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REACTIONS OF AMINES AND RELATED SPECIES WITH TRANSITION METAL PEROXO COMPLEXES *

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Summary

The reactions of amines and related species with molecular oxygen bound to a transition metal centre, are reviewed briefly. New results on the reactions of $Pt(PPh_3)_2O_2$ with amine derivatives such as formanilides and imides are reported; from these reactions new amidohydroperoxoplatinum(II) complexes have been isolated. The related reaction of $Pt(PPh_3)_2O_2$ with phenol is also described. A general mechanism for these deprotonation reactions is discussed.

Introduction

Studies on the reactivity of molecular oxygen bound to a transition metal centre continue to increase [1]. Because of our interest in the chemistry of the metal–nitrogen bond [2], we have studied the reactions of amines and related derivatives with transition metal complexes containing dioxygen as a ligand. We have looked at three types of reaction: (i) those of amines with peroxo-like complexes (η^2-dioxygen); (ii) those of amines with superoxo-like complexes (η^1-dioxygen); and (iii) those of amines bound to a metal centre.

The reactivity of peroxo-like complexes has been extensively investigated because of their importance in the field of catalyzed oxidations; peroxo-like means that molecular oxygen is formally bound as the O_2^{2-} peroxo species, but this represents an extreme situation, and there can be a variable amount of charge delocalized from the metal to the ligand depending on the nature and the oxidation state of the metal centre and on the nature of the ancillary ligands. Below we briefly survey the reactions of amines and related derivatives with transition metal peroxo complexes carried out by our research group and present the results of some new studies of the

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* Dedicated to Professor Lamberto Malatesta in recognition of his important contributions to organometallic chemistry.

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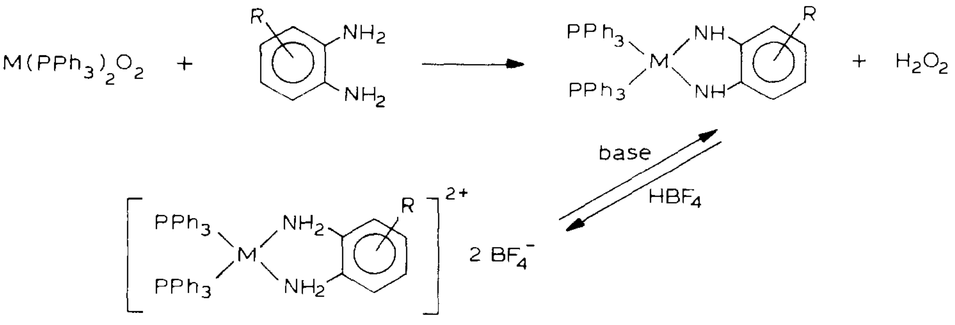


(M = Pd, Pt)

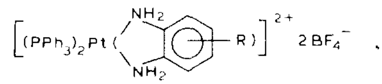
SCHEME 1

reactions of $Pt(PPh_3)_2O_2$ with amine derivatives such as formanilides and imides, and the related reaction involving phenol. Researches related to reactions of type (ii) [3] and (iii) [4] are still in progress in our laboratories.

Results

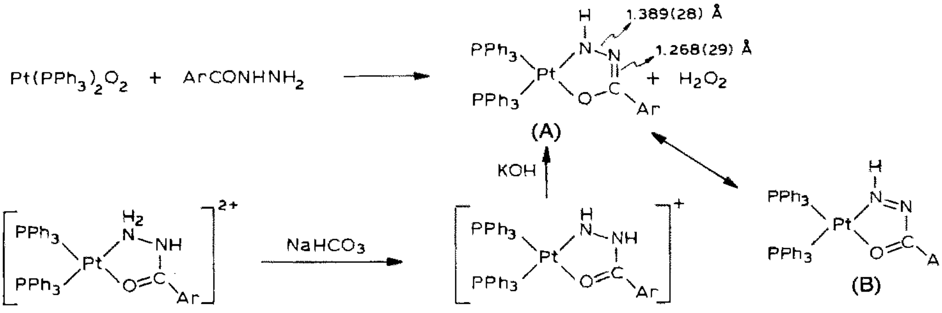
Survey of the previously studied reactions

The palladium and platinum peroxo complexes, $M(PPh_3)_2O_2$ (M = Pd, Pt) readily react with *ortho*-phenylenediamines to give deeply coloured diamido derivatives and hydrogen peroxide [5] (Scheme 1).

In these derivatives the ligand can be mainly regarded as the bis-anion of the starting amine on the basis of spectroscopic data. Thus this reaction can be classified as a deprotonation reaction of the amine by the bound peroxo group. Since other coordinatively saturated peroxo complexes such as $Ru(CO)_2(PPh_3)_2O_2$, $[Rh(PPh_3)_2Cl(O_2)]_2$, $IrCl(CO)(PPh_3)_2O_2$ and $[Ir(Ph_2PCH_2CH_2PPh_2)_2O_2]^+$ do not react with these amines under mild conditions, it is probable that prior coordination of the amine to the metal centre is necessary. Once bonded to the metal the amine becomes similar to an ammonium salt and should more readily transfer a proton to the bound peroxo group. This is indirectly supported by the fact that when bound to platinum in the cationic complex , the amine can be readily deprotonated by a base to give the same diamido complex (Scheme 1).

This deprotonation reaction is rather general, and can be extended to other organic species which readily lose two protons to form chelating ligands [6] (Scheme 2).

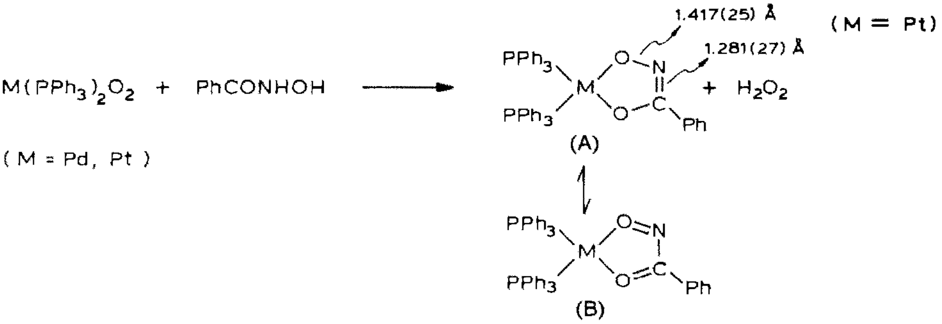
With aroylhydrazines, complexes which can be considered as aroylhydrazidoplatinum(II) derivatives (**A**) or platinum(0) derivatives having the aroyldiazene as ligand (**B**), are formed, together with hydrogen peroxide (Scheme 2). The X-ray structural characterization of one of these derivatives suggests that although the $>$C=N bond distance in the metallocycle is consistent with double bond character, some contribution from form (**B**) must be taken into account since the N–N bond



SCHEME 2

distance is shorter than that in hydrazine (1.453(5) Å). The aroyldiazene, an unstable molecule in the free state, is thus stabilized by coordination to platinum mainly as its bis-anion, although the electron transfer from the metal is incomplete, as is the case in the initial peroxo complex. A species such as an aroylhydrazine can be deprotonated by a base when bound to the metal centre (Scheme 2). With a weak base only one proton is displaced, and this is presumably one of those from bound $-NH_2$ group. With stronger bases even the second proton can be displaced, giving the same product as was obtained in the reaction considered earlier. Other reagents which readily react with the palladium and platinum peroxo complexes are the hydroxylamines (Scheme 3).

With benzoylhydroxylamine, the product can be considered as an aroylhydroxylamidoplatinum(II) complex (**A**), or a zerovalent complex containing *C*-nitrosocarbonylbenzene as ligand (**B**). Again the X-ray structural characterization indicates that although the >C=N-bond distance is consistent with a double bond, the N–O distance is shorter than that in hydroxylamine (1.47(3) Å), suggesting some contribution from form (**B**) to the bonding between the metal and the organic ligand. It is of interest to note that the *C*-nitrosoaroyl intermediates have been postulated as transient species in the oxidative cleavage of phenylhydroxamic acids (or aroylhydroxylamines), and they have been involved in an organic reaction with an appropriate reagent such as a conjugated diene. The reaction shown in Scheme 3 confirms the suggestion that in these oxidations the *C*-nitrosocarbonylbenzene derivative is formed as intermediate and this reaction resembles an organic reaction.



SCHEME 3

Account should be taken of the fact that both oxidant (molecular oxygen) and a trapping agent (a metal) should be present. In our case in the starting complex, the bound O_2 acts as the oxidant. Of the various compounds, which can be deprotonated by the peroxo-platinum complex, phenylhydroxylamine deserves particular attention (Scheme 4):

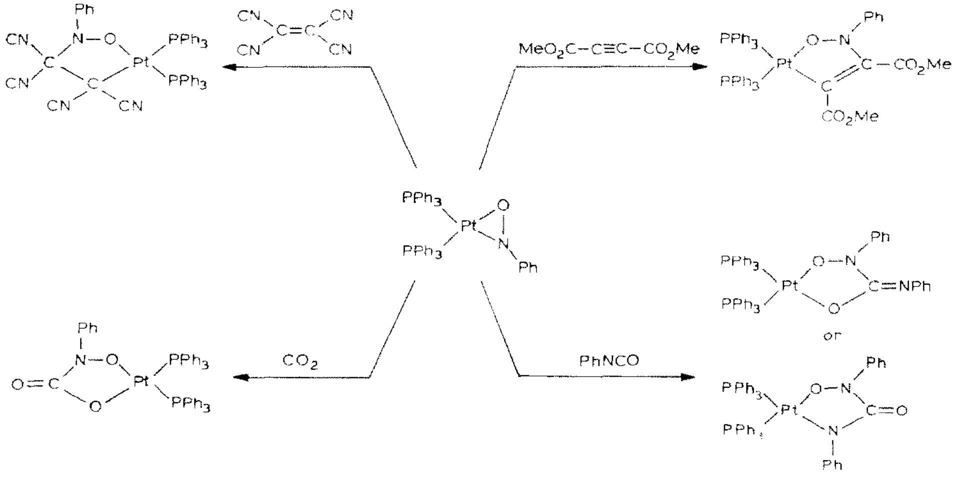
SCHEME 4

The η^2-bonded nitroso ligand was formed in the reaction. In the product the PhNO ligand, which is isoeletronic with dioxygen, can thus be mainly considered as a bis-ionic species bonded to a metal(II) centre.

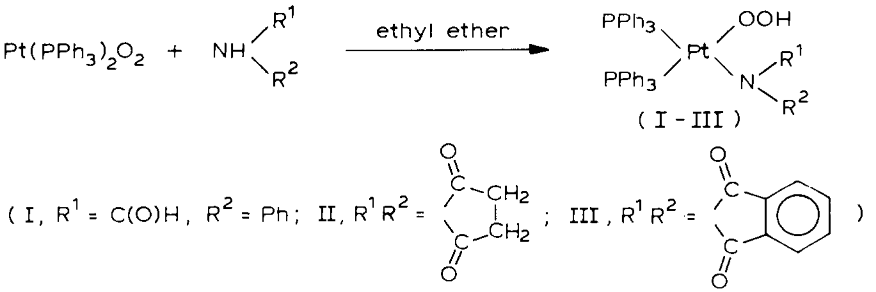
Similar reactions have been reported for a peroxo complex of a metal in a high oxidation state such as molybdenum(VI) [7]. However, in this case the peroxo group is first reduced to an oxo ligand by the hydroxylamine, and then a second molecule of the hydroxylamine gives the η^2-bonded nitroso ligand and water by reaction with the M=O fragment. This emphasizes the difference in reactivity between peroxo complexes of metals in low and high oxidation states. With a low oxidation state, the poor oxophilic character of the metal precludes the formation of a oxo-metal derivative. This means that, in general, while a peroxo complex of a metal in a high oxidation state can transfer only one oxygen atom to the entering molecule, a peroxo complex of a metal in a low oxidation state prefers a substrate which can displace both oxygen atoms of the peroxo group.

As we already pointed out, the PhNO molecule is isoelectronic with dioxygen, and in the $Pt(PPh_3)_2(PhNO)$ derivative it behaves like a peroxo group with respect to unsaturated molecules [8,9,10]. Some complexes are depicted in Scheme 5.

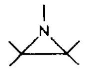
In these reactions the nucleophilic centre in the starting complex, namely nitrogen, attacks the electrophilic carbon atom of the entering molecule to give metallocyclic derivatives. The derivatives obtained with alkenes are model compounds for



SCHEME 5



SCHEME 6

the intermediates which lead to aziridines,  , and oxo-metal derivatives [11], a reaction which corresponds to the epoxidation of alkenes by peroxo transition metal complexes. These results confirm the importance of metallocyclic derivatives in the transfer of ligands or atoms to organic substrates.

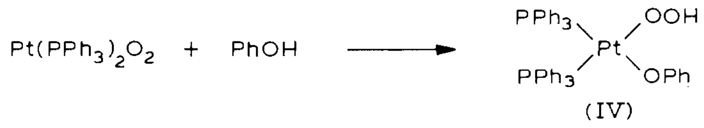
Reactions of $Pt(PPh_3)_2O_2$ with formanilides and imides

The reactions of peroxo transition metal complexes with aliphatic and aromatic monoamines did not lead to readily characterizable isolable products, although there was clearly a reaction. Even ammonia reacts with $Pt(PPh_3)_2O_2$, but we could not identify the product. This is an interesting reaction since ammonia is known to be oxidized to nitric oxide by molecular oxygen with platinum metal as catalyst. However in some cases we were able to isolate products, which can be considered as model compounds for the intermediates which are formed in these deprotonation reactions of amine derivatives by peroxo transition metal complexes. Thus from the reaction of $Pt(PPh_3)_2O_2$ with formanilide, succinimide, or phthalimide in a suspension of ethyl ether, one to one adducts were isolated (Scheme 6) (Tables 1 and 2).

Complexes I–III are formed even when an excess of the organic reactant is used and I–III are formulated as hydroperoxoamido complexes of platinum(II) on the basis of spectroscopic and analytical data. In particular an IR absorption at ca. 3500–3400 cm^{-1} was assigned to the vibration of the hydroperoxo group. However for compound I the alternative formulation as $Pt\{OCH(NPh)\}(OOH)(PPh_3)_2$ cannot be excluded. A similar reaction was observed with phenol, giving raise to $Pt(OPh)(OOH)(PPh_3)_2$ (IV) (Scheme 7) (Tables 1 and 2).

The reaction in Scheme 7 when carried out with *ortho*-$(HO)_2C_6H_4$ instead of phenol gives an *ortho*-diphenolplatinum(II) derivative and hydrogen peroxide [5]. Similar reactions carried out with a series of glycols again gave hydrogen peroxide, but no well characterizable platinum derivatives could be isolated.

The presence of a hydroperoxo group in compounds II, III and IV was confirmed



SCHEME 7

TABLE 1
PHYSICAL AND ANALYTICAL DATA

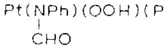
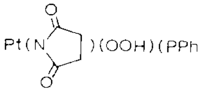
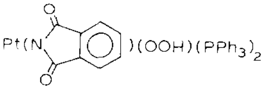
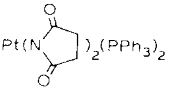
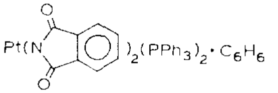
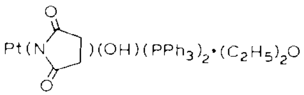
Compound		Colour	M.p. (°C)	Analyses(Found (calcd.)(%))			
				C	H	N	O
(I)	 $\mathrm{Pt(\underset{CHO}{NPh})(OOH)(PPh_3)_2}$	white	150	59.2 (59.2)	4.2 (4.2)	1.6 (1.6)	5.9 (5.5)
(II)		white	190	56.6 (56.5)	4.2 (4.1)	1.6 (1.6)	–
(III)		white	162	58.7 (58.8)	3.9 (3.9)	1.6 (1.6)	–
(IV)	$\mathrm{Pt(OPh)(OOH)(PPh_3)_2}$	light-green	143	60.2 (59.6)	4.3 (4.3)	–	5.4 (5.7)
(V)		white	250	57.3 (57.7)	4.3 (4.2)	3.0 (3.0)	–
(VI)		white	177	64.0 (63.9)	4.3 (4.1)	2.5 (2.6)	–
(VII)		white	236	58.2 (58.2)	4.7 (4.9)	1.4 (1.5)	–

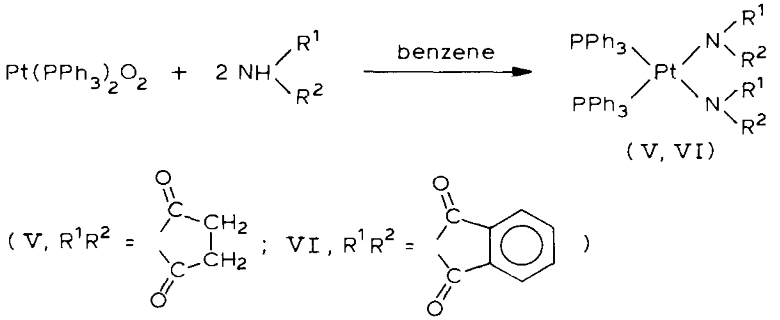
TABLE 2
IR ($\mathrm{cm^{-1}}$, IN NUJOL), ^{1}H AND ^{31}P [a] NMR DATA (δ(ppm), *J* values in Hz)

Compound	IR	NMR data						Solvent
		δ(OOH) [b]	δ(P^1)	δ(P^2)	*J*(P^1–P^2)	*J*(Pt–P^1)	*J*(Pt–P^2)	
I	ν(OOH) 3495.3(w) ν(CO) 1613(s)–1579(s)	6.69 [c]	9.18 [d]	12.87	19.8	3336.6	3541	$CDCl_3$
II	ν(OOH) 3315.9(w) ν(CO) 1625(s)	6.88 [e]	9.10	10.50	15.1	3179	3557.7	CD_2Cl_2
III	ν(OOH) 3378.6(w) ν(CO) 1658(s)	6.73	9.40	11.70	19.8	3184.7	3564.5	CD_2Cl_2
IV	ν(OOH) 3574(w)	6.90	6.55	9.44	21.37	3019.25	4491.45	CD_2Cl_2
V	ν(CO) 1645(s)	[e]	1.35	–	–	3344.6	–	$CDCl_3$
VI	ν(CO) 1664.7(s)	–	2.70	–	–	3332.7	–	CD_2Cl_2
VII	ν(OH) 3574(w) ν(CO) 1635(s)	–	9.78	11.26	18.95	3281	3483.6	CD_2Cl_2

[a] External standard 85% H_3PO_4 in water. [b] These signals disappeared on treatment with D_2O. [c] Signals due to free HC(O)NHPh were present at δ 8.6–9.2 ppm, together with a singlet at δ 8.2 ppm, attributable to the bound HC(O)NPh ligand. [d] Signals due to $\mathrm{Pt(PPh_3)_2O_2}$, were present at δ 14.63 ppm (*J*(Pt–P) 4082.6 Hz). [e] The CH_2 groups of the succinimide ligand gave complex signals between δ 1.5 and 2.2. ppm.

by reaction with potassium iodide and titration with sodium thiosulphate of the formed iodine. The titration gave 100% equivalents in the case of compound II, and 65–70% equivalents in the other two cases. Compounds II–IV are stable in solution but the formanilide derivative I is in equilibrium with the starting peroxo complex, and can be isolated only by carrying out the reaction of Scheme 6 in ethyl ether, in which the product is insoluble. Crystallization of compound I from chloroform/n-hexane or from ethanol/n-hexane gives the peroxo platinum complex and the free amide. This equilibrium in solution is nicely confirmed by the ^{31}P NMR spectrum, which shows not only the expected AX type multiplet of I due to two non equivalent phosphorus atoms, with satellites due to coupling with ^{195}Pt (Table 2), but also a singlet with two satellites [δ(P) 14.63 ppm, J(Pt–P) 4082.6 Hz] attributable to the peroxo platinum complex.

From the relative integrals of the NMR peaks, ca. 50% of the hydroperoxo derivative must be dissociated into the starting peroxo derivative in solution. This equilibrium was confirmed by the ^{1}H NMR spectrum, in which signals from free formanilide were present together with those from complex I (Table 2). The different behaviour of I compared with II and III may be due to the fact that in I the organic ligand is bound to the metal via the oxygen and not the nitrogen atom. It should also be noted that the reaction in Scheme 6 is very sensitive to small electronic and steric changes in the organic molecule, and when $CH_3C(O)NHPh$ or $HC(O)NHC_6H_4CH_3$-*p* was used in the reactions of Scheme 6 we were unable to isolate any product. When the reaction of Scheme 6 was carried out in benzene and with an excess of the ligand, bis-amidoplatinum(II) complexes were isolated (Scheme 8) (Tables 1 and 2).



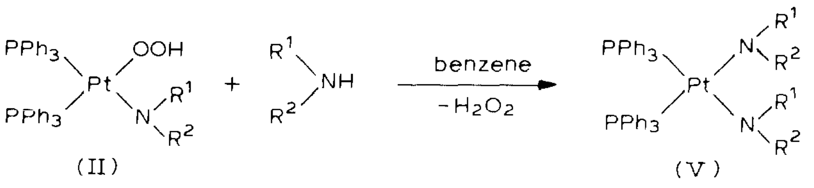
SCHEME 8

The hydroperoxoplatinum(II) complexes II and III are the probable intermediates in this reaction, since we have observed that complex V is also formed when II is treated in benzene with another molecule of the imide (Scheme 9).

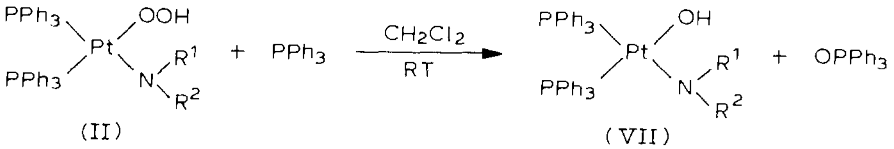
Complexes V and VI are not formed in the reaction of Scheme 6, even when an excess of the imide is used. This is probably due to the insolubility of compounds II and III in diethyl ether, the solvent used for this reaction.

Compounds II and III were treated with a reducing agent such as PPh_3, but only in the case of II was a well defined product obtained (Scheme 10) (Tables 1 and 2).

Complex VII corresponds to a hydroxoamidoplatinum(II) species. The presence of excess phosphine in the reaction of Scheme 10 and the use of more drastic



SCHEME 9



SCHEME 10

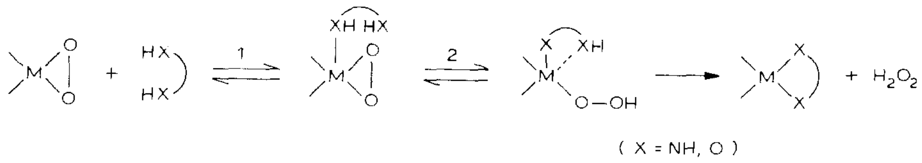
conditions (at reflux in diisopropylether) did not bring about a reductive elimination from VII to give $Pt(PPh_3)_3$ and R^1R^2NOH.

Upon treatment of compounds II and III with an alkene such as cyclooctene we did not observe transfer of the peroxo-oxygen atom to the olefin.

Conclusions

The isolation of hydroperoxoamidoplatinum(II) complexes from the reactions of $Pt(PPh_3)_2O_2$ with imides, and the reversible nature of the reaction with formanilide, enable us to propose a general mechanism for the deprotonation reactions described above (Scheme 11).

Coordination of the entering molecule to the unsaturated metal centre gives a more acidic character (if that is necessary) to the proton bound to the donor atom. A transfer of one proton to the peroxo group takes place, giving the hydroperoxo intermediate. If the entering molecule does not contain another readily deprotonated group, the equilibria 1 and 2 (Scheme 11) can be largely shifted to the left. On the other hand, if another proton can be displaced from the organic ligand, the second donor atom can again interact with the metal centre. The second proton transfer gives the final product and hydrogen peroxide. Thus the metal appears to play a fundamental role in these reactions, and the atom transfer reactions occur at the metal centre. The reactions of amines with superoxo-like complexes proceed via a different route, and the first step of the reaction appears to be the hydrogen abstraction from the amine to give an amino radical [3].



SCHEME 11

Experimental

All reactions were carried out under nitrogen, with stirring. Solvents were dried, purified, and stored under nitrogen. The starting complex $Pt(PPh_3)_2O_2$ was prepared as previously described [12]. The organic reagents were all commercial products. Infrared spectra were recorded on a Beckman 4210 and on a FT Nicolet MX-1 spectrophotometers. ^1H and ^{31}P NMR spectra were obtained on a Bruker VP-80 spectrometer under nitrogen. Elemental analyses were carried out in the analytical laboratories of Milan University, except for the oxygen analyses which were carried out by the Pascher Analytical Laboratories (Bonn).

Compound I–IV and VII were stored under nitrogen. For complexes I–III prolonged drying in vacuo was required in order to remove traces of diethyl ether, otherwise clearly evident in the ^1H NMR spectra.

$Pt(PPh_3)_2(OOH)(HCONPh)$ (I)

A mixture of $Pt(PPh_3)_2O_2$ (0.15 g) and $HC(O)NHPh$ (0.073 g) in diethyl ether (15 ml) was stirred for 3 h at room temperature. The insoluble white product was filtered off, washed repeatedly with diethyl ether, and dried in vacuo giving a 76% yield.

$Pt(PPh_3)_2(OOH)[NC(O)CH_2CH_2C(O)]$ (II)

A mixture of $Pt(PPh_3)_2O_2$ (0.226 g) and $HNC(O)CH_2CH_2C(O)$ (0.0331 g) in diethyl ether 30 ml was stirred for 2 h at room temperature. The insoluble white product was filtered off, washed with diethyl ether, and dried in vacuo giving a 75% yield.

$Pt(PPh_3)_2(OOH)[NC(O)C_6H_4C(O)$ (III)

A mixture of $Pt(PPh_3)_2O_2$ (0.322 g) and $HNC(O)C_6H_4C(O)$ (0.126 g) in diethyl ether (35 ml) was stirred for 4 h at 0°C. The white product was filtered off, washed with ethyl ether, and dried in vacuo giving a 78% yield.

$Pt(PPh_3)_2(OOH)(OPh)$ (IV)

A mixture of $Pt(PPh_3)_2O_2$ (0.287 g) and PhOH (0.058 g) in benzene (25 ml) was stirred for 4 h at room temperature. The light-green precipitate was filtered off from the yellow solution, washed with benzene, and dried in vacuo giving a 71% yield.

$Pt(PPh_3)_2[NC(O)CH_2CH_2C(O)]_2$ (V)

A mixture of $Pt(PPh_3)_2O_2$ (0.249 g) and $HNC(O)CH_2CH_2C(O)$ (0.0662 g) in benzene (20 ml) was stirred for 4 h at room temperature. The colourless solution was evaporated to a small volume, and n-hexane was added. A white compound separated and was filtered off, washed with n-hexane, and dried in vacuo giving a 46% yield. The same compound was obtained by reaction of II (0.188 g) with $HNC(O)CH_2CH_2C(O)$ (0.0252 g) in benzene (25 ml) for 8 h. Some insoluble material was filtered off from the colourless benzene solution before work-up giving a 78% yield.

$Pt(PPh_3)_2[\overline{NC(O)C_6H_4C}(O)]_2$ *(VI)*

A mixture of $Pt(PPh_3)_2O_2$ (0.194 g) and $H\overline{NC(O)C_6H_4C}(O)$ (0.0762 g) in benzene (20 ml) was stirred for 4 h at room temperature. Some insoluble material was filtered off from the colourless benzene solution. The filtrate was evaporated to a small volume. Addition of n-hexane gave a white precipitate which was filtered off, washed with n-hexane, and dried in vacuo giving a 78% yield.

$Pt(PPh_3)_2(OH)[\overline{NC(O)CH_2CH_2C}(O)]$ *(VII)*

A mixture of (II) (0.208 g) and PPh (0.514 g) in CH_2Cl_2 (25 ml) was stirred for 4 h at room temperature. The yellow solution was evaporated to dryness and the residue was treated with diethyl ether (30 ml). The pale pink insoluble product was filtered off, washed with diethyl ether, and dried in vacuo giving a 55% yield. The presence of triphenylphosphine oxide was detected by thin-layer chromatography and IR spectroscopy in the residue obtained by evaporation of the diethyl ether washings to dryness.

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