Insertion of Carbon Dioxide, of CO$_2$-like Molecules, and of Other Unsaturated Compounds into the Platinum–Nitrogen Bond of [Pt(PPh$_3$)$_2$(PhNO)]

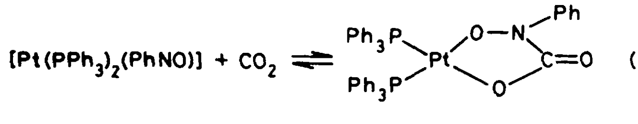
Sergio Cenini,* Francesca Porta, Maddalena Pizzotti, and Corrado Crotti
Dipartimento di Chimica Inorganica e Metallorganica and CNR Center, Via Venezian 21, 20133 Milano, Italy

The compound [Pt(PPh$_3$)$_2$(PhNO)] (**1**) reacts reversibly with carbon dioxide to give [Pt{ON(Ph)C(O)O}(PPh$_3$)$_2$] (**2**). Other CO$_2$-like molecules readily and irreversibly insert into the platinum–nitrogen bond of (**1**); with CS$_2$, PhNCO, and PhNCS the corresponding 1:1 adducts [Pt{ON(Ph)C(S)S}(PPh$_3$)$_2$] (**3**), [Pt{ON(Ph)C(NPh)O}(PPh$_3$)$_2$] (**4**), and [Pt{ON(Ph)C(NPh)S}(PPh$_3$)$_2$] (**5**), respectively have been obtained. Compound (**2**) is an isomer of the insertion product (**6**), [Pt{O$_2$C(NPh)O}(PPh$_3$)$_2$], obtained from the reaction of [Pt(PPh$_3$)$_2$(O$_2$)] with PhNCO. A labile insertion product, [Pt{ON(Ph)CH(Ph)O}(PPh$_3$)$_2$], (**7**), was obtained by reaction of (**1**) with PhCHO, while no reaction was observed between (**1**) and acetone or diethyl carbonate. However, compound (**1**) reacts with EtO$_2$C–N=N–CO$_2$Et to give the substitution product (**8**), [Pt{N(CO$_2$Et)N=C(OEt)O}(PPh$_3$)$_2$]. The reactions of compound (**2**) towards mineral acids, organic acids, benzoyl chloride, and sulphonyl chlorides have been studied. The products are identical to those obtained from the corresponding reactions of (**1**). I.r., ^{1}H, ^{31}P, and ^{195}Pt n.m.r. spectra of the new compounds are reported and discussed.

The activation of carbon dioxide by transition-metal complexes is of obvious interest in the search for alternative chemical feedstocks.[1] In addition the metal-promoted C–N bond formation is a major achievement in the field of hydrocarbon functionalisation.[2] We have previously reported on the reactivity of [Pt(PPh$_3$)$_2$(PhNO)] (**1**), having a η^2-bonded nitroso-ligand, with alkenes and alkynes.[3] From these reactions, compounds in which unsaturated hydrocarbons have been inserted into the platinum–nitrogen bond of (**1**) have been isolated. We report here on the reactivity of complex (**1**) toward carbon dioxide, CO$_2$-like molecules, and other unsaturated compounds. A preliminary report on these reactions has been published.[4]

Results and Discussion

Synthesis of the Complexes.—Compound (**1**) readily reacts with carbon dioxide in methylene chloride at room temperature and atmospheric pressure to give [equation (1)] the 1:1 adduct



(1) (1) (2)

(**2**) (Table 1). Compound (**2**) is isolated with 1 molecule of solvent of crystallisation. The insertion reaction is reversible, and by bubbling dinitrogen into a benzene suspension of (**2**), compound (**1**) and carbon dioxide are quantitatively obtained. Thus, a weak carbon–nitrogen bond in complex (**2**) is indicated. However, disorder in the crystals did not allow a satisfactory refinement of the structural parameters of this compound, although the *X*-ray data unambiguously defined its solid-state structure.[4] On the other hand we have observed that the related 1:1 adduct obtained[5] from [Pt(PPh$_3$)$_2$(O$_2$)] and CO$_2$, [Pt{O$_2$C(O)O}(PPh$_3$)$_2$], is stable in benzene suspension under a stream of dinitrogen.

I.r., ^{1}H and ^{31}P n.m.r. data for compound (**2**) are in agreement with its solid-state structure (Tables 1 and 2). It shows $\nu_{max.}$ at 1 635 cm^{-1} (C=O) as the most significant i.r. band. At 0 °C and under a carbon dioxide atmosphere, the ^{31}P n.m.r. spectrum of (**2**) in CD$_2$Cl$_2$ shows only the expected AX type multiplet with ^{195}Pt satellites. For comparison, the ^{31}P n.m.r. data for [Pt(PPh$_3$)$_2$(CO$_3$)] have also been reported in Table 2; δ(P) and *J*(Pt–P) are very close to those observed for compound (**2**). The ^{195}Pt n.m.r. spectrum of (**2**) under a carbon dioxide atmosphere shows δ(Pt) = $-4\,058$ p.p.m. (upfield from external Na$_2$PtCl$_6$) with the same coupling constants for two non-equivalent phosphorus atoms as observed in the ^{31}P n.m.r. spectrum. On the contrary at 30 °C and under a dinitrogen atmosphere, the ^{31}P n.m.r. spectrum of (**2**) also shows absorptions due to compound (**1**) (Table 2). There is clearly an equilibrium between these compounds in solution. However in chlorinated solvents, in which (**1**) and (**2**) are readily soluble, the ^{31}P n.m.r. spectra at room temperature also show the presence of *cis*-[Pt(PPh$_3$)$_2$Cl$_2$][δ(P) = 14.4 p.p.m., *J*(Pt–P) = 3 679 Hz], formed by reaction with the solvent. For this reason we could not study this equilibrium by ^{31}P n.m.r. On the other hand, compounds (**1**) and (**2**) show very similar electronic spectra in the solid state and in benzene, even under a carbon dioxide atmosphere for (**2**), and thus even in this case the equilibrium could not be studied.

Examples of reversible CO$_2$ insertion into bonds between transition metals and hydrogen, carbon, and oxygen have been reported.[1] The alkali-metal salts of [*N*,*N'*-ethylenebis(salicylideneiminato)]cobaltate ion and related species also reversibly absorb carbon dioxide to give the corresponding salts of cobalt–carboxylic acid complexes.[6] Reaction (1) represents the first genuine example of a reversible carbon dioxide insertion into a metal–nitrogen bond. It has in fact been recognized that what was previously thought to be a CO$_2$ insertion into a M–NR$_2$ bond is actually an amine-catalysed reaction which proceeds *via* the R$_2$NCO$_2$$^-$ anion.[7]

Table 1. Physical, analytical, and i.r. (cm^{-1}, in Nujol) data

Compound	Colour	M.p. (°C)	Analysis[a] (%) C	H	N	
(**2**) $[Pt\{ON(Ph)C(O)O\}(PPh_3)_2]\cdot CH_2Cl_2$	Ochre-yellow	119—121 (decomp.)	55.2(55.3)	3.9(3.9)	1.6(1.5)	1 635 (C=O), 1 260, 995 or 985 (N–O)
(**3**) $[Pt\{ON(Ph)C(S)S\}(PPh_3)_2]\cdot 0.5CH_2Cl_2$	Yellow	159—160	55.6(55.3)	3.8(3.8)	1.4(1.5)	1 047, 999, 962
(**4**) $[Pt\{ON(Ph)C(NPh)O\}(PPh_3)_2]\cdot CH_2Cl_2$	Yellow	200	58.5(58.3)	4.2(4.1)	2.7(2.7)	1 608 (C=N), 1 346, 1 297, 995 or 985 (N–O)
(**5**) $[Pt\{ON(Ph)C(NPh)S\}(PPh_3)_2]$	Orange	251—252	60.9(61.2)	4.1(4.2)	2.9(2.9)	1 530 (C=N), 1 380, 1 345, 1 250
(**6**) $[Pt\{O_2C(NPh)O\}(PPh_3)_2]\cdot CHCl_3$	White	110	53.8(53.4)	3.4(3.6)	1.5(1.4)	1 640 (C=N), 1 310, 1 030, 925, 850
(**7**) $[Pt\{ON(Ph)CH(Ph)O\}(PPh_3)_2]$	Yellow		62.8(63.1)	4.4(4.8)	1.5(1.5)	
(**8**) $[Pt\{N(CO_2Et)N{=}C(OEt)O\}(PPh_3)_2]$	Orange	225—227	56.2(56.4)	4.6(4.5)	3.0(3.1)	1 670 and 1 625 (C=O and C=N), 1 320, 1 300, 1 280
(**9**) $[Pt\{ON(COPh)(Ph)\}(PPh_3)_2]Cl$[b] or $[Pt\{ON(Ph)C(Ph)O\}(PPh_3)_2]Cl$	Pale yellow	205 (decomp.)	60.8(60.8)	4.2(4.1)	1.3(1.5)	1 630 (C=O)
(**10**) $[PtCl\{ON(Ph)(SO_2Me)\}(PPh_3)_2]$	White	130	54.3(54.9)	4.3(4.0)	1.3(1.5)	1 335 (SO_2, asym), 1 150 (SO_2, sym)
(**11**) $[PtCl\{ON(Ph)(SO_2C_6H_4Me\text{-}p)\}(PPh_3)_2]$	Pale brown	150 (decomp.)	57.0(57.9)	4.1(4.1)	1.4(1.4)	1 340 (SO_2, asym), 1 170—1 160 (SO_2, sym)

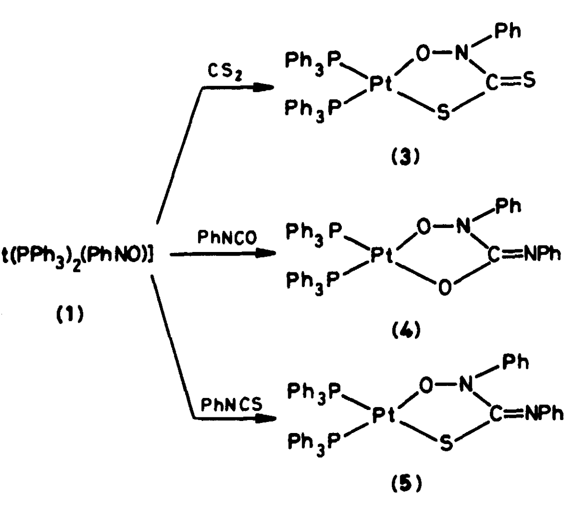
[a] Calculated values are given in parentheses. [b] $\Lambda_M = 23.77\ \Omega^{-1}\ cm^2\ mol^{-1}$ in nitrobenzene.

Table 2. Phosphorus-31[a] and ^{195}Pt[b] n.m.r. data (δ/p.p.m, *J* values in Hz)

Compound	$\delta(P^1)$	$\delta(P^2)$	$J(P^1-P^2)$	$J(Pt-P^1)$	$J(Pt-P^2)$	δ(Pt)	Solvent/atmosphere
(**1**)	16.63	17.06	7.8	4 752	3 929		CD_2Cl_2/N_2
(**2**)	5.48	13.04	26.2	3 454	3 770	−4 058.8[c]	CD_2Cl_2/CO_2 at 0 °C
(**3**)	8.15	20.25	23.0	3 600	2 875		CD_2Cl_2/N_2
(**4**)	7.33	18.23	26.74	3 569	3 262		$CDCl_3/N_2$
(**5**)	9.41	22.2	23.7	3 484	2 973	−4 324.6	$CDCl_3$/air
(**8**)	4.96	15.2	23.7	3 835	3 574	−4 159	C_6D_6/N_2
(**9**)	7.26	6.63	25.3	3 893	3 552	−4 095	$CDCl_3/N_2$
(**10**)	3.29	20.64	21.1	4 188	3 213		$CDCl_3/N_2$
$[Pt(PPh_3)_2(CO_3)]$		6.56			3 698		CD_2Cl_2/air

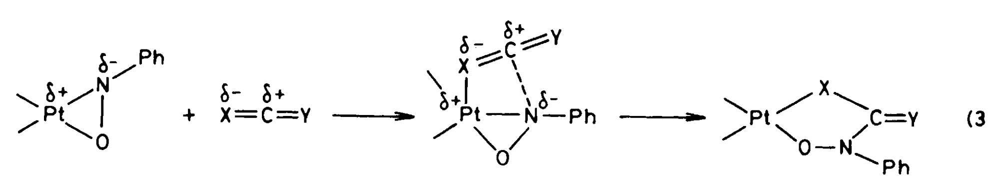
[a] External standard, 85% H_3PO_4 in water. [b] External standard, Na_2PtCl_6 in D_2O. [c] In $CDCl_3$.

Other CO_2-like molecules readily and irreversibly insert [equation (2)] into the platinum–nitrogen bond of complex (**1**) (Table 1). I.r., ^{31}P and ^{195}Pt n.m.r. spectra (Tables 1 and 2) are in agreement with the proposed structures for these derivatives which show the expected AX (^{31}P) or the M component of an AMX (^{195}Pt) type multiplet in the n.m.r. spectra. In the i.r. spectra compounds (**4**) and (**5**) show $\nu_{max.}$ at 1 608 and 1 530 cm^{-1} (C=N) respectively, while compound (**3**) shows three significant bands in the 960—1 050 cm^{-1} region (Table 1), one of these being probably due to $\nu_{max.}$(C=S). Other structures for compounds (**3**)—(**5**) are less probable, not only on the basis of the spectral data (absence in the ^{31}P n.m.r. spectra of signals at low field attributable to phosphorus atoms *trans* to carbon),[3] but also because the proposed formulations fit with the view that compounds (**2**)—(**5**) are formed *via* attack of the nucleophilic centre in (**1**), that is nitrogen, on the electrophilic carbon atom of the entering molecules. Reactions (1) and (2) can be viewed as a dipolar addition of the reactants to compound (**1**) [equation (3)]. This reaction scheme is similar to the main reaction path proposed for the insertion of the carbonyl group of ketones into the platinum–oxygen bond of $[Pt(PPh_3)_2(O_2)]$.[8]



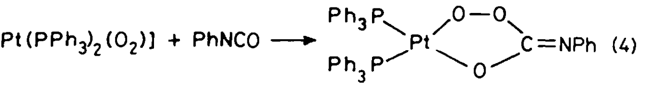
(2)

Compound (**2**) is an isomer of the insertion product (**6**), $[Pt\{O_2C(NPh)O\}(PPh_3)_2]$, obtained from the reaction [equation (4)] of $[Pt(PPh_3)_2(O_2)]$ with PhNCO (Table 1). Compound (**6**) shows in its i.r. spectrum $\nu_{max.}$ at 1 640 cm^{-1} (C=N) as the most significant band, and all the other bands are different from those observed for (**2**).



(3)

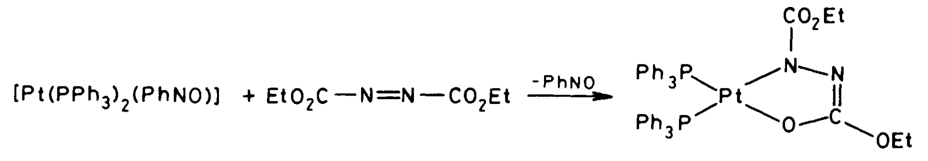
(X = O or S; Y = O, S, or NPh)



(4)

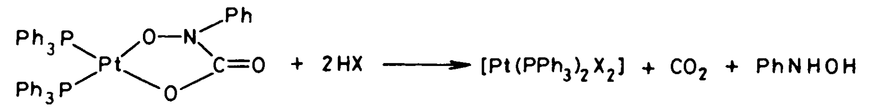
(6)

Compound (1) does not react with acetone or with diethyl carbonate. It reacts with benzaldehyde, to give a labile insertion product, $[Pt\{ON(Ph)CH(Ph)O\}(PPh_3)_2]$ (7). This formulation is based only on the analytical data and on the i.r. spectrum (absence of absorptions attributable to a >C=O group), since in solution this compound decomposes to the free aldehyde. However, in the ^1H n.m.r. spectrum it was possible to detect a signal at δ 5.96 p.p.m., besides the absorption at δ 10.05 p.p.m. due to CHO of the free aldehyde, attributable to the 1:1 insertion product. Another molecule similar to carbon dioxide, cyclohexylcarbodi-imide, does not react with compound (1). On the other hand, the unsaturated molecule $EtO_2C-N=N-CO_2Et$ reacts [equation (5)] with (1), but the product $[Pt\{N(CO_2Et)N=C(OEt)O\}(PPh_3)_2]$, (8), does not contain the PhNO ligand (Table 1). The orange complex (8) shows in the ^{31}P n.m.r. spectrum the usual AX type multiplet with ^{195}Pt satellites, δ(P) and *J*(Pt–P) being similar to those of compounds (2) and (4) (Table 2). However, the satellite bands at low fields were casually coincident. These data support the view that no $Pt-CO_2Et$ groups are present in compound (8), since a phosphorus *trans* to carbon should have much different values of these parameters.[3] The ^1H n.m.r. spectrum showed signals of two different ethyl groups, while its i.r. spectrum is rather complex in the 1 300—1 700 cm^{-1} region, with two strong absorptions at $\nu_{max.}$ 1 670 (C=O) and 1 625 cm^{-1} (C=N). The proposed metallacycle corresponds to the usual mode of bonding of aroylhydrazido-ligands with platinum(II).[9]



(5)

(1) (8)



(6)

(2)

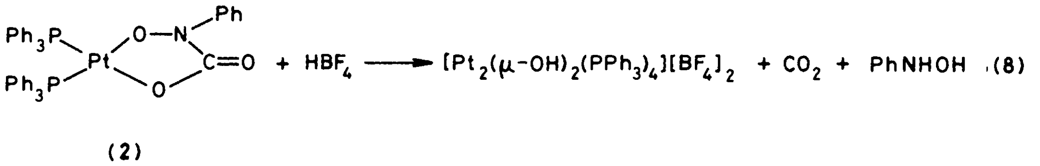
(X = Cl, $X_2 = SO_4^{2-}$)

Reactivity of Compounds (1) *and* (2).—In view of the interest in the activation of carbon dioxide by transition-metal complexes, we have investigated the reactivity of (2) towards several reagents such as mineral acids, organic acids, benzoyl chloride, and sulphonyl chlorides. However, we always observed the loss of CO_2 and the products were identical to those obtained in the reactions of compound (1) with the same reagents.

Organic and mineral acids do not give a protonation product of the metallacycle in (2), but instead the organic ligand is totally displaced [equation (6)]. The same reaction was observed with CF_3CO_2H under a carbon dioxide atmosphere. Analogous products were obtained by protonation of compound (1) [equation (7)]. An acid having a non-co-ordinating anion such as HBF_4 behaves similarly, giving however a dimeric hydroxoplatinum(II) complex with both (1) and (2) [equation (8)]. By reaction [equation (9)] of (2) [or (1)] with 1 equivalent of PhCOCl, an ionic complex (9) (Table 1) was isolated. Compound (9) could be an O,N-bonded hydroxylamido-derivative (9a) or an aroylhydroxylamido-derivative where the carbonyl group of the substituent is involved in co-ordination with platinum (9b). The i.r. spectrum, which shows $\nu_{max.}$ at 1 630 cm^{-1} (C=O), does not clearly distinguish between the two possible formulations. The ^{31}P n.m.r. spectrum is rather

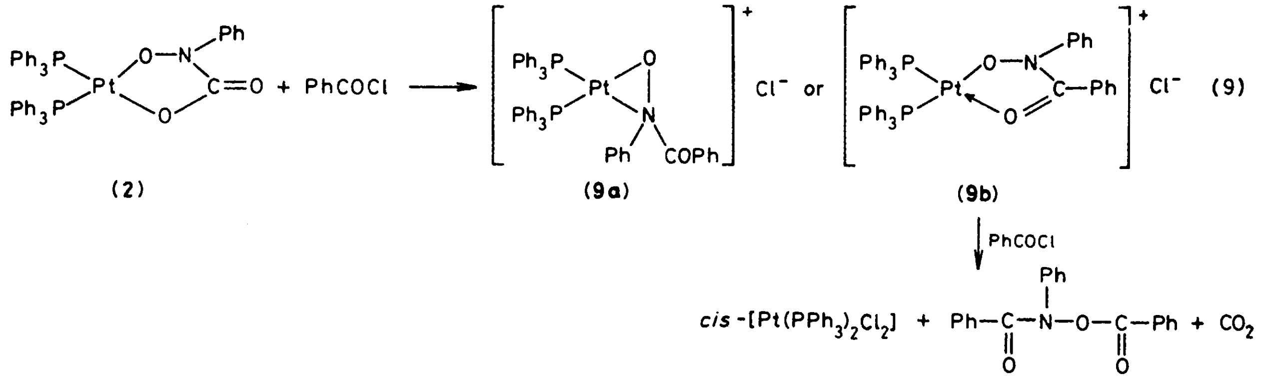
$$[Pt(PPh_3)_2(PhNO)] + 2CR_3CO_2H \longrightarrow [Pt(PPh_3)_2(O_2CCR_3)_2] + PhNHOH \quad (7)$$
(R = H or F)

unusual. It corresponds to an AB system, with the two central lines practically coincident (relative intensities in the apparent triplet *ca.* 1:6:1), with the expected satellites due to coupling with ^{195}Pt. A simulated spectrum with $\delta(P^1) = 7.26$, $\delta(P^2) = 6.63$ p.p.m. $J(P^1-P^2) = 27.28$, $J(Pt-P^1) = 3\,893.02$, and $J(Pt-P^2) = 3\,552.16$ Hz was entirely in agreement with the observed spectrum. The ^{195}Pt n.m.r. spectrum of compound (9) once more confirmed the interpretation of the ^{31}P n.m.r. data (Table 2). By reaction of (9) with another equivalent of PhCOCl [or by conducting reaction (9) with 2 mol of PhCOCl per mol of compound (2)] the organic ligand is displaced as *O,N*-dibenzoyl-*N*-phenylhydroxylamine [equation (9)]. The nature of the formed hydroxylamine was confirmed by elemental analyses, i.r. and mass spectra. The same organic compound is obtained when PhCOCl is treated with PhNHOH in the presence of base.[10]



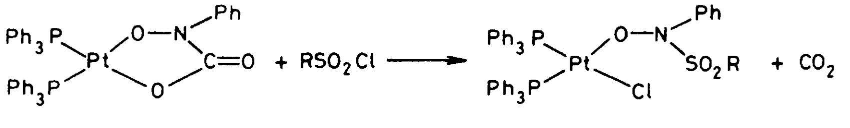
(2)

(8)



(2) (9a) (9b)

(9)



(2)

(10)

(10) R = Me
(11) R = C_6H_4Me-*p*

When compound (**2**) [or (**1**)] was treated with a stoicheiometric amount of RSO_2Cl (R = Me or C_6H_4Me-*p*), non-ionic complexes were isolated [equation (10)]. Complexes (**10**) and (**11**) show $\nu_{max.}$ at *ca.* 1 340 and 1 160 cm^{-1} (SO_2), close to those observed for the starting sulphonyl chlorides, which indicates that the oxygen atoms of the sulphonyl groups are not involved in co-ordination with platinum. On the other hand, the ^{31}P n.m.r. spectrum of (**10**) shows the usual AX type system, in agreement with the proposed formulation (Table 2).

Attempted reactions of complex (**2**) with simple alkenes such as cyclohexene, cyclo-octa-1,3-diene, and 1,4-diphenylbutadiene were unsuccessful, no reaction being observed.

Experimental

All reactions were carried out with magnetic stirring. Solvents were dried, purified, and stored under nitrogen. The complex $[Pt(PPh_3)_2(PhNO)]$ (**1**) was prepared as described.[3] The organic reagents were all commercial products, which were purified by distillation or crystallisation. Infrared spectra were recorded on a Beckman 4210 spectrophotometer. Hydrogen-1, phosphorus-31, and platinum-195 n.m.r. spectra were obtained on a Brucker VP-80 spectrometer, with $SiMe_4$ as internal standard, 85% H_3PO_4 in water, and Na_2PtCl_6 in D_2O as external standard respectively. Elemental analyses were carried out in the analytical laboratories of Milan University.

$[Pt\{ON(Ph)C(O)O\}(PPh_3)_2]\cdot CH_2Cl_2$ (**2**).—To CH_2Cl_2 (30 cm^3), degassed and saturated with carbon dioxide, was added $[Pt(PPh_3)_2(PhNO)]$ (**1**) (0.5 g). The resulting yellow-orange solution was left in a carbon dioxide atmosphere for 4 h. Upon addition of n-hexane saturated with CO_2, the ochre-yellow product precipitated (92.5% yield). It was quickly filtered off, washed with n-hexane, dried *in vacuo*, and stored in a carbon dioxide atmosphere. When exposed to air a new band in the i.r. spectrum appears at 1 680 cm^{-1}, probably due to $[Pt(PPh_3)_2(CO_3)]$.[5] Its ^1H n.m.r. spectrum in $CDCl_3$ showed a signal at 5.3 p.p.m. due to the solvent of crystallisation.

Compound (**2**) (0.42 g) was suspended in benzene (33 cm^3) degassed with dinitrogen. Dinitrogen was bubbled through the orange solution for 3 h and then passed through an aqueous solution of $Ba(OH)_2$. At the end of the reaction the amount of $BaCO_3$ precipitated was equivalent to the amount of starting complex. Upon addition of n-hexane to the benzene solution, $[Pt(PPh_3)_2(PhNO)]$ precipitated. It was recognized by its m.p. and i.r. spectrum, and by reaction with CO_2 in CH_2Cl_2 which gave compound (**2**) as described above.

$[Pt\{ON(Ph)C(S)S\}(PPh_3)_2]\cdot 0.5CH_2Cl_2$ (**3**).—To compound (**1**) (0.2 g) was added a solution of carbon disulphide (0.182 g) in CH_2Cl_2 (10 cm^3) under a nitrogen atmosphere. The initial yellow-orange solution rapidly became canary yellow. After 4 h the solution was evaporated to *ca.* half its volume. Upon addition of n-hexane the yellow product precipitated. It was filtered off, washed with n-hexane, crystallised from CH_2Cl_2–n-hexane, and dried *in vacuo* (80% yield).

$[Pt\{ON(Ph)C(NPh)O\}(PPh_3)_2]\cdot CH_2Cl_2$ (**4**).—To compound (**1**) (0.167 g) in benzene (20 cm^3) was added a solution of PhNCO (0.026 g) in benzene (5 cm^3) under nitrogen. After a few minutes the yellow product precipitated from the orange solution. After 1 h it was filtered off under nitrogen and crystallised from CH_2Cl_2–n-hexane under nitrogen. It was stored under a nitrogen atmosphere. Its ^1H n.m.r. spectrum in

$CDCl_3$ showed a signal at δ 5.3 p.p.m. due to the solvent of crystallisation.

$[Pt\{ON(Ph)C(NPh)S\}(PPh_3)_2]$ **(5)**.—To compound **(1)** (0.25 g) were added PhNCS (0.045 g) and benzene (20 cm^3) under nitrogen. After 1 h the yellow-orange solution was evaporated to a small volume. Upon adding n-hexane under a nitrogen atmosphere the orange complex precipitated. It was filtered off, washed with n-hexane, and dried *in vacuo*. It was crystallised from $CHCl_3$–hexane.

$[Pt\{O_2C(NPh)O\}(PPh_3)_2]\cdot CHCl_3$ **(6)**.—To $[Pt(PPh_3)_2(O_2)]$ (0.4 g) in benzene (15 cm^3) was added a solution of PhNCO (0.07 g) in benzene (5 cm^3) under nitrogen. The reaction was carried out in the dark. The yellow suspension became a colourless solution and after a few minutes a white precipitate was formed. After 0.5 h the product was filtered off, washed with benzene, and dried *in vacuo*. It was crystallised from $CHCl_3$–n-hexane under nitrogen (85% yield). It was stored under nitrogen in the dark. The crude compound contains 1 mol of benzene of crystallisation (Found: C, 61.6; H, 4.4; N, 1.3; O, 5.1. Calc. for $C_{49}H_{41}NO_3P_2Pt$: C, 62.0; H, 4.3; N, 1.5; O, 5.1%).

$[Pt\{ON(Ph)CH(Ph)O\}(PPh_3)_2]$ **(7)**.—To compound **(1)** (0.3 g) was added a solution of benzaldehyde (0.078 g) in benzene (30 cm^3) under nitrogen. After 20 h the orange-brown solution was evaporated to a small volume and n-hexane degassed with dinitrogen was added. The yellow precipitate was filtered off under nitrogen, washed with n-hexane degassed with dinitrogen, and dried *in vacuo*. The compound was stored under nitrogen. The same reaction carried out in toluene gave a complex which contains toluene, as shown by the ^1H n.m.r. spectrum under a nitrogen atmosphere [$\delta(CH_3)$ 2.37 p.p.m. in $CDCl_3$]. In the same n.m.r. spectrum it was possible to detect the signals due to the CHO group (free, δ 10.05; complexed, δ 5.96 p.p.m.).

$[Pt\{N(CO_2Et)N{=}C(OEt)O\}(PPh_3)_2]$ **(8)**.—To compound **(1)** (0.5 g) were added $EtO_2C{-}N{=}N{-}CO_2Et$ (0.116 g) and toluene (20 cm^3) under nitrogen. The orange suspension became brownish. After 18 h the orange precipitate was filtered off, washed with toluene and n-hexane, and dried *in vacuo* at 40 °C for 24 h (62% yield).

$[Pt\{ON(COPh)(Ph)\}(PPh_3)_2]Cl$ **(9a)** *or*
$[Pt\{ON(Ph)C(Ph)O\}(PPh_3)_2]Cl$ **(9b)**.—To compound **(1)** (0.3 g) was added a solution of PhCOCl (0.0584 g) in benzene (25 cm^3) under nitrogen. A canary-yellow suspension was formed immediately. After 2 h the yellow precipitate was filtered off, washed with diethyl ether, and dried *in vacuo* at 30 °C for 10 h. The compound was crystallised from $CHCl_3$–diethyl ether under nitrogen and stored under nitrogen. Compound **(9)** was also obtained from the reaction of **(2)** with PhCOCl under a carbon dioxide atmosphere. In the mother-liquor of the reaction, small amounts of *cis*-$[Pt(PPh_3)_2Cl_2]$ and of PhC(O)N(Ph)OC(O)Ph were detected. These compounds were the only products of the reaction when compound **(2)** was treated with PhCOCl in a molar ratio of 1 : 2.2 for 22 h, under a carbon dioxide atmosphere. Under these conditions a white precipitate was obtained, which was shown to be *cis*-$[Pt(PPh_3)_2Cl_2]$ by its i.r. spectrum. The solution was evaporated to dryness and treated with diethyl ether. Some *cis*-$[Pt(PPh_3)_2Cl_2]$ was filtered off. The ether solution was evaporated to dryness and the oily residue was left under stirring after addition of a saturated solution of $NaHCO_3$ in water. A pale brown powder was obtained, which was shown to be PhC(O)N(Ph)OC(O)Ph by its m.p., elemental analyses, i.r. and mass spectra.

$[PtCl\{ON(Ph)(SO_2Me)\}(PPh_3)_2]$ **(10)**.—To compound **(1)** (0.284 g) in benzene (25 cm^3) was added a solution of $MeSO_2Cl$ (0.044 g) in benzene (5 cm^3) under nitrogen. After 1 h the colourless solution was evaporated to a small volume. Upon addition of n-hexane under nitrogen a white precipitate was obtained. It was filtered off, washed with n-hexane, and dried *in vacuo* (90% yield). Compound **(10)** is a non-conductor in nitrobenzene. Its ^1H n.m.r. spectrum in $CDCl_3$ showed a signal at δ 8.0 p.p.m. due to the methyl group. The same complex was obtained by conducting the reaction under a carbon dioxide atmosphere with compound **(2)** instead of **(1)**.

$[PtCl\{ON(Ph)(SO_2C_6H_4Me\text{-}p)\}(PPh_3)_2]$ **(11)**.—To compound **(1)** (0.282 g) were added *p*-$MeC_6H_4SO_2Cl$ (0.072 g) and benzene (25 cm^3) under nitrogen. After 2 h small amounts of *cis*-$[Pt(PPh_3)_2Cl_2]$ were filtered off from the yellow suspension. The solution was evaporated to a small volume and upon addition of n-hexane the yellow product precipitated. It was filtered off, crystallised under nitrogen from benzene–n-hexane, and dried *in vacuo*. It is a non-conductor in nitrobenzene. After crystallisation the colour became pale brown, possibly due to some decomposition, although the elemental analysis was still in agreement with the proposed formulation (Table 1). The ^1H n.m.r. spectrum in C_6D_6 showed $\delta(CH_3)$ 1.80 p.p.m. The same complex was obtained by reaction of **(2)**, in a carbon dioxide atmosphere, with *p*-$MeC_6H_4SO_2Cl$. The crude product was crystallised from benzene–n-hexane in order to eliminate some unreacted starting material.

Protonation Reactions of Complex **(2)**.—(*a*) *With* HX ($X = Cl^-$ *or* $CF_3CO_2^-$) *and* H_2SO_4. By reaction of complex **(2)** under nitrogen in ethanol with hydrochloric or sulphuric acid in water, carbon dioxide is evolved [confirmed by trapping the gas with $Ba(OH)_2$], and *cis*-$[Pt(PPh_3)_2Cl_2]$ and $[Pt(PPh_3)_2(SO_4)]$ were obtained (i.r. spectra identical to those of authentic samples). By reaction of complex **(2)** with CF_3CO_2H under a carbon dioxide atmosphere, $[Pt(PPh_3)_2(O_2CCF_3)_2]$ was isolated; it was crystallised from $CHCl_3$–n-hexane and dried *in vacuo*, m.p. 242—245 °C (Found: C, 51.3; H, 3.3. Calc. for $C_{40}H_{30}F_6O_4P_2Pt$: C, 50.8; H, 3.2%); $\nu_{max.}$ of 1 720 (C=O), 1 195, and 1 180 cm^{-1} (C–O), in Nujol. It is a non-conductor in nitrobenzene.

By reaction of **(1)** with CF_3CO_2H in ethanol under nitrogen the same compound was obtained. Similarly, the reaction of **(1)** with $MeCO_2H$ in ethanol yielded $[Pt(PPh_3)_2(O_2CMe)_2]$, $\nu_{max.}$ 1 628 (C=O) and 1 092 cm^{-1} (C–O) in Nujol. $\delta(CH_3) = 1.22$ p.p.m. in $CDCl_3$. It is a non-conductor in nitrobenzene.

(*b*) *With* HBF_4. By reaction of complex **(2)** under nitrogen in ethanol with HBF_4 (40% in water), carbon dioxide is evolved (confirmed with the usual test) and from the solution a pale brown material precipitated. It was filtered off and crystallised from CH_2Cl_2–n-hexane, giving a white product. This was shown to be $[Pt_2(\mu\text{-}OH)_2(PPh_3)_4][BF_4]_2$ by its i.r. spectrum, identical to that of an authentic sample.[11] The same complex (i.r. evidence) was obtained when the protonation reaction was carried out on **(1)** under the same experimental conditions.

Acknowledgements

We are particularly grateful to Mrs. Maria Bonfà for the n.m.r. spectra.

References

1 R. Eisemberg and D. E. Hendriksen, *Adv. Catal.*, 1979, **28**, 79; S. Incue and N. Yamazaki (eds.), 'Organic and Bio-Organic Chemistry of Carbon Dioxide,' Kodansha Ltd., Tokio, Halsted Press, New York, 1982.

2 M. Tsutsui and R. Ugo (eds.), 'Fundamental Research in Homogeneous Catalysis,' Plenum Press, New York and London, 1977.

3 S. Cenini, F. Porta, M. Pizzotti, and G. La Monica, *J. Chem. Soc., Dalton Trans.*, 1984, 355.

4 P. L. Bellon, S. Cenini, F. Demartin, M. Pizzotti, and F. Porta, *J. Chem. Soc., Chem. Commun.*, 1982, 265.

5 P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Am. Chem. Soc.*, 1970, **92**, 5873.

6 S. Gambarotta, F. Arena, C. Floriani, and P. R. Zanazzi, *J. Am. Chem. Soc.*, 1982, **104**, 5082.

7 M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, 1977, **99**, 792.

8 R. Ugo, G. M. Zanderighi, A. Fusi, and D. Carreri, *J. Am. Chem. Soc.*, 1980, **102**, 3745.

9 P. L. Bellon, S. Cenini, F. Demartin, M. Manassero, M. Pizzotti, and F. Porta, *J. Chem. Soc., Dalton Trans.*, 1980, 2060.

10 L. Horner and H. Steppan, *Liebigs Ann. Chem.*, 1957, **606**, 24.

11 S. Cenini, R. Ugo, and G. La Monica, *J. Chem. Soc. A*, 1971, 3441.

Received 19*th March* 1984; *Paper* 4/439