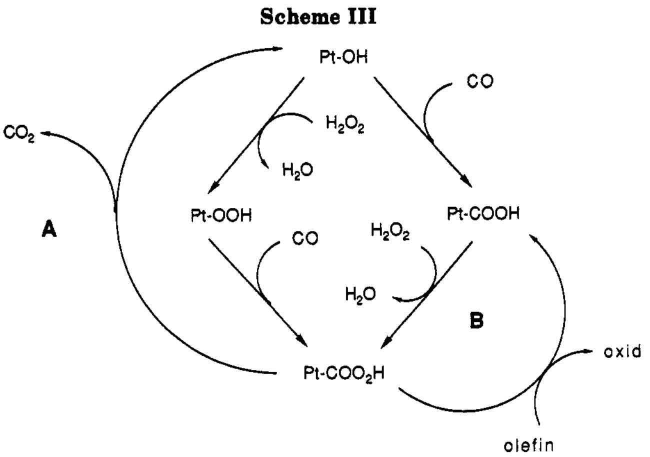
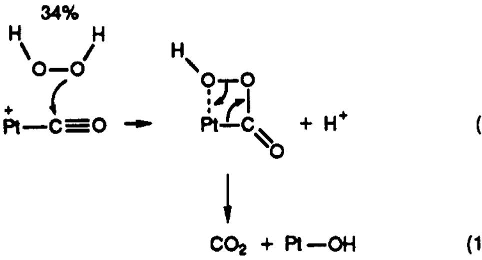
Scheme III



plex would account for the formation of the dimer.

In a second experiment $[(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{CO})]\text{ClO}_4$ was treated with a stoichiometric amount of 34% H_2O_2. The initial ^{19}F NMR spectrum was run at −70 °C in CD_2Cl_2 (0.1 M); after addition of 34% H_2O_2 nothing happened until the temperature was raised to −20 °C. At this temperature the initial carbonyl species slowly disappeared and was replaced by the signals characteristic of (diphoe)Pt(CF_3)(OH) and $[(\text{diphoe})\text{Pt}(\text{CF}_3)(\text{CH}_2\text{Cl}_2)]^+$ (PtOH, δ −27.40 dd, $^3J_{\text{FP}_{\text{cis}}} = 9.1$ Hz, $^3J_{\text{FP}_{\text{trans}}} = 57.6$ Hz, $^2J_{\text{FPt}} = 596$ Hz; Pt$^+$, δ −29.36 dd, $^3J_{\text{FP}_{\text{cis}}} = 8.6$ Hz, $^3J_{\text{FP}_{\text{trans}}} = 56.7$ Hz, $^2J_{\text{FPt}} = 518$ Hz).[7] The reaction was complete in about 1 h, and carbon dioxide was found in the gas phase. Reactions 9 and 10 show a plausible pathway that accounts for the products observed. Again, these observations seem to suggest the intermediacy of the hydroperoxy carbonyl species.



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(10)

Reactions with H_2O_2 have been carried out also on the methyl esters and on the carboxy dimers. The results are summarized in the lower part of Scheme II and do not differ greatly from those obtained with the PtCOOH complexes, indicating that the CF_3 derivatives are generally more reluctant to undergo decarboxylation. Most likely, these reactions proceed through prior hydrolysis of the starting complexes followed by the chemistry already described for the PtCOOH complexes.

Catalytic Reactions. The possible involvement of platinum peracids in the above reactions seems to suggest that the oxidizing ability of these species could indeed be exploited only if the oxygen transfer to an organic substrate were faster than the oxidation of the carbonyl. In order to make our ultimate goal (i.e. organic oxidation) more likely, we have devised a catalytic system consiting of (diphoe)Pt(CF_3)(OH), hydrogen peroxide, and an olefin under a carbon monoxide atmosphere, which should provide for the formation of the necessary PtCOOH complex and compensate for losses of active species due to oxidation of the carbonyl to CO_2. Under these conditions two possible catalytic cycles can take place (Scheme III): one leading to the oxidation of carbon monoxide (A) and the other one to the oxidation of the olefin to products (B).

This system has been checked in the oxidation of simple olefins such as cyclohexene and 1-octene in THF with 72% H_2O_2. The reactions have been carried out either at −25 °C or at −10 °C; they were monitored with GLC for 5 days, but no organic oxidation products were detected. Modest amounts of CO_2 were produced at −25 °C, while at −10 °C massive formation of carbon dioxide took place (virtually all the H_2O_2 introduced was consumed to give CO_2) in about 4 h. At the end of these tests the catalyst was recovered and characterized. It consisted of a ~1/1 mixture of PtOH and PtCOOH with minor amounts of PtOOH. This reaction is indeed a catalytic process, since blank tests carried out under the same experimental conditions or even at 25 °C in the absence of Pt complex gave only negligible amounts of CO_2.

The mechanism for decarboxylation in the present system may be similar to processes in the water-gas shift reaction, for which two possibilities have been suggested: (i) a concerted "β-elimination" type of mechanism (reaction 11) and (ii) a stepwise mechanism via deprotonation (reaction 12).[9] Although in most cases the hydroxycarbonyl

$$\text{L}_n\text{M–COOH} \rightarrow \text{L}_n\text{M–H} + \text{CO}_2 \tag{11}$$

$$\text{L}_n\text{M–COOH} \rightarrow \text{H}^+ + \text{L}_n\text{M–CO}_2^- \rightarrow \text{CO}_2 + \text{L}_n\text{M}^- + \text{H}^+ \tag{12}$$

complexes described in this paper seem to be reluctant to undergo reaction 11, a similar β-hydroxy rearrangement following nucleophilic attack (as in reaction 9) seems the most favorable pathway for decarboxylation, since a behavior analogous to reaction 12 would require in this case the unlikely formation of HO$^+$. Reaction 10 can be considered the decomposition of an intermediate quasi peroxy metallacycle, which was suggested as the key step in the epoxidation of olefins with H_2O_2 by use of the same P_2-Pt(CF_3)(OH) catalysts.[7]

Of the two possible catalytic cycles shown in Scheme III, only cycle A seems to work, which suggests that the internal nucleophilic attack on the carbonyl is overwhelming compared to the oxygen transfer to the external olefin.

Conclusions

The study reported here has allowed the synthesis of a variety of carboxylic complexes and the suggestion of an intriguing chemistry concerning peroxy species; however, the organometallic carboxylic acids synthesized are not useful as catalysts for the oxidation of organic substrates. In fact, we have observed that, even if there is repeated, although indirect, evidence for the intermediacy of peroxycarboxylic species in the reactions with H_2O_2, their reactivity seems to be dominated by the tendency to undergo intramolecular oxidation, which is overriding with respect to any other oxidation process. We believe that the main reason for this behavior lies in the very weak (if any) acidic character of the carboxylic group, even in those complexes containing strongly electron-withdrawing ligands.

Although the present approach to organometallic peroxy acids has failed, we still believe that these species, which in principle combine around the same metal center the peracidic function and the ability to activate the substrate, might be a plausible new way to transition-metal-catalyzed organic oxidations.

Experimental Section

Apparatus. IR spectra were taken on a Perkin-Elmer 683 spectrophotometer and on a Digilab FTS 40 interferometer either in Nujol mulls CsI plates or in CH_2Cl_2 solution CaF_2 windows. ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectra were recorded on a Varian FT

Table VII. Microanalytical Data for New Complexes

compd	% C calcd (found)	% H calcd (found)
(dppe)Pt(Ph)(OH)	55.89 (55.78)	4.40 (4.32)
(dppe)Pt(CF_3)(COOH)	47.53 (47.45)	3.56 (3.61)
(dppp)Pt(CF_3)(COOH)	48.27 (48.40)	3.77 (3.75)
trans-(PPh_2Me)$_2$Pt(CF_3)(COOH)	47.39 (47.28)	3.84 (3.78)
trans-(PPh_3)$_2$Pt(CF_3)(COOH)	54.75 (54.82)	3.75 (3.82)
(diphoe)Pt(Me)(COOH)	51.62 (51.70)	4.02 (4.10)
(dppe)Pt(Ph)(COOH)	55.39 (55.31)	4.22 (4.29)
trans-(PCy_3)$_2$Pt(Me)(COOH)	55.93 (55.85)	8.65 (8.68)
(dppe)Pt(CF_3)(COOMe)	48.27 (48.21)	3.77 (3.81)
(dppp)Pt(CF_3)(COOMe)	48.98 (49.04)	3.97 (4.02)
(diphoe)Pt(Me)(COOMe)	52.33 (52.21)	4.24 (4.20)
(diphoe)$_2$Pt$_2$(CF_3)$_2$(μ-CO_2)	48.40 (48.47)	3.25 (3.28)
(dppe)$_2$Pt$_2$(CF_3)$_2$(μ-CO_2)	48.25 (48.22)	3.53 (3.48)

80A spectrometer operating in the FT mode, using as external references TMS, $CFCl_3$, and 85% H_3PO_4, respectively. $^{13}C\{^1H\}$ NMR spectra at −40 °C were recorded on a Bruker AM 400 spectrometer operating in the FT mode, using as an external reference TMS. Negative chemical shifts are upfield from the reference. UV-vis spectra were registered on a Perkin-Elmer Lambda 5 spectrophotometer in the 220–450-nm region. GLC measurements were taken on a Hewlett-Packard 5790A gas chromatograph equipped with a 3390 automatic integrator. GM-MS experiments were performed on a Carlo Erba HRGC 5160 gas chromatograph equipped with a Hewlett-Packard 5970 mass selective detector. Identification of products was made with GLC by comparison with authentic samples. pH measurements were performed on a Orion 701 digital pH meter.

Materials. Solvents were dried and purified according to standard methods. 1-Octene (Fluka) was purified by passing through neutral alumina, distilled, and stored under N_2 in the dark. $H_2{}^{18}O$ (95% isotopic purity from Cambridge Isotope Laboratories), hydrogen peroxide (35% from Fluka, 72% from Degussa), and diphoe (*cis*-1,2-bis(diphenylphosphino)ethylene), dppe (1,2-bis(diphenylphosphino)ethane), dppp (1,3-bis(diphenylphosphino)propane), PPh_3, PPh_2Me, and PCy_3 (all from Strem) were commercial products and were used without purification.

The following compounds were prepared according to literature procedures: (dppe)Pt(Ph)Cl,[30] (dppe)Pt(CF_3)(OH),[10] (dppp)Pt(CF_3)(OH),[6d] *trans*-(PPh_2Me)$_2$Pt(CF_3)(OH),[10] *trans*-(PPh_3)$_2$Pt(CF_3)(OH),[10] (diphoe)Pt(Me)(OH),[23] *trans*-(PCy_3)$_2$Pt(Me)(OH),[6b] (diphoe)Pt(CF_3)(COOH),[10] and (diphoe)Pt(CF_3)(COOMe).[10]

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 the complexes, except one, were found to be air-stable once isolated. All complexes gave satisfactory elemental analyses (Table VII).

(dppe)Pt(Ph)(OH). (dppe)Pt(Ph)Cl (1.70 g, 2.38 mmol) was suspended in acetone, and the suspension was degassed and placed under N_2. $AgBF_4$ (2.4 mL of a 1 M solution in acetone) was added dropwise. After 1 h AgCl was filtered off and to the concentrated solution was added KOH (0.094 g, 2.4 mmol) dissolved in H_2O (10 mL) dropwise with stirring. The mixture darkened quickly and after 1 h was brought to dryness in vacuo. The solid residue was extracted with a CH_2Cl_2/toluene (1:2 v/v) mixture, and the resulting solution was concentrated in vacuo and then placed at −20 °C overnight. The white solid obtained was filtered, washed with hexane, and dried. Recrystallization was from CH_2Cl_2/Et_2O (yield 40%).

(dppe)Pt(CF_3)(COOH). (dppe)Pt(CF_3)(OH) (0.50 g, 0.70 mmol) was partially dissolved in 150 mL of toluene. The system was degassed and saturated with CO, with stirring. In a few minutes the solid dissolved completely and stirring was continued at room temperature for 24 h. The solvent was removed in vacuo to about 50 mL. The precipitation was completed by addition of Et_2O. The white solid was filtered, washed with Et_2O, and dried. Recrystallization was from CH_2Cl_2/Et_2O (yield 65%).

(dppp)Pt(CF_3)(COOH). The complex could be obtained by starting from the corresponding hydroxo derivative (0.50 g, 0.69 mmol) according to the procedure described for (dppe)Pt(CF_3)(COOH), but the reaction time was 6 h (yield 68%).

***trans*-(PPh_2Me)$_2$Pt(CF_3)(COOH).** The complex could be obtained by starting from the corresponding hydroxo derivative (0.70 g, 0.98 mmol) according to the procedure described for (dppp)Pt(CF_3)(COOH) (yield 75%).

***trans*-(PPh_3)$_2$Pt(CF_3)(COOH).** *trans*-(PPh_3)$_2$Pt(CF_3)(OH) (0.50 g, 0.62 mmol) was partially dissolved in 150 mL of toluene. The system was degassed and saturated with CO, with stirring. Complete dissolution took place in a few minutes, while after 30 min a white solid precipitated out of solution. Stirring was continued at room temperature for a further 5 h. The solvent was removed in vacuo to about 5 mL. The precipitation was completed by addition of hexane. The white solid was filtered, washed with hexane, and dried. Recrystallization was from CH_2Cl_2/hexane (yield 70%).

(diphoe)Pt(Me)(COOH). The complex could be obtained by starting from the corresponding hydroxo derivative (0.40 g, 0.62 mmol) according to the procedure described for (dppp)Pt(CF_3)(COOH) (yield 65%).

(dppe)Pt(Ph)(COOH). (dppe)Pt(Ph)(OH) (0.55 g, 0.80 mmol) was partially dissolved in 5 mL of dry THF. The mixture was degassed, saturated with CO, which caused immediate complete dissolution, and stirred for 45 min at room temperature. The white precipitate was filtered, washed with Et_2O, and dried in vacuo. Recrystallization was from CH_2Cl_2/Et_2O (yield 45%).

***trans*-(PCy_3)$_2$Pt(Me)(COOH).** The complex could be obtained by starting from the corresponding hydroxo derivative (0.50 g, 0.64 mmol) according to the procedure described for (dppp)Pt(CF_3)(COOH) (yield 65%).

(dppe)Pt(CF_3)(COOMe). (dppe)Pt(CF_3)(OH) (0.50 g, 0.72 mmol) was dissolved in MeOH (40 mL) and 0.10 mL of NEt_3 was added to the solution. The solution was then degassed by several freeze and thaw cycles, saturated with CO, and stirred for 15 h. The white solid obtained was filtered, washed with Et_2O, and dried in vacuo (yield 62%).

(dppp)Pt(CF_3)(COOMe). The complex could be obtained by starting from the corresponding hydroxo derivative (0.50 g, 0.73 mmol) according to the procedure described for (dppe)Pt(CF_3)(COOMe) (yield 55%).

(diphoe)Pt(Me)(COOMe). The complex could be obtained by starting from the corresponding hydroxo derivative (0.50 g, 0.80 mmol) according to the procedure described for (dppe)Pt(CF_3)(COOMe). The reaction was complete in 30 min (yield 55%).

[(diphoe)Pt(CF_3)]$_2$(μ-CO_2). (diphoe)Pt(CF_3)(OH) (0.15 g, 0.22 mmol) and (diphoe)Pt(CF_3)(COOH) (0.16 g, 0.22 mmol) were dissolved in 15 mL of dry THF. The solution was degassed, N_2-saturated, and stirred for 3 h. The solution was concentrated in vacuo, and addition of Et_2O resulted in the precipitation of a white solid. This was filtered, washed with Et_2O, and dried in vacuo. Recrystallization was from THF/Et_2O (yield 86%).

[(dppe)Pt(CF_3)]$_2$(μ-CO_2). The complex could be obtained by starting from the corresponding hydroxo (0.055 g, 0.081 mmol) and hydroxycarbonyl (0.055 g, 0.081 mmol) derivatives according to the procedure described for (diphoe)$_2$Pt$_2$(CF_3)$_2$(μ-CO_2) (yield 55%).

(diphoe)(CF_3)Pt(μ-CO_2)Pt(CF_3)(dppp). The procedure described above for (diphoe)$_2$Pt$_2$(CF_3)$_2$(μ-CO_2) starting from (diphoe)Pt(CF_3)(COOH) (0.15 g, 0.21 mmol) and (dppp)Pt(CF_3)(OH) (0.15 g, 0.21 mmol) gave a product consisting of an equilibrium mixture of starting complexes and the dimeric complex described.

[(diphoe)Pt(CF_3)(CO)]ClO_4. [(diphoe)Pt(CF_3)(CH_2Cl_2)]ClO_4 (0.15 g, 0.18 mmol) was dissolved in CH_2Cl_2 (5 mL), degassed, and saturated with CO. Evaporation of the solvent under a stream of CO yielded a white solid (yield 95%).

(diphoe)Pt(CF_3)($CO^{18}OH$). The synthesis was performed in glassware that was dried in the oven for 2 h and then flushed with dry N_2 prior to use. Manipulation and contact with solvent was reduced to the minimum. (diphoe)Pt(CF_3)(OH) (0.20 g, 0.28 mmol) was dissolved in dry CH_2Cl_2 and the solution placed under N_2. To the stirred solution was added 0.2 mL of $H_2{}^{18}O$, and the mixture was stirred. The solution was sampled periodically and analyzed by IR spectroscopy in the 3800–3400-cm^{-1} region. After 10 h the solution was evaporated to dryness in vacuo and the white solid was partially dissolved in 50 mL of dry toluene under a CO

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(30) Baird, M. C.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 865.

atmosphere. After the solution was stirred for 5 h, the solvent was removed in vacuo to give a white solid.

Reaction with PtOOH. (diphoe)Pt(CF_3)($CO^{18}OH$) (0.050 g, 0.071 mmol) and (diphoe)Pt(CF_3)(OOH) (0.049 g, 0.071 mmol) were placed as the solids in a Schlenk tube bearing a screw-capped silicone septum. The system was evacuated and filled with N_2. Dry, N_2-saturated, chilled THF (10 mL) was added and the reaction mixture stirred for 2 h. The gas phase was then sampled with a gastight syringe and the sample injected into a GC–MS system.

Reactions with H_2O_2. Reactions of (diphoe)Pt(Me)(COOH), (dppe)Pt(Ph)(COOH), (diphoe)Pt(CF_3)(COOH), (dppe)Pt(CF_3)(COOH), (dppp)Pt(CF_3)(COOH), *trans*-(PPh_3)$_2$Pt(CF_3)(COOH), *trans*-(PPh_2Me)$_2$Pt(CF_3)(COOH), (diphoe)Pt(CF_3)(COOMe), (dppe)Pt(CF_3)(COOMe), (dppp)Pt(CF_3)(COOMe), (diphoe)$_2$Pt$_2$(CF_3)$_2$(μ-CO_2), and (dppe)$_2$Pt$_2$(CF_3)$_2$(μ-CO_2) with H_2O_2 were carried out, according to the general procedure described here, in a round-bottomed flask equipped with two stopcocks for gas inlet and outlet, a side arm fitted with a screw-capped silicone septum to allow sampling, and an external jacket connected to the external circulation of a thermostat; stirring was performed with a Teflon-coated bar driven externally by a magnetic stirrer.

In the reactor 0.1 mmol of complex was suspended in 15 mL of dry THF. The system was degassed, N_2-saturated, and thermostated at 0 °C. To the stirred mixture was added 100 μL of H_2O_2 (34% or 72%), and the reaction was carried out for 20 h. The presence of CO_2 in the gas phase was determined by flushing the reaction vessel with N_2 and bubbling the gas through a water solution containing $Ba(OH)_2$. The weight of $BaCO_3$, which can be recovered by filtration, gave a semiquantitative estimate of the CO_2 evolved. The reaction mixture was then concentrated, and addition of Et_2O yielded a solid, which was filtered and analyzed.

Catalytic Reactions. The catalytic reactions were carried out in the same reactors described above according to the following procedure with either (diphoe)Pt(CF_3)(OH) or (dppe)Pt(CF_3)(OH) as catalyst and either 1-octene or cyclohexene as substrate.

A 0.05-mmol amount of the complex was dissolved in 3 mL of dry THF. The system was degassed by several freeze and thaw cycles, saturated with CO admitted from a gas reservoir (~1 L) connected to the system, and thermostated at the required temperature (either −25 or −10 °C). Through the septum was added 50 μL of 72% H_2O_2 and 1 mL of olefin. The mixture was stirred for up to 5 days and sampled periodically. The liquid phase was analyzed with a 30-m HP-5 capillary column, while the gas phase was analyzed with a 3-m Porapak Q packed column. At the end of the reaction the solution was concentrated and addition of Et_2O yielded a solid, which was filtered and analyzed.

Acknowledgment. This work was supported jointly by the European Economic Community (Brussels, Belgium) and Degussa AG (Frankfurt, Germany) through the special program BRITE. Degussa AG also provided a free sample of 72% H_2O_2. Special thanks are expressed to Drs. G. Goor and M. Schmidt (Degussa AG), to Professor W. Drenth (University of Utrecht), and to Professor J. W. Buchler (University of Darmstadt) for stimulating discussions. Dr. R. Bertani (CNR, Padua, Italy) is gratefully acknowledged for running the ^{13}C NMR spectra.

Direct Evidence for the Formation of a Disiladiferracyclic Compound through Dimerization of an Iron–Silylene Intermediate

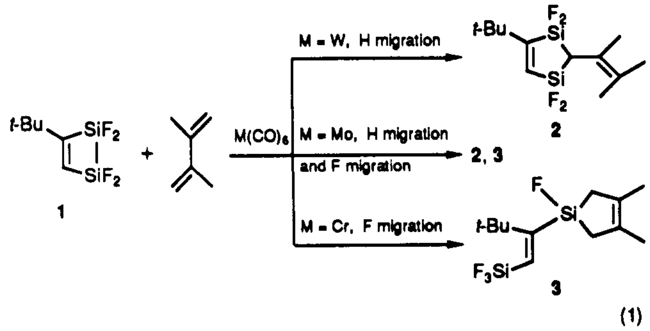
K. M. Horng, S. L. Wang, and C. S. Liu*

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China

Received May 3, 1990

In the reaction between tetrafluorodisilacyclobutene (1) and [(η^5-C_5H_5)Fe(CO)$_2$]$_2$, a metal-mediated intramolecular fluorine migration results in an Fe–silylene intermediate that rapidly dimerizes to a disiladiferracyclic compound (6). The structure of 6 is determined by spectroscopies in solution and X-ray diffraction of a single crystal. The Fe–silylene intermediate can be stabilized (in the form of 7) by weak donor solvents such as tetrahydrofuran (THF), acetonitrile, and hexamethylphosphoric triamide (HMPT).

Recently we proposed that during cycloaddition reactions between tetrafluorodisilacyclobutene (1) and conjugated dienes mediated by metal carbonyls,[1-3] a η^3-allyl–η^3-silaallyl complex intermediate might facilitate either hydride or fluorine migration depending on the hardness of the central metal. For example, the cycloaddition between 1 and 2,3-dimethylbuta-1,3-diene mediated by group 6 metal carbonyls resulted in the product from H migration (2) or F migration (3) according to the hardness of the metal (Cr > Mo > W) (eq 1).



(1)

If one tunes the hardness of the metal horizontally across the periodic table, the harder Mn would facilitate F mi-

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0276-7333/91/2310-0631$02.50/0