

Further investigations of the reactivity of η^2 -bonded nitroso complexes of platinum. The crystal structure of $\text{Pt}(\text{PPh}_3)_2(\text{PhNO})$ *

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Abstract

The crystal structure of $\text{Pt}(\text{PPh}_3)_2(\text{PhNO})$ (I) has been determined. This is the first example of a structure determination for a monomeric complex of a metal in a low oxidation state and bearing an η^2 -bonded nitroso ligand. Compound I crystallizes in the monoclinic space group $P2_1/c$ (no.14) with a 14.228(4), b 13.914(3), c 17.855(4) Å, β 100.31(2)°, V 3478(3) Å³ and $Z = 4$. Final R and R_w indices are 0.026 and 0.030 for 3609 observed reflections ($I \geq 3 \sigma(I)$).

The new complexes $\text{Pt}(\text{PPh}_3)_2(\text{RNO})$ ($\text{R} = \text{Bu}^t$ (II), CF_3 (III)) have been synthesized and their reactions with CO_2 , CS_2 , PhNCO , PhNCS , CO , alkenes and dimethyl acetylenedicarboxylate have been investigated and compared with those of the previously studied compound I. Preliminary observations on the synthesis and reactivity of $\text{Pd}(\text{PPh}_3)_2(\text{CF}_3\text{NO})$ (IV) are also reported.

Introduction

Studies on the reactions of complexes containing an η^2 -bonded nitroso ligand are of interest from several points of view. In the first place nitroso compounds, RNO , are the probable intermediates in the reduction by carbon monoxide of nitro compounds, RNO_2 , catalysed by transition metal complexes [1]; such reductive carbonylation reaction is of practical interest for the search for a route to iso-

* Dedicated to Professor Luigi Sacconi in recognition of his important contributions to organometallic chemistry.

cyanates, RNCO, which does not involve the reaction of the dangerous and corrosive phosgene, COCl_2 , with amines [1]. In the second place, nitroso compounds are isoelectronic with dioxygen, and their reactions with transition metal complexes can give information on the activation of this important molecule by metal centres.

We have previously studied the reactions of $\text{Pt}(\text{PPh}_3)_2(\text{PhNO})$ (I) with unsaturated hydrocarbons [2,3], carbon dioxide, and CO_2 -like species [2,4,5]. We report here the crystal and molecular structure of compound I, which represents the first example of determination of a structure of a monomeric complex of a metal in a low oxidation state and containing an η^2 -bonded nitroso ligand. We also describe the syntheses of the new complexes $\text{M}(\text{PPh}_3)_2(\text{RNO})$ ($\text{M} = \text{Pt}$, $\text{R} = \text{Bu}^t$ (II), $\text{R} = \text{CF}_3$ (III); $\text{M} = \text{Pd}$, $\text{R} = \text{CF}_3$ (IV)). Their reactions with carbon oxides, CO_2 -like molecules, and unsaturated hydrocarbons have been investigated, and the influence of the R group in these reactions is discussed.

Description of the structure of $\text{Pt}(\text{PPh}_3)_2(\text{PhNO})$ (I)

The molecular structure of $\text{Pt}(\text{PPh}_3)_2(\text{PhNO})$ is shown in Fig. 1. Selected bond distances and angles are listed in Table 1.

The discrete mononuclear molecules contain a three-coordinate platinum atom bearing two triphenylphosphine ligands and bound to a phenylnitroso ligand in an η^2 -fashion to give a three-membered platinaoxaziridine ring. The Pt–P(1) distance, approximately *trans* to O, of 2.239(2) Å, is slightly shorter than the Pt–P(2) one, *trans* to N (2.272(2) Å). In spite of the similarities in Pt–P distances observed here with those for square-planar platinum complexes $(\text{PPh}_3)_2\text{PtL}$ (with *cis*-triphenylphosphine ligands and L a chelating ligand), a significant enlargement of the

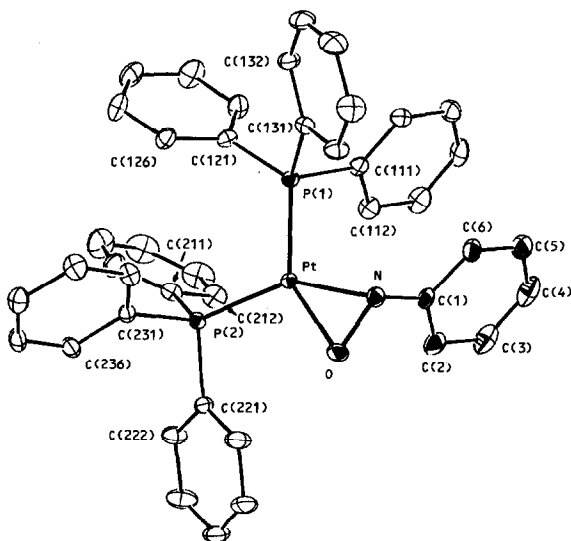


Fig. 1. ORTEP drawing of $\text{Pt}(\text{PPh}_3)_2(\text{PhNO})$ (I).

Table 1
Selected bond distances (Å) and angles (°) for compound I

Pt–P(1)	2.239(2)	P(1)–Pt–P(2)	106.52(6)
Pt–P(2)	2.272(2)	P(1)–Pt–N	106.1(2)
Pt–N	2.084(5)	P(1)–Pt–O	146.2(1)
Pt–O	2.031(4)	P(2)–Pt–N	147.3(2)
N–O	1.410(7)	P(2)–Pt–O	107.3(1)
N–C(1)	1.412(9)	O–Pt–N	40.0(2)
C(1)–C(2)	1.382(10)	O–N–C(1)	110.9(5)
C(2)–C(3)	1.390(12)	Pt–N–O	68.0(3)
C(3)–C(4)	1.367(14)	Pt–O–N	72.0(3)
C(4)–C(5)	1.366(13)	Pt–N–C(1)	109.7(4)
C(5)–C(6)	1.380(12)		
C(6)–C(1)	1.394(10)		
P(1)–C(1i1) _{av.}	1.829		
P(2)–C(2i1) _{av.}	1.825		

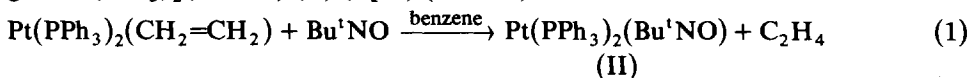
P–Pt–P angle can be seen in complex I: the value of 106.52(6)° is outside the range of values usually found for (PPh₃)₂PtL tetra-coordinate complexes [5–7].

The N and O atoms lie on the same side 0.054(6) and 0.057(6) Å out of the plane defined by atoms Pt, P(1) and P(2), indicating a very slight pyramidal distortion of the coordination geometry.

The pattern of bond distances and angles within the platinaoxaziridine ring (see Table 1) is consistent with an *sp*³-hybridization for the N atom. The Pt–N distance (2.084(5) Å) is longer than that found in PtCl₂[(CH₃)₃C(NO)]₂ [8] (1.967(9) Å) for a *N*-coordinated nitroso ligand, and is comparable with a Pt–N(aminic) interaction. The values of both the N–O and N–C(1) bond lengths suggest a predominant single bond character. The length of the N–O bond can be compared with that of the corresponding bond in oxo(*N*-phenyl-hydroxylamido-*O,N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphoramidomolybdenum (VI), (1.416(7) Å) [9] and in bis[tricarbonyl-(3-chloro-2-methylnitrosobenzene)iron], (1.40(1) Å) [10], it is slightly longer than that in [Pd(PhNO)(PBU^t)₃]₃, (1.35(1) Å) [11]. The Pt–O bond length (2.031(4) Å) agrees well with the value of 2.044(5) Å found in Pt{ON(Ph)C(NPh)S}(PPh₃)₂ [5] obtained by insertion of PhN=C=S into the platinum–nitrogen bond of complex I. The phenyl ring of the aryl nitroso ligand is slightly twisted about the N–C(1)···C(4) axis (torsional angle O–N–C(1)–C(2) 5°) and faces the almost parallel C(111)–C(116) phenyl plane at a distance corresponding to a “graphitic” interaction (see Fig. 1).

Synthesis of the complexes M(PPh₃)₂(RNO) (M = Pt, R = Bu^t (II), CF₃ (III); M = Pd, R = CF₃ (IV))

Reaction of Pt(PPh₃)₂(CH₂=CH₂) with Bu^tNO in benzene under dinitrogen gave Pt(PPh₃)₂(Bu^tNO) (II) (eq. 1) (Table 2).

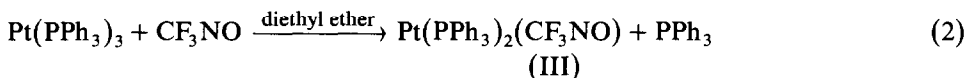


It is noteworthy that the reaction of Bu^tNO with ethylene bound to platinum(II) gives a σ -alkyl-nitron complex, derived by attack of the nitroso compound on the electrophilic alkene [12].

Table 2
Physical, analytical and IR data

Compound	M.p. (°C)	Analysis (Found (calc) (%))			ν (cm ⁻¹) (in Nujol)
		C	H	N	
Pt(PPh ₃) ₂ (Bu ¹ NO)·0.5C ₆ H ₆ (II)	123	61.0 (61.1)	5.0 (5.0)	1.6 (1.7)	960 (NO)
Pt(PPh ₃) ₂ (CF ₃ NO) (III)	174	54.9 (54.3)	3.8 (3.7)	1.5 (1.7)	840 (NO)
Pd(PPh ₃) ₂ (CF ₃ NO) (IV)	157	60.4 (60.9)	4.2 (4.1)	1.9 (1.9)	845 (NO)
Pt{ON(Bu ¹)C(O)O}(PPh ₃) ₂ (V)	158–160	57.6 (57.9)	4.7 (4.6)	1.8 (1.6)	1608 (C=O)
Pt{ON(Bu ¹)C(S)S}(PPh ₃) ₂ (VI)	199	55.6 (55.8)	4.6 (4.4)	1.7 (1.6)	960 (C=S)
Pt{ON(CF ₃)C(S)S}(PPh ₃) ₂ (VII)	219	50.5 (51.0)	3.3 (3.4)	1.9 (1.6)	980 (C=S)
Pt{ON(Bu ¹)C(O)NPh}(PPh ₃) ₂ C ₆ H ₆ (VIII)	183	62.0 (61.0)	4.8 (4.8)	2.9 (3.0)	1730 (C=O)
Pt{ON(CF ₃)C(O)NPh}(PPh ₃) ₂ (IX)	194	56.5 (56.6)	3.9 (3.7)	2.8 (3.0)	1646 (C=O)
Pt{ON(Bu ¹)C(NPh)S}(PPh ₃) ₂ (X)	257	61.0 (60.0)	4.8 (4.7)	2.8 (3.0)	1530 (C=N)
Pt{ON(CF ₃)C(NPh)S}(PPh ₃) ₂ (XI)	266	54.8 (55.5)	3.6 (3.7)	3.0 (2.9)	1570 (C=N)
Pt{ON(Bu ¹)CH(Ph)C(CN) ₂ }(PPh ₃) ₂ (XII)	129	62.4 (62.5)	5.0 (4.7)	4.0 (4.4)	2200 (C≡N)
Pt{ON(CF ₃)CH(Ph)C(CN) ₂ }(PPh ₃) ₂ (XIII)	194	57.3 (58.0)	3.9 (3.7)	3.9 (4.3)	2210 (C≡N)
Pt{ON(CF ₃)C(CN) ₂ C(CN) ₂ }(PPh ₃) ₂ (XIV)	198	54.2 (54.5)	3.4 (3.2)	6.7 (7.4)	2220 (C≡N)
Pt{ON(Bu ¹)C(CO ₂ Me)=C(CO ₂ Me)}- (PPh ₃) ₂ (XV)	180	57.0 (58.2)	4.7 (4.7)	1.3 (1.5)	1715 (C=O)

Compound II could not be obtained by reaction of Bu¹NO with Pt(PPh₃)₃. On the other hand, the enhanced π -acidic character of CF₃NO allowed the synthesis of Pt(PPh₃)₂(CF₃NO) (III) directly from Pt(PPh₃)₃ [13] in diethyl ether (eq. 2) (Table 2).



Similarly, Pd(PPh₃)₂(CF₃NO) (IV) was obtained by reaction of CF₃NO with Pd(PPh₃)₄ in diethyl ether; the reaction of Pt(PPh₃)₄ with CF₃NO in benzene has been reported to give an unstable, purple, paramagnetic complex of stoichiometry Pt(PPh₃)₂(CF₃)(NO) [14]. Repeated attempts to characterize the red-orange material obtained from the reaction of Pd(PPh₃)₄ with PhNO were unsuccessful. Compound II shows a band at 960 cm⁻¹ in its IR spectrum attributable to ν (NO) of the η^2 -bonded nitroso ligand (Table 2). For compound I this band is observed at 975 cm⁻¹. In compounds III and IV ν (NO) is lowered to 840–845 cm⁻¹, which suggests a substantial reduction in the N–O bond order in these derivatives with respect to compounds I and II, as one would expect since the CF₃ group is strongly electron-

Table 3

¹H, ³¹P^a and ¹⁹F^b NMR data (δ (ppm), J values in Hz), CD₂Cl₂ as solvent

Compound	δ(¹ H) (Me)	δ(¹⁹ F)	δ(P(1))	δ(P(2))	J(Pt-P(1))	J(Pt-P(2))	J(P(1)-P(2))
Pt(PPh ₃) ₂ (Bu ^t NO)·0.5C ₆ H ₆ (II)	1.0	-	-	-	-	-	-
Pt(PPh ₃) ₂ (CF ₃ NO) (III)	-	-60.7 ^c	-	-	-	-	-
Pd(PPh ₃) ₂ (CF ₃ NO) (IV)	-	-63.38 ^d	-	-	-	-	-
Pt{ON(Bu ^t)C(O)O}(PPh ₃) ₂ (V)	1.03	-	-	-	-	-	-
Pt{ON(Bu ^t)C(S)S}(PPh ₃) ₂ (VI)	1.22	-	9.43	19.42	3643	2802.6	23.7
Pt{ON(CF ₃)C(S)S}(PPh ₃) ₂ (VII)	-	-61.97	-	-	-	-	-
Pt{ON(Bu ^t)C(O)NPh}(PPh ₃) ₂ ·C ₆ H ₆ (VIII)	0.93	-	9.03	16.42	3502	3274.4	27.6
Pt{ON(CF ₃)C(O)NPh}(PPh ₃) ₂ (IX)	-	-66.6	7.44	15.24	3545.8	3337.5	27.5
Pt{ON(Bu ^t)C(NPh)S}(PPh ₃) ₂ (X)	1.02	-	11.17	21.95	3445	2987	22.87
Pt{ON(CF ₃)C(NPh)S}(PPh ₃) ₂ (XI)	-	-66.2	8.71	22.80	3430.9	3067.9	21.7
Pt{ON(Bu ^t)CH(Ph)C(CN) ₂ }(PPh ₃) ₂ (XII)	0.41 ^e	-	-	-	-	-	-
Pt{ON(CF ₃)CH(Ph)C(CN) ₂ }(PPh ₃) ₂ (XIII)	-	-69.31	-	-	-	-	-
Pt{ON(CF ₃)C(CN) ₂ C(CN) ₂ }(PPh ₃) ₂ (XIV)	-	-69.84	-	-	-	-	-
Pt{ON(Bu ^t)C(CO ₂ Me)=C(CO ₂ Me)}·(PPh ₂) ₂ (XV)	0.81 ^f	-	14.21	29.91	3722.3	2354.6	18.32

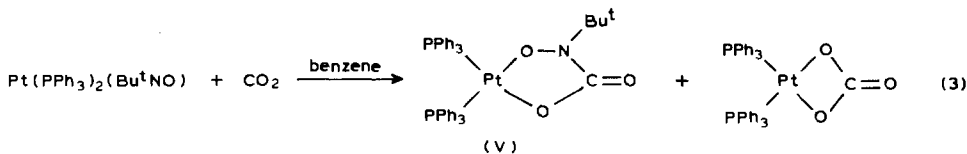
^a External standard: 85% H₃PO₄. ^b Standard: CFCl₃. ^c Multiplet due to the coupling of ¹⁹F with P-*cis* and P-*trans*: J(F-P-*trans*) 15 Hz. J(F-P-*cis*) 13 Hz. ^d Multiplet due to the coupling of ¹⁹F with P-*trans*, P-*cis* and ¹⁹⁵Pt: J(F-P-*trans*) 12.5 Hz; J(F-Pt) 56.0 Hz; J(F-P-*cis*) was not clearly detected. ^e δ (CH) 3.74 with satellites due to coupling with ¹⁹⁵Pt, J(Pt-H) 25.46 Hz. ^f δ(OCH₃) 2.28(s); 3.56(s).

withdrawing. The absorptions due to ν(CF) were observed in the 1000–1300 cm⁻¹ region. In its ¹H NMR spectrum compound II shows a singlet at δ 1 ppm due to the equivalent methyl groups (Table 3). The ¹⁹F NMR spectrum of III shows a complex signal at ca. -60.75 ppm (CFCl₃ as reference) due to fluorine atoms coupled with P-*trans* and P-*cis*, and with satellites due to coupling with ¹⁹⁵Pt (J(Pt-F) 56 Hz). The ¹⁹F NMR spectrum of IV shows an apparent triplet at -63.38 ppm, due to coupling with the two non-equivalent phosphorus atoms.

Reactions of compounds II and III

With carbon dioxide

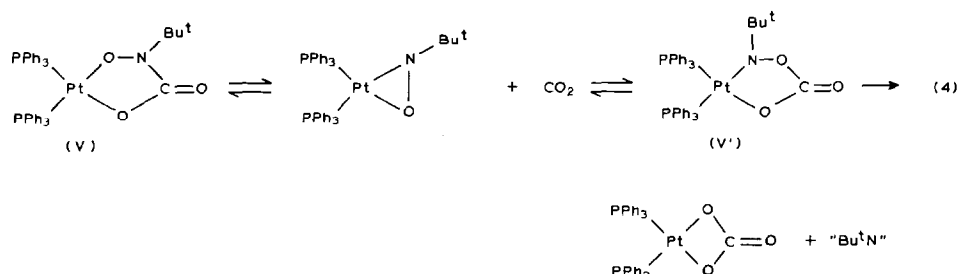
Reaction of Pt(PPh₃)₂(Bu^tNO) (II) with CO₂ in benzene at room temperature gave a ca. 1 : 1 mixture of Pt(PPh₃)₂(CO₃) [15] and of Pt{ON(Bu^t)C(O)O}(PPh₃)₂ (V) (eq. 3):



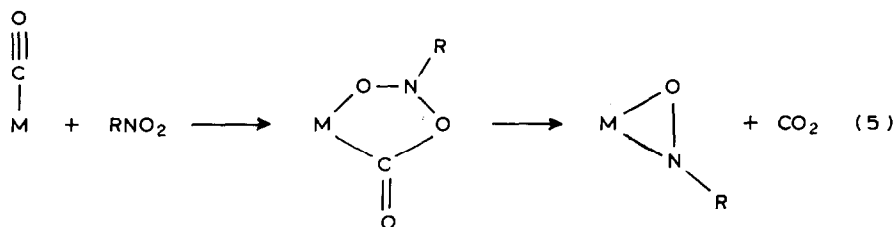
A similar reaction carried out with Pt(PPh₃)₂(CF₃NO) (III) led to isolation of only the carbonato complex Pt(PPh₃)₂(CO₃).

When reaction 3 was carried out at ca. 5°C, nearly pure V, containing traces of $\text{Pt}(\text{PPh}_3)_2(\text{CO}_3)$, was isolated. Compound V is formulated as an insertion product of CO_2 into the Pt–N bond of II on the basis of its IR spectrum, which in the $\nu(\text{CO})$ stretching frequency region is close to that of the insertion product of CO_2 into the Pt–N bond of I [4]. The structure of the latter compound has been confirmed by an X-ray structural study [2].

When compound V was dissolved in benzene at room temperature under a dinitrogen atmosphere, it was slowly and quantitatively transformed into the carbonato complex, $\text{Pt}(\text{PPh}_3)_2(\text{CO}_3)$. Repeated attempts to determine the fate of the Bu^tN nitrene residue in this reaction were unsuccessful. When dinitrogen was bubbled into a benzene suspension of V carbon dioxide was evolved, and compound II was isolated from the solution. These results indicate that the insertion of CO_2 into the Pt–N bond of II is reversible, as it is in the reaction of CO_2 with compound I [4].



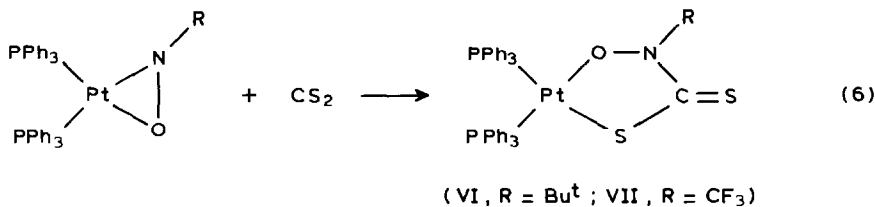
The formation of the carbonato complex in reaction 3 suggests either that the insertion product of CO_2 into the Pt–O bond of II (V') must be present in solution (eq. 4), or that the insertion product with CO_2 (V') is the only compound formed from II and CO_2 . The latter possibility is supported by the observation that with compound III, in which the CF_3 group will reduce the nucleophilic character of the nitrogen of the nitroso ligand, only the carbonato complex was isolated. However several insertion products obtained by reaction of III with CO_2 -like molecules (see later) are derived from the attack of the nitrogen of the nitroso ligand to the electrophilic carbon atom of the entering molecule, as was observed for the analogous reactions of compound I [2,4,5]. The metallocycles obtained by the reactions with CO_2 are of particular interest because they are the isomers of the intermediate postulated in the deoxygenation reactions of nitro compounds by coordinated carbon monoxide [1] (eq. 5):



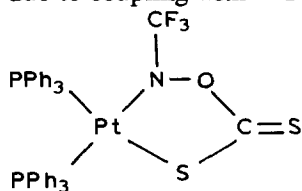
With carbon disulphide

Reaction of II and III with CS_2 led to isolation of the insertion products VI and

VII (eq. 6) (Tables 2 and 3):



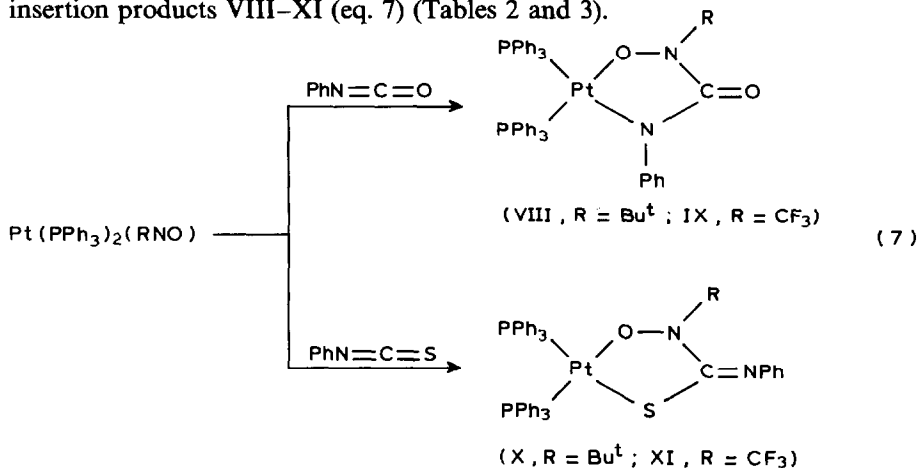
These derivatives show IR bands at 960–980 cm⁻¹, probably due to $\nu(\text{C}=\text{S})$. The ¹⁹F NMR spectrum of VII shows a singlet at -61.97 ppm which has no satellites due to coupling with ¹⁹⁵Pt. This excludes a formulation for VII such as



since in this case coupling with ¹⁹⁵Pt (and even with ³¹P) should be observed, as for compound III. As expected, the ³¹P NMR spectrum of VI shows two *cis* non-equivalent phosphorus atoms, with satellites bands due to coupling with ¹⁹⁵Pt (Table 3). The ³¹P NMR parameters are comparable with those for Pt{ON(Ph)C(S)S}(PPh₃)₂ [4].

With PhN=C=X (X = O, S)

The reaction of compounds II and III with PhN=C=X (X = O, S) gave the insertion products VIII–XI (eq. 7) (Tables 2 and 3).



The X-ray structures of the corresponding insertion products with R = Ph were determined previously, and the reasons for the difference in the reaction of PhNCO (cycloaddition to the C=N bond) and that of PhNCS (cycloaddition to the C=S bond) discussed [5].

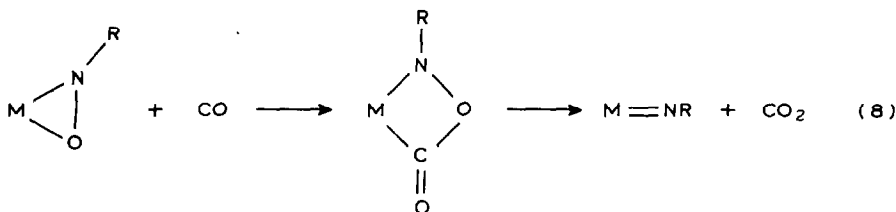
In Pt{ON(Ph)C(O)N(Ph)}(PPh₃)₂, $\nu(\text{CO})$ appears at 1608 cm⁻¹, a low value which was initially attributed to a $\nu(\text{C}=\text{N})$ band [4]. In compounds VIII and IX, the $\nu(\text{CO})$ band appears at 1730 and 1646 cm⁻¹, respectively. Thus in these metallo-

cycles $\nu(\text{CO})$ decreases in the order: $\text{Bu}^t > \text{CF}_3 > \text{Ph}$, and there are no apparent reasons for these marked variations. On the other hand, the ^{31}P NMR spectra of compounds VIII and IX are very similar with that of $\text{Pt}\{\text{ON}(\text{Ph})\text{C}(\text{O})\text{NPh}\}(\text{PPh}_3)_2$ [4]. The ^{19}F NMR spectrum of IX shows a singlet at $\delta -66.6$ ppm, confirming the conclusion that insertion has taken place into the Pt–N and not the Pt–O bond of III.

For compounds X and XI the $\nu(\text{C}=\text{N})$ frequency ($1530\text{--}1570\text{ cm}^{-1}$) and the ^{31}P NMR parameters are again entirely in agreement with those of $\text{Pt}\{\text{ON}(\text{Ph})\text{C}(\text{NPh})\text{S}\}(\text{PPh}_3)_2$ [4]; a singlet was observed at $\delta -66.2$ ppm in the ^{19}F NMR spectrum of XI.

With CO

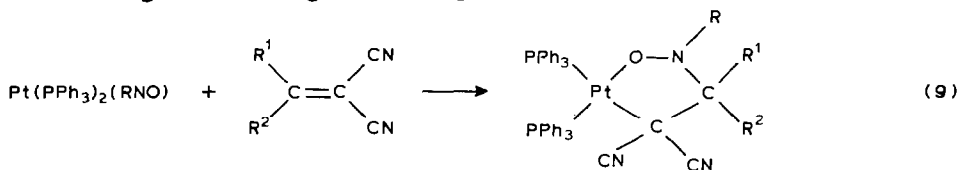
The reactions of compounds I–III with CO were examined carefully, since the reaction of carbon monoxide with a coordinated nitroso compound corresponds to the final stage of the catalytic deoxygenation of nitro compounds [1] (eq. 8):



However the results, from several repeated reactions, were unsatisfactory for several reasons. Firstly, although CO_2 was evolved ($\text{R} = \text{Ph}, \text{CF}_3$) its amount was always less than that required by the stoichiometry of the reaction. Secondly, the only platinum derivative obtained was a known cluster carbonyl containing no nitrogen, viz. $\text{Pt}_3(\text{CO})_3(\text{PPh}_3)_x$ ($x = 3$ and/or 4) [16]. Finally the fate of the RN nitrene residue was not established. The carbonylation of III gave a product showing a strong IR absorption at 2220 cm^{-1} , which must be attributed to a NCO group directly bonded to platinum, since no absorptions due to $\nu(\text{CF})$ were detected. The intermediate proposed in eq. 8 is not consistent with the results previously reported, since we always observed an attack of the nucleophilic centre in I–III, that is the nitrogen atom, on the electrophilic carbon of the entering molecule, except possibly for the reaction with CO_2 (see above). Reaction with CO of a σ -nitrogen-bonded nitroso ligand in equilibrium with the η^2 -bonded nitroso compound could perhaps account for the results obtained [1].

With alkenes and dimethylacetylenedicarboxylate

Reaction of compounds II and III with alkenes activated by strong electron-withdrawing substituents gave the complexes XII–XIV (eq. 9) (Tables 2 and 3):



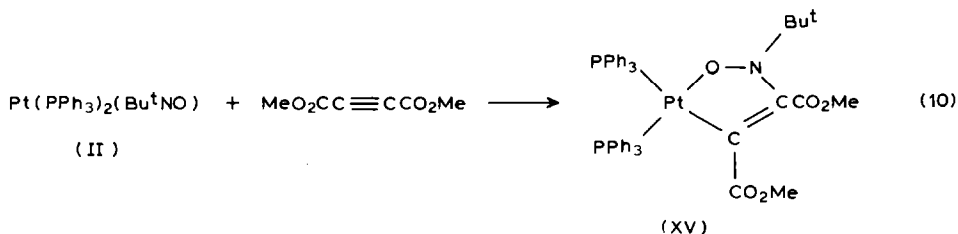
(XII, $\text{R} = \text{Bu}^t$, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$;

XIII, $\text{R} = \text{CF}_3$, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$;

XIV, $\text{R} = \text{CF}_3$, $\text{R}^1 = \text{R}^2 = \text{CN}$)

Compounds XIII and XIV show the usual singlet in the ^{19}F NMR spectrum, while the Pt–H(R^2) coupling constant observed in the ^1H NMR spectrum of XII indicates that the carbon bearing this atom is not directly bonded to platinum [3]. Compound XIV proved to be particularly stable, and was recovered unchanged after prolonged refluxing of its benzene solution. Transfer of the nitrene residue to the inserted alkene should give the corresponding aziridine and a metal oxo derivative [3].

An insertion product (XV) was also obtained from the reaction of II with dimethyl acetylenedicarboxylate (eq. 10) (Tables 2 and 3). The IR, ^1H and ^{31}P NMR data for compound XV are very similar to those observed for the analogous insertion product obtained by reaction of I with $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ [3].



Reactions of $\text{Pd}(\text{PPh}_3)_2(\text{CF}_3\text{NO})$ (IV)

In order to see where not only the substituents in the nitroso ligand but also the metal influence the reactivity of η^2 -bonded nitroso complexes, we also initiated a study of the reactions of $\text{Pd}(\text{PPh}_3)_2(\text{CF}_3\text{NO})$ (IV). We were rather surprised to find that compound IV does not react with CO and CO_2 under the conditions used for compounds I–III. It does react with PhNCO , but give a product which has not yet been fully characterized. Further studies of the reactions of IV are planned.

Experimental

Magnetic stirring was used in all reactions. The complexes $\text{Pt}(\text{PPh}_3)_3$ and $\text{Pt}(\text{PPh}_3)_2(\text{CH}_2=\text{CH}_2)$ were prepared as described previously [17,18]. The CF_3NO and Bu^tNO were commercial products (Aldrich and Merck, respectively). All reactions were carried out under dinitrogen in dried solvents.

Elemental analyses were carried out by the Analytical Laboratories of Milan University. Infrared spectra were recorded on a Beckman IR 4210 spectrophotometer. The ^1H and ^{31}P NMR spectra were recorded on a Bruker VP-80 spectrometer, with SiMe_4 and 85% H_3PO_4 , respectively, as external standards. ^{19}F NMR spectra were recorded on a Varian XL 300 and Varian XL 200 with CFCl_3 as internal standard. All compounds were stored under dinitrogen.

$\text{Pt}(\text{PPh}_3)_2(\text{Bu}^t\text{NO}) \cdot 0.5\text{C}_6\text{H}_6$ (II)

A solution of $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ (300 mg) in benzene (15 ml) degassed with dinitrogen was cooled in a dry ice-acetone bath and Bu^tNO (100 mg) was added. The solution was kept in the dark and allowed to warm slowly to room temperature. After 5 h the green solution was evaporated to ca. half its volume, and n-hexane was added to produce a yellow-green precipitate. This was filtered off under dinitrogen, washed with n-hexane, degassed with dinitrogen, and dried in vacuo.

Pt(PPh₃)₂(CF₃NO) (III)

Gaseous CF₃NO was bubbled for about 5 min into dry diethyl ether (30 ml) (any of the gas emerging being bubbled into a KOH solution). Pt(PPh₃)₃ (1 g) was added, and after few minutes the bubbling was stopped. After 5 h the yellow precipitate was filtered off, washed with diethyl ether, and dried in vacuo.

Pd(PPh₃)₂(CF₃NO) (IV)

Gaseous CF₃NO was bubbled for 5 min into dry diethyl ether (20 ml) (any emerging gas again being bubbled into a KOH solution.) The Pd(PPh₃)₄ (311 mg) was added, and after few minutes the bubbling was stopped. After 5 h the yellow-orange product was filtered off under dinitrogen, washed with diethyl ether, degassed with dinitrogen, and dried in vacuo.

Pt{ON(Bu¹)C(O)O}(PPh₃)₂ (V)

Dinitrogen and CO₂ were bubbled through benzene (25 ml), cooled in ice, and Pt(PPh₃)₂(Bu¹NO) (490 mg) was then added. After 45 min the suspended solid was filtered under dinitrogen, washed with benzene, degassed with CO₂, and dried in vacuo. The yellow-orange compound obtained contained a little of the carbonato complex Pt(PPh₃)₂(CO₃).

When the reaction was carried out at room temperature gave the carbonato complex in an amount comparable to that of the insertion product V.

When a similar procedure (at 0 °C) was carried out in THF but with the complex Pt(PPh₃)₂(CF₃NO), the carbonato complex Pt(PPh₃)₂(CO₃) was the only product.

Pt{ON(Bu¹)C(S)S}(PPh₃)₂ (VI)

A solution of CS₂ (188 mg) in CH₂Cl₂ (10 ml) was degassed with dinitrogen and Pt(PPh₃)₂(Bu¹NO) (200 mg) was added. After 4 h the orange solution was evaporated to half its volume and n-hexane was added to give a yellow orange precipitate. This was filtered off under dinitrogen, washed with n-hexane, and dried in vacuo.

Pt{ON(CF₃)C(S)S}(PPh₃)₂ (VII)

A solution of CS₂ (185 mg) in CH₂Cl₂ was degassed with dinitrogen (10 ml) and Pt(PPh₃)₂(CF₃NO) (200 mg) was added. After 4 h the yellow solution was evaporated to half its volume and n-hexane was added to give the yellow precipitate. This was filtered off, washed with n-hexane, and dried in vacuo; it was recrystallized from CH₂Cl₂/n-hexane under dinitrogen.

Pt{ON(Bu¹)C(O)NPh}(PPh₃)₂ · C₆H₆ (VIII)

To Pt(PPh₃)₂(Bu¹NO) (300 mg) was added a solution of PhNCO (133 mg) in benzene (18 ml) degassed with dinitrogen. After 3.5 h the red-orange solution was evaporated to small volume and n-hexane was added to give a yellow-orange precipitate. This was filtered off under dinitrogen, washed with n-hexane, and isopropyl ether, and dried in vacuo. It was recrystallized from benzene/n-hexane under dinitrogen.

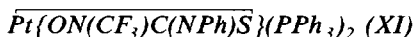
Pt{ON(CF₃)C(O)NPh}(PPh₃)₂ (IX)

To Pt(PPh₃)₂(CF₃NO) (325 mg) was added a solution of PhNCO (142 mg) in benzene (20 ml) degassed with dinitrogen. After 4 h the pale-yellow product was

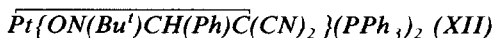
filtered off under dinitrogen, washed with benzene, and dried in vacuo. It was recrystallized from benzene/n-hexane under dinitrogen.



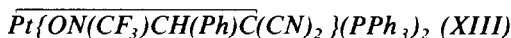
To $Pt(PPh_3)_2(Bu^1NO)$ (180 mg) was added a solution of $PhNCS$ (90.5 mg) in benzene (12 ml). After 4 h the red-orange solution was evaporated to small volume, and n-hexane, was added, to give an orange precipitate. This was filtered off, washed with n-hexane, and dried in vacuo. It was recrystallized from benzene/n-hexane under dinitrogen.



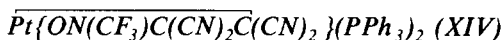
To $Pt(PPh_3)_2(CF_3NO)$ (194 mg) was added a solution of $PhNCS$ (96 mg) in benzene (18 ml). After 3.5 h the yellow solution was evaporated to small volume and n-hexane degassed with dinitrogen was added to give a yellow precipitate. This was filtered off under dinitrogen, washed with n-hexane, and dried in vacuo. It was recrystallized from benzene/n-hexane under dinitrogen.



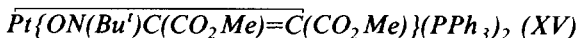
Benzene (20 ml) was added to a mixture of $Pt(PPh_3)_2(Bu^1NO)$ (300 mg) and $PhCH=C(CN)_2$ (115 mg). After 3.5 h the yellow solution was evaporated to small volume and n-hexane was added to give a yellow precipitate. This was filtered off, washed with n-hexane, and dried in vacuo. It was recrystallized from benzene/n-hexane under dinitrogen.



Benzene (30 ml) was added to a mixture of $Pt(PPh_3)_2(CF_3NO)$ (300 mg) and $PhCH=C(CN)_2$ (113 mg). After 3.5 h the yellow solution was evaporated to small volume and n-hexane was added to give a white precipitate. This was filtered off, washed with n-hexane, and dried in vacuo. It was recrystallized from benzene/n-hexane under dinitrogen.



Benzene (20 ml), degassed with N_2 , was added to a mixture of $Pt(PPh_3)_2(CF_3NO)$ (300 mg) and $(CN)_2C=C(CN)_2$ (59 mg). After 3 h a yellow precipitate was filtered off under dinitrogen, washed with benzene, and dried in vacuo. It was recrystallized from CH_2Cl_2 /n-hexane under dinitrogen.



To a solution of $Pt(PPh_3)_2(Bu^1NO)$ (308 mg) in benzene (20 ml) was added a solution of $MeO_2CC\equiv CCO_2Me$ (108 mg) in benzene (5 ml). After 3 h the orange solution was evaporated to small volume and n-hexane was added to give an orange precipitate. This was filtered off, washed with n-hexane, and dried in vacuo. It was recrystallized from benzene/n-hexane under dinitrogen.



CO was bubbled through benzene (20 ml) for few minutes and $Pt(PPh_3)_2(RNO)$ was then added (ca. 300 mg). The gas evolved was bubbled into a solution of

Table 4

Crystal data and intensity collection parameters

Compound	Pt(PPh ₃) ₂ (PhNO) (I)
Formula	C ₄₂ H ₃₅ NOP ₂ Pt
FW (amu)	826.79
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (nr. 14)
<i>a</i> (Å)	14.228(4)
<i>b</i> (Å)	13.914(3)
<i>c</i> (Å)	17.855(4)
β (°)	100.31(2)
<i>U</i> (Å ³)	3478(3)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.579
μ (Mo- <i>K</i> α) (cm ⁻¹)	41.99
Min. transmission factor	0.93
Crystal dimensions (mm)	0.12 × 0.13 × 0.15
Scan mode	ω
ω -scan width (°)	1.0 + 0.35 tan θ
θ -range (°)	3–24
Octants of reciprocal space explored	$\pm h, +k, +l$
Measured reflections	6086
Unique observed reflections with $I > 3\sigma(I)$	3609
final <i>R</i> and <i>R</i> _w indices ^a	0.026, 0.030
No. of variables	424
ESD ^b	0.957

^a $R = [\sum(F_0 - k|F_c|)/\sum F_0]$; $R_w = [\sum w(F_0 - k|F_c|)^2/\sum wF_0^2]^{1/2}$. ^b $ESD = [\sum w(F_0 - k|F_c|)^2/(NO - NV)]^{1/2}$.

Ba(OH)₂ to permit detection of CO₂. After 17 h (R = Bu¹) the solution was evaporated to small volume, then n-hexane was added to give an orange precipitate. No formation of CO₂ was observed. The orange compound was filtered off, washed with n-hexane and dried in vacuo. Its IR data and elemental analysis were consistent with the formulation Pt₃(CO)₃(PPh₃)_x (*x* = 3 or 4) [16]. The same orange compound was obtained from the carbonylation of Pt(PPh₃)₂(RNO) (R = Ph, CF₃). In the latter case, however, CO₂ was detected among the products.

Structure determination

Crystal data and details of the procedures used in determination of the structure of compound I are summarized in Table 4. The diffraction experiments were carried out on an Enraf–Nonius CAD-4 diffractometer at room temperature using Mo-*K* α radiation (λ 0.71073 Å). The unit cell parameters were determined by least-squares refinement of the setting angles of 25 high- θ reflections. The diffraction intensities were corrected for Lorentz, polarization, and absorption (empirical correction [19]). Anomalous dispersion corrections for atomic scattering factors were taken from ref. 20. The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares, the minimized function being $\sum w(F_0 - k|F_c|)^2$. Weights assigned to individual observations were $w = 1/(\sigma F_0)^2$ where $\sigma(F_0) = [\sigma^2(I) + (0.04 \cdot I)^2]^{1/2}/2F_0Lp$. In the last cycles of the refinement the hydrogen

Table 5
Positional parameters for non-hydrogen atoms with esd's in parentheses

Atom	x	y	z
Pt	0.18106(2)	0.01681(2)	0.24540(1)
P(1)	0.2929(1)	0.0243(1)	0.35083(8)
P(2)	0.0804(1)	0.1422(1)	0.25127(9)
O	0.1346(3)	-0.0526(4)	0.1456(3)
N	0.2173(4)	-0.1000(4)	0.1832(3)
C(1)	0.2972(5)	-0.0763(4)	0.1500(3)
C(2)	0.2974(6)	-0.0102(5)	0.0923(4)
C(3)	0.3812(7)	0.0059(5)	0.0644(4)
C(4)	0.4638(6)	-0.0425(7)	0.0919(5)
C(5)	0.4632(6)	-0.1092(6)	0.1480(5)
C(6)	0.3809(5)	-0.1273(5)	0.1764(4)
C(111)	0.4090(4)	0.0416(4)	0.3229(3)
C(112)	0.4175(5)	0.1111(5)	0.2685(4)
C(113)	0.5049(6)	0.1267(6)	0.2457(5)
C(114)	0.5821(5)	0.0723(6)	0.2750(4)
C(115)	0.5743(5)	0.0023(5)	0.3282(4)
C(116)	0.4891(5)	-0.0119(5)	0.3515(4)
C(121)	0.2949(5)	0.1123(4)	0.4277(3)
C(122)	0.3746(5)	0.1681(5)	0.4540(4)
C(123)	0.3763(7)	0.2284(6)	0.5156(5)
C(124)	0.2973(7)	0.2366(5)	0.5496(4)
C(125)	0.2174(6)	0.1830(6)	0.5234(4)
C(126)	0.2163(5)	0.1209(5)	0.4635(4)
C(131)	0.3050(4)	-0.0897(4)	0.4023(4)
C(132)	0.3457(5)	-0.0967(5)	0.4792(4)
C(133)	0.3564(6)	-0.1844(5)	0.5152(4)
C(134)	0.3279(6)	-0.2663(5)	0.4762(5)
C(135)	0.2881(7)	-0.2626(5)	0.3995(5)
C(136)	0.2755(5)	-0.1744(5)	0.3626(4)
C(211)	0.1320(5)	0.2549(4)	0.2912(4)
C(212)	0.2058(5)	0.2939(5)	0.2587(5)
C(213)	0.2491(6)	0.3782(6)	0.2876(6)
C(214)	0.2220(7)	0.4220(6)	0.3497(6)
C(215)	0.1513(7)	0.3842(6)	0.3819(5)
C(216)	0.1055(6)	0.3003(5)	0.3530(4)
C(221)	0.0183(4)	0.1761(5)	0.1561(3)
C(222)	-0.0066(6)	0.2700(5)	0.1355(4)
C(223)	-0.0530(6)	0.2895(5)	0.0622(4)
C(224)	-0.0785(6)	0.2180(6)	0.0098(4)
C(225)	-0.0553(7)	0.1254(6)	0.0309(4)
C(226)	-0.0079(6)	0.1042(6)	0.1034(4)
C(231)	-0.0172(4)	0.1168(4)	0.3019(3)
C(232)	-0.0145(4)	0.0349(4)	0.3452(4)
C(233)	-0.0874(5)	0.0137(5)	0.3850(4)
C(234)	-0.1644(5)	0.0755(5)	0.3801(4)
C(235)	-0.1678(5)	0.1559(5)	0.3369(4)
C(236)	-0.0955(5)	0.1787(5)	0.2969(4)

atoms were included at calculated positions with C-H 0.95 Å. All the computations were carried out on a PDP 11/34 computer using the Enraf-Nonius SDP package of programs [21].

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