

Reactivity of Hydroxo, Hydroperoxo and Peroxo Platinum(II) Derivatives towards Carbon Oxides

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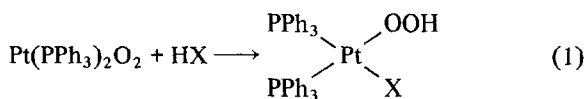
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Abstract

The reaction of the complexes $\text{Pt}(\text{PPh}_3)_2(\text{OOH})\text{X}$ (HX = succinimide (I), phthalimide (II), PhOH (III), $p\text{-MeC}_6\text{H}_4\text{OH}$ (IV)) and $\text{Pt}(\text{PPh}_3)_2(\text{OH})\text{X}$ (HX = succinimide (V), phthalimide (VI)) with CO and CO_2 have been studied. In order to clarify some reaction pathways, the reactivity of $\text{Pt}[\text{O}_2\text{C}(\text{O})\text{O}](\text{PPh}_3)_2$ (VII) and of $\text{Pt}[\text{O}_2\text{CMe}_2\text{O}](\text{PPh}_3)_2$ (VIII) with succinimide and phthalimide has also been investigated. ^{17}O NMR and IR spectra of some of these compounds and of $\text{Pt}[\text{OC}(\text{O})\text{O}](\text{PPh}_3)_2$ (IX) have been recorded.

Introduction

We recently reported on the reactivity of the peroxo platinum(II) complex, $\text{Pt}(\text{PPh}_3)_2\text{O}_2$, with imides and phenol [1]. From these reactions hydroperoxo platinum(II) complexes have been obtained (eqn. (1))



HX = succinimide (I), phthalimide (II), PhOH (III)

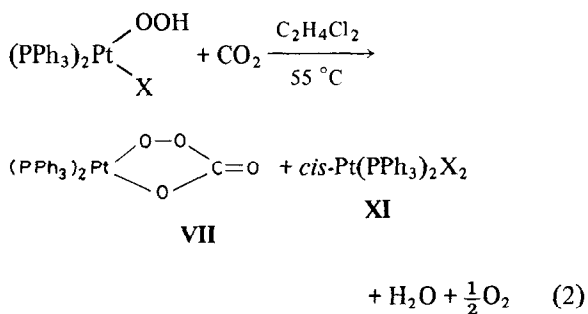
The related complex with $\text{HX} = p\text{-MeC}_6\text{H}_4\text{OH}$ (IV) has been obtained in the present work. Compound I when treated with PPh_3 gave $\text{Pt}(\text{PPh}_3)_2(\text{OH})\text{X}$ (HX = succinimide (V)), and the related complex with HX = phthalimide (VI) has now been similarly obtained. Upon treatment of compounds I and II with an alkene such as *cis*-cyclooctene we did not observe the transfer of the peroxo-oxygen atom

to the olefin [1]. However, on considering the growing interest in the chemistry of monomeric metal hydroxides, alkoxides and amides [2], we decided to investigate the reactivity of compounds I–VI towards carbon oxides. Moreover, in order to clarify some reaction pathways, the reactivity of $\text{Pt}[\text{O}_2\text{C}(\text{O})\text{O}](\text{PPh}_3)_2$ (VII) and of $\text{Pt}[\text{O}_2\text{CMe}_2\text{O}](\text{PPh}_3)_2$ (VIII) with succinimide and phthalimide has also been investigated. ^{17}O NMR and IR spectra of some of these compounds and of $\text{Pt}[\text{OC}(\text{O})\text{O}](\text{PPh}_3)_2$ (IX) are also reported and discussed.

Results and Discussion

Reactions with Carbon Dioxide

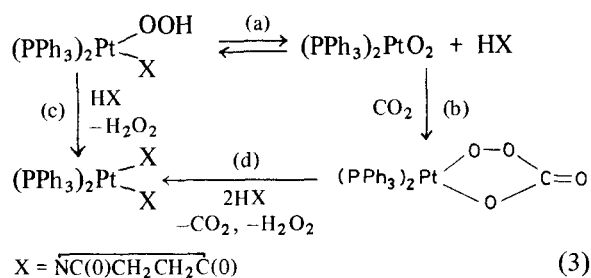
Compound I reacts with carbon dioxide only at $T > 55^\circ\text{C}$ in $\text{C}_2\text{H}_4\text{Cl}_2$ (eqn. (2))



$\text{X} = \overline{\text{NC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})}$ (I)

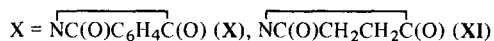
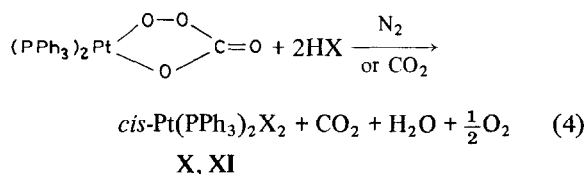
The peroxocarbonato complex VII [3] and the bis-amido complex XI are obtained. Hydrogen peroxide was not present in solution; it probably decomposes to water and dioxygen under the reaction conditions. Compounds VII and XI are not formed in equimolar amounts (4:1), and their formation can follow different routes (eqn. (3))

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Compound I could be in equilibrium with the peroxo platinum complex, which is known to react with CO₂ giving the peroxocarbonato derivative (paths (a) and (b)). The equilibrium (a) has been demonstrated in the case of X = $\text{Ph}-\text{N}-\text{CHO}$ [1]. The succinimide thus

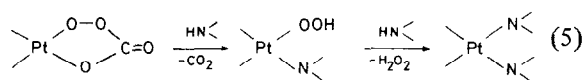
formed can then react with compound I giving the bis-amido complex XI (path (c)), a reaction which has been already verified [1]. However even the reaction of the peroxocarbonato complex with HX (path (d)) could be involved. In fact this reaction has been independently demonstrated (eqn. (4))



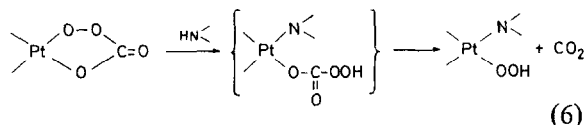
Compound X crystallizes with some solvent clathrated in the lattice, giving uncertain elemental analyses. For this reason and since only the IR spectrum of this compound was not conclusive as far as its formulation is concerned, we have prepared crystals of compound X by slow diffusion of n-hexane into a CH₂Cl₂ solution of X under a di-nitrogen atmosphere. Preliminary results are indicative of a monomeric complex containing two triphenylphosphine and two phthalimido ligands in cis-square planar arrangement [4].

By using in reaction (4) two moles of HX per mole of the peroxocarbonato complex, the reaction is complete and the stoichiometric amount of CO₂ is evolved*. If a one to one ratio of the reactants is used, compounds X and XI are again obtained, together with some unreacted starting material. Reaction (4) presumably proceeds via protonation of the peroxo group (eqn. (5))

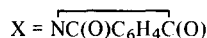
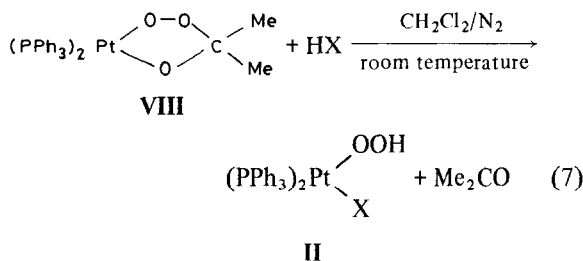
*For determination of the CO₂ evolved, see the reaction of III with CO in 'Experimental'.



A referee has suggested an alternative route (eqn. (6))

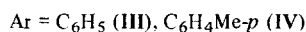
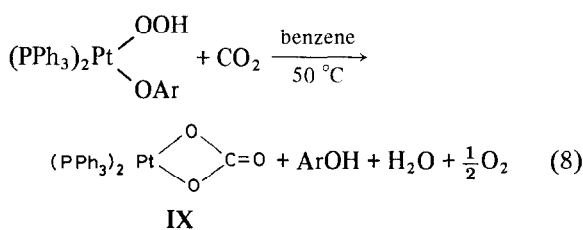


Under the reaction conditions, the peroxocarbonato complex does not eliminate CO₂ in the absence of the amide to give Pt(PPh₃)₂O₂. Nevertheless IR studies failed to detect the intermediate formation of a metal-carbamate, a type of complex which is known to readily lose carbon dioxide [2, 5]. For this reason we also studied the reaction of phthalimide with the acetone adduct of Pt(PPh₃)₂O₂ [3, 6] (eqn. (7))

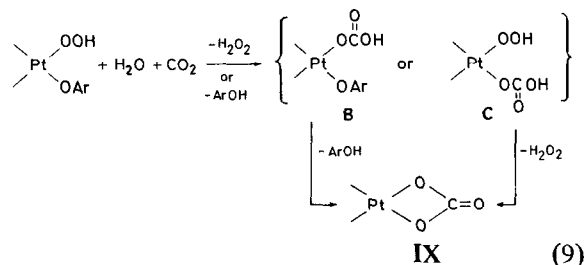


By using a one to one ratio of the reactants, even in this case no intermediates containing acetone could be detected by IR spectroscopy and the product isolated from the solution was the hydroperoxo complex II, while free acetone was also formed. This finding supports the route proposed in eqn. (5). A reaction in CH₂Cl₂ was also carried out on compound VIII with acetic acid (1 to 2) with the aim of obtaining AcOC(OH)Me₂. However the only products were again free acetone and Pt(PPh₃)₂(OAc)₂ [8].

The reactions with carbon dioxide were also studied with the hydroperoxo complexes III and IV (eqn. (8))

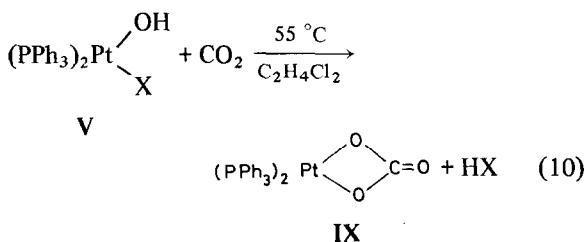


The carbonato complex IX is obtained, while the presence of ArOH was detected in the mother liquor. Compounds III and IV do not lose ArOH to give intermediately the peroxo complex, $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ (IR and ^{31}P NMR evidences), and in fact the formation of the peroxocarbonato complex, $\text{Pt}[\text{O}_2\text{C}(\text{O})\text{O}](\text{PPh}_3)_2$, was never observed in this reaction. In order to explain the formation of the carbonato derivative IX [3], we suggest the reactions reported in eqn. (9)



In both possible reaction paths, an intermediate bicarbonato complex B or C is formed [2, 7], due to adventitious moisture present in the reaction medium. Elimination of ArOH from B or of H_2O_2 (that is $\text{H}_2\text{O} + \frac{1}{2}\text{O}_2$) from C, gives the final product IX. As a matter of fact, reaction (8) proceeds much more rapidly when water is added to the reaction mixture. It should also be noted that compound III does not react with water under a dinitrogen atmosphere. Finally, insertion of CO_2 into the Pt—OAr bond of III and IV should not explain the formation of IX.

The hydroxo complex VI does not react with CO_2 , while with compound V a reaction was observed, leading again to the carbonato complex IX (eqn. (10))

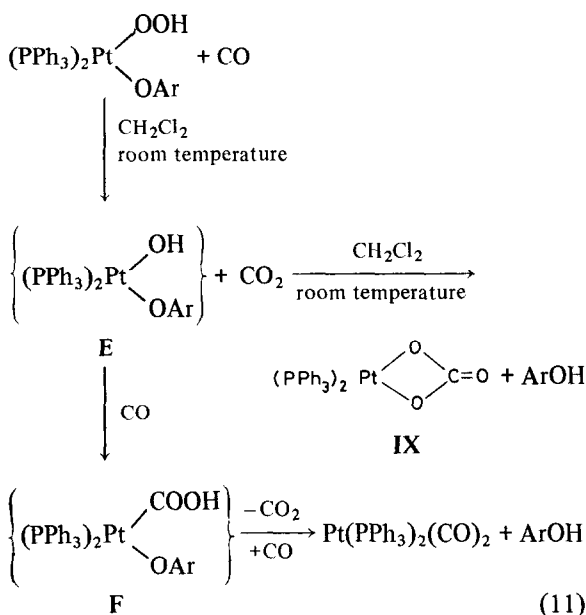


The intermediate formation of the bicarbonato complex analogous to B, eqn. (9), by formal insertion of CO_2 into the Pt—OH bond of V [2], seems the most probable pathway.

Reactions with Carbon Monoxide

The hydroxo complexes V and VI and the hydroperoxo complex II do not react with carbon monoxide at atmospheric pressure and room temperature. On the other hand a reaction was observed

with the hydroperoxo complexes III and IV (eqn. (11))



Ar = C_6H_5 (III), $\text{C}_6\text{H}_4\text{Me-}p$ (IV)

The products are ArOH, the carbonato complex IX, presumably formed via the intermediate formation of E (a reaction which corresponds to the oxidation of CO to CO_2 by the starting hydroperoxo complex) and a zerovalent carbonyl complex, *cis*- $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$, probably formed via the intermediate formation of an hydrido—alkoxide, unstable under the carbon monoxide atmosphere. In reaction (11) carbon dioxide is formed in about half the molar amount of the starting hydroperoxo complex. Indirect evidence for the intermediate formation of the metallorganic carboxylic acid F [2] has been obtained by conducting reaction (11) in methanol. In this solvent complex IX is not formed, while a material was obtained showing $\nu(\text{C=O}) = 1630$, $\nu(\text{C—O}) = 1025 \text{ cm}^{-1}$ and $\delta(\text{CH}_3) = 7.39$, which are typical absorptions of a carbomethoxy group bound to platinum [9].

IR and ^{17}O NMR Spectra

The complexes $\text{Pt}(\text{PPh}_3)_2\text{O}_2^*$ (XII)*, $\text{Pt}[\text{O}_2^*\text{C}(\text{O})\text{O}](\text{PPh}_3)_2$ (VII)* and $\text{Pt}[\text{O}^*\text{C}(\text{O})\text{O}^*](\text{PPh}_3)_2$ (IX) have been prepared by using labelled dioxygen, with the following composition (from the mass spectrum): $^{16}\text{O}_2$ (14.6%), $^{16}\text{O}-^{17}\text{O}$ (3.6%), $^{16}\text{O}-^{18}\text{O} + ^{17}\text{O}-^{17}\text{O}$ (23.1%), $^{17}\text{O}-^{18}\text{O}$ (21.4%) and $^{18}\text{O}_2$ (37.1%).

Compound XII* shows in its IR spectrum in the $780\text{--}830 \text{ cm}^{-1}$ region a series of absorptions which can be assigned to the vibration of the peroxo group as reported in Table 1, assuming a simple diatomic harmonic oscillator, with reference to $\nu(^{18}\text{O}-^{18}\text{O}) =$

TABLE 1. Infrared absorptions (cm^{-1} , nujol) involving oxygen motion^a

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})_{\text{asym}}$	$\nu(\text{C}-\text{O})_{\text{sym}}$	π	$\nu(\text{O}-\text{O})$
$\text{Pt}[\text{O}_2\text{C}(\text{O})\text{O}](\text{PPh}_3)_2$ (VII) ^b	1680	1248	980	840	780
$\text{Pt}[\text{O}_2^*\text{C}(\text{O})\text{O}](\text{PPh}_3)_2$ (VII)	1680	1248	981 971–965	845	780
$\text{Pt}[\text{OC}(\text{O})\text{O}](\text{PPh}_3)_2$ (IX) ^b	1685	1185	980	815	
$\text{Pt}[\text{O}^*\text{C}(\text{O})\text{O}^*](\text{PPh}_3)_2$ (IX)	1680	1180	975	825 812–801 790–778	
	$\nu(\text{O}-\text{O})$				
	$^{16}\text{O}-^{16}\text{O}$	$^{16}\text{O}-^{17}\text{O}$	$^{16}\text{O}-^{18}\text{O}$ $^{17}\text{O}-^{17}\text{O}$	$^{17}\text{O}-^{18}\text{O}$	$^{18}\text{O}-^{18}\text{O}$
$\text{Pt}(\text{PPh}_3)_2\text{O}_2$ (XII) ^b	825				
$\text{Pt}(\text{PPh}_3)_2\text{O}_2^*$ (XII)*	827.5 (829.6)	815.9 (817.4)	805.3 (806.2–804.9)	792.8 (793.6)	782.2

^aValues in parentheses are calculated assuming a simple diatomic harmonic oscillator, with reference to $\nu(^{18}\text{O}-^{18}\text{O}) = 782.2 \text{ cm}^{-1}$ for $\text{Pt}(\text{PPh}_3)_2\text{O}_2$.

^bData taken from ref. 3 and compared with those of samples prepared in the present work.

782.2 cm^{-1} . This absorption is in agreement with the value reported by Collman *et al.* [10] and more close to the one observed by Brill [11], who has conducted some IR studies by using oxygen-18.

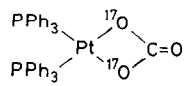
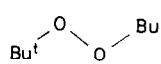
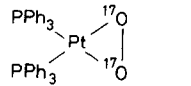
The labelled peroxocarbonato complex VII*, showed $\nu(\text{O}-\text{O})$ at 780 cm^{-1} (Table 1), practically coincident with the absorption of the ^{16}O analogue. The π deformation [3] is shifted to higher frequencies, while $\nu(\text{C}-\text{O})_{\text{asym}}$ is again insensitive to the presence of a mixture of labelled peroxo groups. On the other hand the $\nu(\text{C}-\text{O})_{\text{sym}}$ splits into a triplet, with the two absorptions at 971 and 965 cm^{-1} attributable to the presence of $\text{C}-^{17}\text{O}$ and $\text{C}-^{18}\text{O}$ groups, respectively in the molecule.

In the carbonato complex IX*, $\nu(\text{C}-\text{O})_{\text{asym}}$ and $\nu(\text{C}-\text{O})_{\text{sym}}$ both shift slightly to lower frequencies with respect to IX. The deformation splits into five absorptions, which are difficult to assign.

The ^{17}O NMR spectra of compounds VII*, IX* and XII* have been recorded. The carbonato complex IX* showed a signal at δ 137 (Table 2), while so far we have been unable to detect ^{17}O NMR signals for the peroxocarbonato complex VII*. On the other hand for the peroxo complex XII* we could record a broad ^{17}O signal at δ 451, having a linewidth at half height of 6990 Hz, in agreement with the ^{17}O NMR spectrum of XII* recently reported having a linewidth at half height of 5000 Hz [12]. However in these spectra a signal due to $\text{Ph}_3\text{P}=\text{O}$ at δ 50 was always detected together with the ^{17}O resonance of the peroxo complex.

Comparing the ^{17}O chemical shifts of the compounds reported here with those of other 'side-on' peroxometals [13] (Table 2), one might be tempted

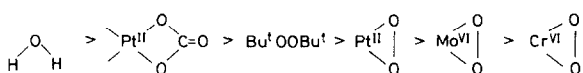
TABLE 2. ^{17}O NMR (27.12 MHz) chemical shifts and linewidth for carbonato and peroxo derivatives

Compound	δ ^a	$(\Delta_{1/2})$ ^b	Solvent	Reference
	137	(750)	CH_2Cl_2	this work
	267	(560)	CHCl_3	13
	451	(6990)	CH_2Cl_2	this work
$\text{MoO}(\text{O}_2)_2(\text{HMPA})$	468	(2000)	CHCl_3	13
$\text{CrO}(\text{O}_2)_2(\text{HMPA})$	770 818	(890) (870)	CHCl_3	13

^aChemical shifts (ppm) are referred to external deionized water at 25°C .

^bLinewidths at half-height.

to suggest that the electron density at peroxidic oxygen decreases in the order



This seems to indicate that a peroxide moiety bound to a metal in a relatively low oxidation state (platinum(II)) is more electron-rich and thus more nucleophilic than a peroxidic group bound to a metal in a high oxidation state such as chromium(VI) and, to a lesser extent, molybdenum(VI). This seems in

agreement with what is known concerning the reactivity of these complexes towards, for example, unsaturated hydrocarbons [14]. In fact, while $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ reacts readily only with alkenes bearing electron-withdrawing groups, the molybdenum peroxo complex transfers one oxygen atom to unsubstituted alkenes.

Experimental

Unless otherwise stated, all reactions and manipulations were carried out under dinitrogen, with magnetic stirring. Solvents were dried, purified and stored under dinitrogen. The starting complexes, $\text{Pt}(\text{PPh}_3)_2\text{O}_2$, $\text{Pt}[\text{O}_2\text{C}(\text{O})\text{O}](\text{PPh}_3)_2$ and $\text{Pt}[\text{O}_2\text{CMe}_2\text{O}](\text{PPh}_3)_2$ were prepared by the methods reported in the literature [3]. The hydroperoxo and hydroxo complexes were prepared as previously described [1].

Infrared spectra were recorded on Beckman 4210 and on Nicolet MX-1 FT spectrophotometers. ^1H and ^{31}P NMR spectra were recorded on Bruker VP-80 or Bruker AC-200 spectrometers with TMS as internal standard. ^{17}O NMR spectra were recorded on a Varian XL-200 instrument, equipped with a 16 mm probe, at 27.12 MHz. The S2PUL sequence was used in all cases and typical operating conditions were: spectral width 50 000 Hz, acquisition time 0.02 s, 90° r.f. pulse, number of transitions 615 000. The pre-acquisition delay was kept at 20 μs and left-shift of the FID was performed to reduce pulse-breakthrough effects. Chemical shifts are referred to H_2^{17}O as external standard. Concentration: 0.02 M in CH_2Cl_2 .

Synthesis of the Complexes

$\text{Pt}(\text{PPh}_3)_2(\text{OOH})(\text{OC}_6\text{H}_4\text{Me-}p)(\text{IV})$

To a solution of $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ (601 mg, 0.80 mmol) in benzene (24 ml), *p*- $\text{MeC}_6\text{H}_4\text{OH}$ (86.2 mg, 0.80 mmol) was added. The yellow suspension was left at room temperature for 0.5 h, then it was cooled to 5°C and stirred for 5 h. The insoluble yellow product was filtered off, washed with benzene and dried *in vacuo* giving a 46% yield. The product was stored under nitrogen. Melting point (m.p.) = 134°C . Non-conductor in PhNO_2 . *Anal.* Found: C, 59.7; H, 4.3. Calc. for $\text{C}_{43}\text{H}_{38}\text{O}_3\text{P}_2\text{Pt}$: C, 60.1; H, 4.4%. IR (cm^{-1} , nujol): 3565, $\nu(\text{OOH})$; 1270, $\nu(\text{C}-\text{O})$; 827, $\nu(\text{O}-\text{O})$. ^1H NMR (δ , CDCl_3 , under nitrogen): 2.16 (3 H, s, CH_3); 6.75 (1 H, d, $J = 9.15$ Hz, C-H); 6.89 (1 H, d, $J = 9.15$ Hz, C-H); 6.82 (1 H, s, OOH, this signal disappears on addition of D_2O). ^{31}P NMR (δ , CDCl_3 , under nitrogen): 8.48 (P_1 , dt, $J(\text{Pt}-\text{P}_1) = 3026$ Hz); 6.05 (P_2 , dt, $J(\text{Pt}-\text{P}_2) = 4487$ Hz); $J(\text{P}_1-\text{P}_2) = 20.8$ Hz. To a solution of 50 mg of compound IV in ethanol (15 ml), HCl (36%, 2 ml) and H_2SO_4 (2 N, 5 ml) were added. After the addition of

an excess of KI, the formed iodine was titrated with $\text{Na}_2\text{S}_2\text{O}_3$ 0.01 N. The titration gave 88% equivalents of the starting hydroperoxo complex.

$\text{Pt}(\text{PPh}_3)_2(\text{OH})[\text{NC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})](\text{VI})$

To a solution of $\text{Pt}(\text{PPh}_3)_2(\text{OOH})[\text{NC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})](\text{II})$ (476 mg, 0.53 mmol) in CH_2Cl_2 (85 ml), PPh_3 (883 mg, 3.37 mmol) was added. The yellow solution was stirred for 4 h and then evaporated to dryness. The residue was treated with diethyl ether (20 ml). The yellow insoluble product was filtered off and washed with diethyl ether. The crude product was crystallized from CH_2Cl_2 /diethyl ether giving the analytically pure product (73% yield). The presence of triphenylphosphine oxide was detected by thin-layer chromatography and IR spectroscopy in the residue obtained by evaporation to dryness of the diethyl ether washings. m.p. = 239°C . *Anal.* Found: C, 60.2; H, 4.0; N, 1.7. Calc. for $\text{C}_{44}\text{H}_{35}\text{NO}_3\text{P}_2\text{Pt}$: C, 59.9; H, 4.0; N, 1.6%. IR (cm^{-1} , nujol): 3480, $\nu(\text{O}-\text{H})$; 1655, $\nu(\text{C}=\text{O})$.

Reactions with Carbon Dioxide

$\text{Pt}(\text{PPh}_3)_2(\text{OOH})[\text{NC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})](\text{I})$ with CO_2

CO_2 was bubbled in $\text{C}_2\text{H}_4\text{Cl}_2$ (23 ml) for 2 min, then solid $\text{Pt}(\text{PPh}_3)_2(\text{OOH})[\text{NC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})](\text{I})$ (227 mg, 0.27 mmol) was added. The white suspension was heated at 55°C . After 0.5 h a yellow solution was obtained. It was stirred at 55°C for 4.5 h, then evaporated to a small volume and *n*-hexane was added. The white precipitate was filtered off and washed with *n*-hexane. The crude product was crystallized from CH_2Cl_2 /diethyl ether giving the white product $\text{Pt}[\text{O}_2\text{C}(\text{O})\text{O}](\text{PPh}_3)_2$ (VII), m.p. = 165°C , 68% yield. To the mother liquors, evaporated to a small volume, CH_2Cl_2 and diethyl ether were added, obtaining a pale brown precipitate of $\text{Pt}(\text{PPh}_3)_2[\text{NC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})]_2(\text{XI})$ (16% yield).

$\text{Pt}(\text{PPh}_3)_2(\text{OOH})(\text{OC}_6\text{H}_5)(\text{III})$ with CO_2

CO_2 was bubbled in benzene (25 ml) for 2 min, then solid $\text{Pt}(\text{PPh}_3)_2(\text{OOH})(\text{OC}_6\text{H}_5)(\text{III})$ (202 mg, 0.24 mmol) was added. The yellow suspension was heated at 50°C for 6 h, then it was stirred at room temperature for 18 h. The white insoluble product $\text{Pt}[\text{OC}(\text{O})\text{O}](\text{PPh}_3)_2$ (IX) was filtered off, washed with benzene and dried *in vacuo* (86% yield). It was identified by comparison with an authentic sample [8]. The mother liquors, evaporated to dryness, gave a mixture of PhOH and PPh_3O (IR, ^1H NMR and thin-layer chromatography evidences).

$\text{Pt}(\text{PPh}_3)_2(\text{OOH})(\text{OC}_6\text{H}_4\text{Me-}p)(\text{IV})$ with CO_2

CO_2 was bubbled in benzene (13 ml) for 2 min, then solid $\text{Pt}(\text{PPh}_3)_2(\text{OOH})(\text{OC}_6\text{H}_4\text{Me-}p)(\text{IV})$ (100.7 mg, 0.12 mmol) was added. The yellow suspension

was heated at 50 °C for 6 h. The white insoluble product $\text{Pt}[\text{OC}(\text{O})\text{O}](\text{PPh}_3)_2$ was obtained [8] (83% yield). The yellow mother liquors were evaporated to dryness, giving a mixture of *p*-MeC₆H₄OH and PPh₃O (IR, ¹H NMR and thin-layer chromatography evidences).

Pt(PPh₃)₂(OH)[NC(O)CH₂CH₂C(O)] (V) with CO₂

CO₂ was bubbled in C₂H₄Cl₂ (14 ml) for 2 min, then solid $\text{Pt}(\text{PPh}_3)_2(\text{OH})[\text{NC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})]$ (V) (140.4 mg, 0.17 mmol) was added. The yellow solution was heated at 55 °C and stirred for 7 h. The yellow solution was evaporated to a small volume; by adding n-hexane, the white compound $\text{Pt}[\text{OC}(\text{O})\text{O}](\text{PPh}_3)_2$ [8] (66% yield) was obtained. In the mother liquors, evaporated to dryness, succinimide was detected by IR and ¹H NMR spectroscopy ($\delta(\text{CH}_2) = 2.76$ ppm in CDCl₃).

Reactions with CO

Pt(PPh₃)₂(OOH)(OC₆H₅) (III) with CO

CO was bubbled in CH₂Cl₂ (15 ml) for 2 min then solid $\text{Pt}(\text{PPh}_3)_2(\text{OOH})(\text{OC}_6\text{H}_5)$ (III) (200.4 mg, 0.24 mmol) was added. A yellow solution was immediately formed. The reaction was followed by IR spectroscopy, evidencing the formation of two strong bands at 1970 and 1940 cm⁻¹, attributable to $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$ [15] and the strong band at 1670 cm⁻¹ of $\text{Pt}[\text{OC}(\text{O})\text{O}](\text{PPh}_3)_2$. The solution was stirred for 4 h, then evaporated to a small volume. By adding n-hexane a light pink precipitate was obtained. The crude product, washed with benzene, gave the white product $\text{Pt}[\text{OC}(\text{O})\text{O}](\text{PPh}_3)_2$ (65% yield) [8]. The CO₂ evolved was bubbled into a solution of Ba(OH)₂. The weight of the collected BaCO₃ was 25.8 mg (0.11 mmol). In the mother liquor the presence of PhOH and of PPh₃O was detected by thin-layer chromatography.

*Pt(PPh₃)₂(OOH)(OC₆H₄Me-*p*) (IV) with CO*

CO was bubbled in CH₂Cl₂ (15 ml) for 2 min, then solid $\text{Pt}(\text{PPh}_3)_2(\text{OOH})(\text{OC}_6\text{H}_4\text{Me-}p)$ (IV) (98 mg, 0.11 mmol) was added. An orange solution was formed. The reaction was followed by IR spectroscopy. After 2 h it was possible to detect two strong bands at 1970 and 1940 cm⁻¹, attributable to $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$ [15] and the strong band at 1670 cm⁻¹ of $\text{Pt}[\text{OC}(\text{O})\text{O}](\text{PPh}_3)_2$. The orange solution was stirred for 6 h and then evaporated to a small volume. By adding n-hexane a light pink precipitate was obtained. This crude material, washed with benzene, gave the white complex $\text{Pt}[\text{OC}(\text{O})\text{O}](\text{PPh}_3)_2$ (61% yield). The mother liquor showed the presence of *p*-MeC₆H₄OH and PPh₃O (IR and thin-layer chromatography evidences).

Reactions of $\text{Pt}[\text{O}_2\text{C}(\text{O})\text{O}](\text{PPh}_3)_2$ (VII) with HX
(X = $\text{NC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})$, $\text{NC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})$)

With $\text{HNC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})$

CO₂ was bubbled in C₂H₄Cl₂ (25 ml) for 2 min. $\text{Pt}[\text{O}_2\text{C}(\text{O})\text{O}](\text{PPh}_3)_2$ (VII) (249 mg, 0.31 mmol) and $\text{HNC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})$ (68 mg, 0.70 mmol) were added. The yellow solution was stirred at 55 °C for 5 h, then it was evaporated to a small volume. By adding n-hexane a pale brown precipitate was obtained. It was crystallized from CH₂Cl₂/n-hexane giving the white complex $\text{Pt}(\text{PPh}_3)_2[\text{NC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})]_2$ (75% yield). The complex was identified by comparison with an authentic sample [1]. The same product was obtained conducting the reaction under a dinitrogen atmosphere.

With $\text{HNC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})$

CO₂ was bubbled in C₂H₄Cl₂ (20 ml) for 2 min. $\text{Pt}[\text{O}_2\text{C}(\text{O})\text{O}](\text{PPh}_3)_2$ (VII) (200 mg, 0.25 mmol) and $\text{HNC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})$ (37.3 mg, 0.25 mmol) were added. The light yellow solution was heated at 55 °C for 2 h obtaining the white precipitate $\text{Pt}(\text{PPh}_3)_2[\text{NC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})]_2$ (75% yield). The nature of this complex is being investigated by X-ray crystallography (see text). The same product was obtained conducting the reaction under a dinitrogen atmosphere.

Reactions of $\text{Pt}[\text{O}_2\text{CMe}_2\text{O}](\text{PPh}_3)_2$ (VIII)

With $\text{HNC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})$

Solid $\text{Pt}[\text{O}_2\text{CMe}_2\text{O}](\text{PPh}_3)_2$ (VIII) (60.2 mg, 0.074 mmol) and $\text{HNC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})$ (10.9 mg, 0.074 mmol) were added to CH₂Cl₂ (6 ml). The colourless solution was stirred for 24 h. The reaction was followed by IR spectroscopy evidencing the formation of free acetone. After 1 h, half volume of this solution was withdrawn and evaporated to dryness *in vacuo*. The obtained white solid was identified as $\text{Pt}(\text{PPh}_3)_2(\text{OOH})[\text{NC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})]$ (II) (37% yield) by comparison with an authentic sample (IR evidence) [1]. At the end of the reaction the remaining pale yellow solution was evaporated to dryness *in vacuo*. A light yellow residue was obtained, consisting of the main product $\text{Pt}(\text{PPh}_3)_2[\text{NC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})]_2$ [1], contaminated by some $\text{Pt}(\text{PPh}_3)_2(\text{OOH})[\text{NC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})]$ and some unreacted starting complex.

With CH₃COOH

To a solution of $\text{Pt}[\text{O}_2\text{CMe}_2\text{O}](\text{PPh}_3)_2$ (VIII) (156 mg, 0.193 mmol) in CH₂Cl₂ (15 ml), CH₃COOH (23.1 mg, 22.05 μl, 0.385 mmol) was added by a microsyringe. The reaction was followed by IR spectroscopy. The complete and immediate formation of $\text{Pt}(\text{PPh}_3)_2(\text{CH}_3\text{COO})_2$ was evidenced by the presence of the new IR stretching at 1628 cm⁻¹ ($\nu(\text{COO})$ of the coordinated acetate group) and the disappearance

of the IR stretching at 968 cm^{-1} ($\nu(\text{C}=\text{O})_{\text{sym}}$) of the starting complex. A strong band was also present at 1714 cm^{-1} . It could be assigned to the $\nu(\text{C}=\text{O})$ of CH_3COCH_3 or of the dimeric form of CH_3COOH . However, by treatment of part of this solution with NEt_3 , only a small decrease in the intensity of this band was observed, confirming that it is due mostly to acetone. The pale yellow solution was evaporated to dryness *in vacuo*, giving a pale yellow solid (88% yield) identified as $\text{Pt}(\text{PPh}_3)_2(\text{CH}_3\text{COO})_2$ by comparison of its IR spectrum in nujol with that reported in the literature [8].

Synthesis of the Oxygen-labelled Complexes

$\text{Pt}(\text{PPh}_3)_2\text{O}_2^* (\text{XII})^*$

A 50 ml flask containing benzene (16 ml) was cooled with dry ice/acetone and evacuated (0.1 mmHg); then the temperature was raised to 20°C and dinitrogen was admitted. This procedure was repeated three times. Solid $\text{Pt}(\text{PPh}_3)_3$ (422 mg, 0.43 mmol) was added to the cooled benzene under a dinitrogen atmosphere. The flask was then evacuated and filled with labelled dioxygen [composition from the mass spectrum: $^{16}\text{O}_2$ (14.6%), $^{16}\text{O}-^{17}\text{O}$ (3.6%), $^{16}\text{O}-^{18}\text{O} + ^{17}\text{O}-^{17}\text{O}$ (23.1%), $^{17}\text{O}-^{18}\text{O}$ (21.4%), $^{18}\text{O}_2$ (37.1%) Cambridge Isotope Laboratories], by a gas burette. The temperature was then allowed to rise to 20°C . The yellow solution was reacted under a labelled dioxygen atmosphere for 0.5 h; a pale yellow suspension was obtained. This suspension was cooled with dry ice/acetone; the labelled dioxygen in excess was recovered and the temperature was allowed to rise to 20°C . The white precipitate was filtered off under dinitrogen and washed with n-hexane degassed with dinitrogen (45% yield). The product was stored under dinitrogen.

$\text{Pt}[\text{O}_2^*\text{C}(\text{O})\text{O}]/(\text{PPh}_3)_2 (\text{VII})^*$

CO_2 was bubbled for 5 min in benzene (12 ml), then solid $\text{Pt}(\text{PPh}_3)_2\text{O}_2^* (\text{XII})^*$ (150 mg, 0.20 mmol) was added. The white suspension was reacted for 1 h.

The white precipitate was filtered off under dinitrogen, washed with benzene degassed with dinitrogen and dried *in vacuo*, m.p. = 151°C , 37% yield. The product was stored under dinitrogen.

$\text{Pt}[\text{O}^*\text{C}(\text{O})\text{O}]/(\text{PPh}_3)_2 (\text{IX})^*$

CO was bubbled for 5 min in benzene (5 ml), then solid $\text{Pt}(\text{PPh}_3)_2\text{O}_2^* (\text{XII})^*$ was added. The pink suspension was reacted at 15°C for 2 h. The white precipitate was filtered off under dinitrogen, m.p. = 186°C , 40% yield. The product was stored under dinitrogen.

References

- 1 S. Cenini, F. Porta and M. Pizzotti, *J. Organomet. Chem.*, **296** (1985) 291.
- 2 H. E. Bryndza and W. Tam, *Chem. Rev.*, **88** (1988) 1163, and refs. therein.
- 3 P. J. Hayward, D. M. Blake, G. Wilkinson and C. J. Nyman, *J. Am. Chem. Soc.*, **92** (1970) 5873.
- 4 F. Demartin, personal communication.
- 5 A. Behr, *Angew. Chem., Int. Ed. Engl.*, **27** (1988) 661.
- 6 R. Ugo, F. Conti, S. Cenini, R. Mason and G. B. Robertson, *J. Chem. Soc., Chem. Commun.*, (1968) 1498.
- 7 G. La Monica, M. A. Angaroni, F. Cariatì and S. Cenini, *Inorg. Chim. Acta*, **143** (1988) 239, and refs. therein.
- 8 C. J. Nyman, C. E. Wymore and G. Wilkinson, *J. Chem. Soc. A*, (1968) 561.
- 9 W. Beck, W. Rieber, S. Cenini, F. Porta and G. La Monica, *J. Chem. Soc., Dalton Trans.*, (1974) 298.
- 10 R. W. Horn, E. Weissberger and J. C. Collman, *Inorg. Chem.*, **9** (1970) 367.
- 11 W. F. Brill, *J. Mol. Catal.*, **19** (1983) 69.
- 12 H. C. Lee and E. Oldfield, *J. Magn. Reson.*, **69** (1986) 367.
- 13 (a) R. Curci, G. Fusco, O. Sciacovelli and L. Troisi, *J. Mol. Catal.*, **32** (1985) 251; (b) M. Camporeale, L. Cassidei, R. Mello, O. Sciacovelli, L. Troisi and R. Curci, in W. Ando and Y. Moro-oka (eds.), *The Role of Oxygen in Chemistry and Biochemistry*, Studies in Organic Chemistry Ser. 33, Elsevier, Amsterdam, 1988, p. 201.
- 14 H. Mimoun, *Angew. Chem., Int. Ed. Engl.*, **21** (1982) 734.
- 15 (a) F. Cariatì and R. Ugo, *Chim. Ind.*, **48** (1966) 1288; (b) P. Chini and G. Longoni, *J. Chem. Soc. A*, (1970) 1542.