# Insertion of Unsaturated Hydrocarbons into the Platinum–Nitrogen Bond of $[Pt(PPh_3)_2(PhNO)]$

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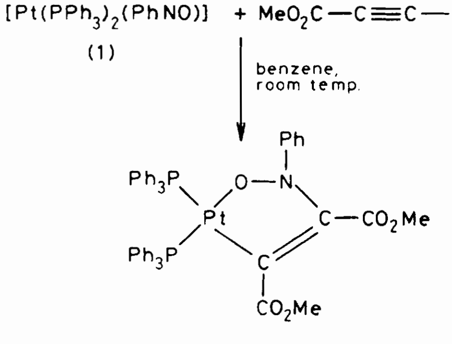
$[Pt(PPh_3)_2(PhNO)]$ (1) reacts with unsaturated hydrocarbons such as dimethyl acetylenedicarboxylate, tetracyanoethylene, and β,β-dicyanostyrene to give the corresponding 1 : 1 adducts $[Pt\{ON(Ph)C(CO_2Me)=C(CO_2Me)\}(PPh_3)_2]$ (2) and $[Pt\{ON(Ph)CR^1R^2C(CN)_2\}(PPh_3)_2]$ [$R^1 = R^2 = CN$ (3); $R^1 = H$, $R^2 = Ph$ (4)], respectively. Fumaronitrile (NCCH=CHCN) reacts with (1) to give a mixture of the 1 : 1 adduct and of the substitution product, $[Pt(PPh_3)_2(NCCH=CHCN)]$, while *p*-benzoquinone gave only $[Pt(PPh_3)_2(OC_6H_4O\text{-}p)]$. *X*-Ray studies on compound (2) have confirmed that the entering molecule is inserted into the platinum–nitrogen bond of the $\eta^2$-bonded nitroso-ligand of compound (1). The reactions of (2) with mineral acids have been studied. I.r., $^1H$ n.m.r., and $^{31}P$ n.m.r. spectra of the new compounds are reported and discussed.

The metal promoted C–N bond formation between amines and alkenes has been extensively investigated. Recently the C–N bond formation within the co-ordination sphere of a transition metal has been achieved by using nitroso-compounds as the nitrogen source.[1–3] In the reactions of molybdenum [1] and niobium [2] aryl- and alkyl-nitroso-derivatives with alkenes, the transfer of the RN residue of the $\eta^2$-bonded nitroso-ligand to the olefin was observed, a reaction favoured by the oxophilic character of these metals in a high oxidation state. On the other hand, 2-methyl-2-nitrosopropane gives a σ-alkylnitrone complex by reaction with ethylene co-ordinated to platinum(II).[3] As a continuation of our investigations on the complexes having a metal–nitrogen bond,[4–6] we have studied the reactions of $[Pt(PPh_3)_2(PhNO)]$ (1), having a $\eta^2$-bonded nitroso-ligand, with unsaturated hydrocarbons. In a preliminary report, the insertion reactions of carbon dioxide and of carbon disulphide with compound (1) have also been reported, and the *X*-ray crystal structure determination carried out on $[Pt\{ON(Ph)C(O)O\}(PPh_3)_2]$ has established that carbon dioxide is inserted into the platinum–nitrogen bond of (1).[7]

## Results and Discussion

Compound (1), formally a platinum(0) derivative, can be obtained from $[Pt(PPh_3)_2(C_2H_4)]$ and nitrosobenzene,[8] and no reaction is observed between the alkene and the nitroso-ligand. It can be obtained more conveniently from $[Pt(PPh_3)_3]$ (see Experimental section). Compound (1) readily reacts with an activated alkyne such as dimethyl acetylenedicarboxylate, to give the 1 : 1 adduct (2) [Table, equation (i)].



(i)

(2)

The structure of the yellow complex (2) suggested in equation (i) has been confirmed by an *X*-ray structural determination. The co-ordination around platinum is square planar, with the alkyne inserted into the platinum–nitrogen bond of the $\eta^2$-bonded arylnitroso-ligand.[9]

Compound (2) shows the expected absorptions in the i.r., $^1H$ n.m.r., and $^{31}P$ n.m.r. spectra. It shows $\nu_{max.}$ at 1 725 (C=O), 1 655 (C=C), 1 210 (C–O), and 900 $cm^{-1}$ (N–O). In its $^1H$ n.m.r. spectrum two distinct signals in 1 : 1 ratio were observed at δ 3.65 and 2.35, attributable to the methyl groups in different chemical environments. The $^{31}P$ n.m.r. spectrum shows an AX type multiplet with $^{195}Pt$ satellites [$\delta(P^1) = 14.9$ for P *trans* to oxygen, $\delta(P^2) = 30.48$ for P *trans* to carbon, downfield from external 85% $H_3PO_4$; $J(P^1\text{–}P^2) = 19.5$, $J(Pt\text{–}P^1) = 3\,851$, $J(Pt\text{–}P^2) = 2\,275$ Hz]. The strong *trans* labilizing influence of the olefinic carbon in compound (2) is confirmed not only by the marked low-field shift of $P^2$ and by the small coupling constant with $^{195}Pt$, but also by the long $Pt\text{–}P^2$ distance [2.307(4) Å] with respect to $Pt\text{–}P^1$ [2.239(4) Å].[9]

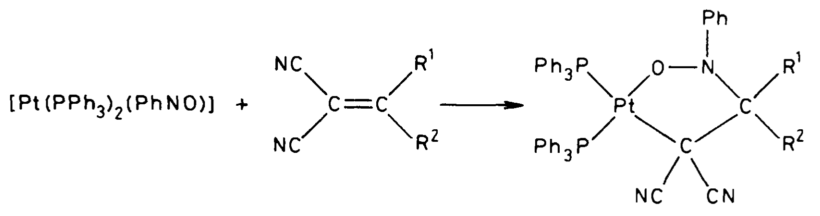
Compound (2) was recovered unchanged after a prolonged reflux in toluene under a nitrogen atmosphere or by treatment with carbon monoxide in chloroform solution. However, when it was repeatedly crystallized from hydrocarbon solutions, a complex (2a), with marked differences in the i.r. spectrum but with elemental analyses identical to those of (2) was isolated. In particular, $\nu_{max.}$ for the olefinic bond was observed at 1 698 $cm^{-1}$. However, compounds (2) and (2a) exhibit the same i.r. spectrum when dissolved in benzene or chloroform. The differences in the solid state may be due to changes in the conformation of the metallocycle or to different packing of molecules in the crystal lattices. Accordingly, compounds (2) and (2a) show the same $^1H$ n.m.r. spectrum at room temperature; $^1H$ n.m.r. spectra of (2) from −90 to +112 °C did not show any significant change of the methyl resonances. The i.r. spectrum of the crystals employed for the *X*-ray structure determination was identical to that of (2).

Compound (1) does not react with methylphenylacetylene. It does, however, react with hexafluorobut-2-yne, to give a mixture of products. In this mixture, $[Pt(PPh_3)_2(CF_3C{\equiv}CCF_3)]$ [10] was not present (absence of i.r. absorptions in the region 1 650—1 800 $cm^{-1}$). The need for a strongly electrophilic carbon atom in order that N–C bond formation should be promoted by (1) is confirmed by the fact that compound (1) does not react with β-cyano-β-phenylstyrene, but more activated alkenes such as tetracyanoethylene and β,β-dicyanostyrene are readily inserted to give the corresponding 1 : 1 adducts (3) and (4) [Table, equation (ii)].

**Table.** Physical and analytical data

| Complex | M.p. ($\theta_c$/°C) | Colour | Analysis[a] (%) | | |
|---|---|---|---|---|---|
| | | | C | H | N |
| (2) $[Pt\{ON(Ph)C(CO_2Me)=C(CO_2Me)\}(PPh_3)_2]\cdot0.5C_6H_6$ | 218—220 | Yellow | 60.4 (60.8) | 4.6 (4.4) | 1.4 (1.4) |
| (2a) $[Pt\{ON(Ph)C(CO_2Me)=C(CO_2Me)\}(PPh_3)_2]\cdot0.5C_6H_6$ | 228 | Yellow | 60.4 (60.8) | 4.4 (4.4) | 1.4 (1.4) |
| (3) $[Pt\{ON(Ph)C(CN)_2C(CN)_2\}(PPh_3)_2]$ | 180 | White | 59.8 (60.4) | 3.8 (3.7) | 7.2 (7.3) |
| (4) $[Pt\{ON(Ph)CH(Ph)C(CN)_2\}(PPh_3)_2]\cdot0.5C_6H_6$ | 155 | Pale yellow | 64.9 (64.8) | 4.5 (4.4) | 4.4 (4.1) |
| (5) $[Pt\{ONH(Ph)C(CO_2Me)=C(CO_2Me)\}(PPh_3)_2]BF_4$[b] | 182 | White | 54.1 (54.6) | 4.0 (4.0) | 1.4 (1.3) |

[a] Calculated values are given in parentheses. [b] $\Lambda_M$ = 26.0 cm$^2$ mol$^{-1}$ in nitrobenzene.



(ii)

(3) $R^1 = R^2 = CN$
(4) $R^1 = H, R^2 = Ph$

The $^1H$ n.m.r. spectrum of compound (4) shows the resonance of the proton $R^1$ at $\delta$ 4.7 as a quartet, due to coupling with two non-equivalent phosphorus atoms, and with $^{195}Pt$ satellites [$J(Pt-H)$ = 41.3, $J(P^1-H)$ = 2.0, $J(P^2-H)$ = 3.6 Hz]. These n.m.r. data suggest that the carbon bearing the hydrogen atom is not directly bound to platinum.[11,12] This is also in agreement with the structure proposed for the corresponding 1 : 1 adduct obtained from $[Pt(PPh_3)_2(O_2)]$ and $PhCH=C(CN)_2$.[13]

Compound (4) could be also described as a complex having a C–O instead of a C–N bond. However, the known structures of two related compounds, the $CO_2$ insertion product [7] and compound (2), have shown that nitrogen is the nucleophilic centre in (1). The $^{31}P$ n.m.r. spectrum of (4) shows the expected AX type multiplet with $^{195}Pt$ satellites [$\delta(P^1)$ 7.81 for P *trans* to oxygen, $\delta(P^2)$ 20.46 for P *trans* to carbon, downfield from external 85% $H_3PO_4$; $J(P^1-P^2)$ = 20.1, $J(Pt-P^1)$ = 3 365, $J(Pt-P^2)$ = 2 855 Hz]. The coupling constant for $P^1$ *trans* to oxygen in (4) is close to that observed for compound (2). On the other hand, the $^{31}P$ n.m.r. spectrum of (1) has shown $\delta(P^1)$ 17.01 [$J(Pt-P^1)$ = 3 919 Hz] and $\delta(P^2)$ 16.3 [$J(Pt-P^2)$ = 4 784 Hz], suggesting that $P^1$ is *trans* to oxygen, and that phosphorus *trans* to nitrogen requires a much higher coupling constant with platinum. On the basis of the observed $\delta(P^2)$ and $J(Pt-P^2)$ in compound (4), a less *trans* labilizing influence of the alkane carbon in (4) with respect to the alkene carbon in (2) can be suggested.

When reaction (ii) was conducted with fumaronitrile, NCCH=CHCN, the corresponding 1 : 1 adduct was obtained. However, it was in a mixture with the substitution product, $[Pt(PPh_3)_2(NCCH=CHCN)]$,[14] as seen by the i.r., $^1H$ n.m.r., and $^{31}P$ n.m.r. spectra. The n.m.r. spectra are also complicated by other absorptions, since when left in chloroform solution this mixture further reacts to give unidentified products, showing in the i.r. spectral bands due to a CN group directly bound to the metal. This behaviour was also observed for the tetracyanoethylene derivative (3). This compound, which is insoluble in the common solvents and shows $\nu_{max.}$ at 2 225 cm$^{-1}$ (CN), when left in a chloroform suspension at reflux gave a new soluble material, showing $\nu_{max.}$ at 2 223 and 2 152 (CN), and 1 675vs cm$^{-1}$, besides other by-products.

Finally, when reaction (2) was conducted with *p*-benzoquinone, only the substitution product, $[Pt(PPh_3)_2(OC_6H_4O\text{-}p)]$ [15] was obtained.

Compound (2) reacts with tetrafluoroboric acid, to give the cationic complex (5) [equation (iii)]. The site of protonation is probably the nitrogen atom of the metallocycle.

$$\underset{(2)}{[Pt\{ON(Ph)C(CO_2Me)=C(CO_2Me)\}(PPh_3)_2]} \underset{NEt_3}{\overset{HBF_4}{\rightleftharpoons}} \underset{(5)}{[Pt\{ONH(Ph)C(CO_2Me)=C(CO_2Me)\}(PPh_3)_2]BF_4} \quad (iii)$$

However, in the i.r. spectrum no bands were observed in the region 3 500—3 050 cm$^{-1}$, and by treatment of (5) with $D_2O$ no significant changes were observed for the i.r. absorptions. Other structures could be proposed for compound (5), *e.g.* $[Pt\{ON(Ph)C(CO_2Me)=CHC(OMe)O\}(PPh_3)_2]BF_4$. However, this reaction is reversible, and by treatment of (5) with $NEt_3$ compound (2a) was readily obtained. This suggests that in the protonation reaction there is no substantial change in the structure of the metallocycle. The i.r. absorptions of (5) in the region 1 800—1 600 cm$^{-1}$ are similar to those of (2a) (see Experimental section). The $^1H$ n.m.r. spectrum of (5) in $CDCl_3$ is rather complex. Two distinct signals in 1 : 1 ratio were observed at $\delta$ 3.57 and 3.41, attributable to the methyl groups. Other small signals were observed in the region $\delta$ 3.6—3.8, and at $\delta$ 2.17; the low-field signals change or disappear on treatment with $D_2O$. Moreover, the region $\delta$ 4—7 is clear, supporting the view that olefinic protons are absent in compound (5).

When (2) or (2a) was treated with gaseous hydrochloric acid in benzene, *cis*-$[Pt(PPh_3)_2Cl_2]$ was obtained, together with two organic materials which we were unable to obtain in analytically pure form (see Experimental section).

## Conclusions

Complexes (3) and (4) are model compounds for intermediates which lead to aziridines and metal–oxo-derivatives,[2] and confirm the importance of metallocycle derivatives for the transfer of ligands to organic substrates. The formation of the aziridine has not been observed with the platinum complexes here reported, since the metal has not enough oxophilic character to promote them.

It is worth mentioning our observation that (hexamethylphosphoramide)oxo(*N*-phenylhydroxylamido-*ON*)(pyridine-2,6-dicarboxylato)molybdenum(VI) does not react with tetracyanoethylene and dimethyl acetylenedicarboxylate at room temperature, while analogous molybdenum compounds transfer on heating the RN residue of the nitroso-ligand to simple alkenes, to yield allylic amines, however, rather than the expected aziridines.[1] This may be due on the one hand to the absence of the vacant site at the molybdenum centre, and on the other hand to the fact that the transfer of the nitrene residue from molybdenum to the alkene does not proceed *via* a metallocycle similar to (3) or (4).

## Experimental

All reactions were carried out under an atmosphere of pure nitrogen, unless stated otherwise, with magnetic stirring. Solvents were dried and purified. The starting complex $[Pt(PPh_3)_2(PhNO)]$ was prepared and described in the literature [8] or by a simplified procedure as reported below.

Dimethyl acetylenedicarboxylate, tetracyanoethylene and fumaronitrile were commercial products while β,β-dicyanostyrene was prepared as described below. Infrared spectra were recorded on a Beckman i.r. 4210 spectrophotometer. Hydrogen-1 and phosphorus-31 n.m.r. spectra were recorded on a Brucker VP-80 spectrometer, with $SiMe_4$ as internal standard and 85% $H_3PO_4$ as external standard respectively. Elemental analyses were carried out in the analytical laboratories of Milan University.

$PhCH{=}C(CN)_2$.—PhCHO (5.23 g) and $CH_2(CN)_2$ (1.32 g) were stirred until a clear solution was obtained. Piperidine (three drops) was then added. After 30 min an orange gelatinous suspension was formed. The white product was filtered off and crystallized from boiling ligroin (88% yield), m.p. 83 °C (Found: C, 77.9; H, 4.0; N, 18.4. Calc. for $C_{10}H_6N_2$: C, 77.9; H, 3.9; N, 18.2%). I.r. (Nujol): $\nu_{max.}$ at 2 230 (CN) and 1 565 cm$^{-1}$ (C=C).

$[Pt(PPh_3)_2(PhNO)]$ (1).—To $[Pt(PPh_3)_3]$ (2 g) and PhNO (0.24 g), diethyl ether (150 cm$^3$) was added. After 1 h the yellow precipitate was filtered off, washed with diethyl ether and dried *in vacuo* (69% yield), m.p. 166 °C. I.r. (Nujol): $\nu_{max.}$ at 975 cm$^{-1}$ (NO). Phosphorus-31 n.m.r. spectrum ($CDCl_3$): δ($P^1$) 17.01, δ($P^2$) 16.3; $J(P^1{-}P^2)$ = 8.5, $J(Pt{-}P^1)$ = 3 919, $J(Pt{-}P^2)$ = 4 784 Hz. This procedure avoids the transformation of $[Pt(PPh_3)_3]$ into $[Pt(PPh_3)_2(O_2)]$ and the subsequent reduction with $NaBH_4$ in the presence of ethylene to give $[Pt(PPh_3)_2(C_2H_4)]$, before the reaction with PhNO.[8]

$[Pt\{ON(Ph)C(CO_2Me){=}C(CO_2Me)\}(PPh_3)_2]{\cdot}0.5C_6H_6$ (2).—To a solution of $[Pt(PPh_3)_2(PhNO)]$ (1) in benzene (20 cm$^3$), $MeO_2C{-}C{\equiv}C{-}CO_2Me$ (0.086 g), dissolved in benzene (5 cm$^3$) was added. After 3 h the solution was evaporated to *ca.* half the volume and n-hexane was added. The yellow precipitate was filtered off, washed with n-hexane and dried *in vacuo* (75% yield). I.r. (Nujol): $\nu_{max.}$ at 1 725 (C=O), 1 655 (C=C), 1 210 (C–O), and 900 cm$^{-1}$ (NO). Hydrogen-1 n.m.r. spectrum ($CDCl_3$): δ($CH_3$) 3.65 and 2.35. Phosphorus-31 n.m.r. spectrum ($CDCl_3$): δ($P^1$) 14.9, δ($P^2$) 30.48; $J(P^1{-}P^2)$ = 19.5, $J(Pt{-}P^1)$ = 3 851, $J(Pt{-}P^2)$ = 2 275 Hz.

After repeated crystallizations of (2) from benzene–n-hexane a yellow compound (2a) showing $\nu_{max.}$ at 1 720 (C=O) and 1 698 cm$^{-1}$ (C=C) in the i.r. spectrum, was obtained. Its elemental analyses were practically coincident with those of (2) (Table).

$[Pt\{ON(Ph)C(CN)_2C(CN)_2\}(PPh_3)_2]$ (3).—To $[Pt(PPh_3)_2(PhNO)]$ (1) (0.3 g) and tetracyanoethylene (0.058 g), benzene (20 cm$^3$) was added. The initial brown solution rapidly became a green suspension. After 2 h the solution was evaporated to *ca.* half the volume, and the white precipitate was filtered off, washed with n-hexane and dried *in vacuo* (75% yield). I.r. (Nujol): $\nu_{max.}$ at 2 225 (CN) and 930 cm$^{-1}$ (NO).

$[Pt\{ON(Ph)CH(Ph)C(CN)_2\}(PPh_3)_2]{\cdot}0.5C_6H_6$ (4).—To $[Pt(PPh_3)_2(PhNO)]$ (1) (0.3 g) and $PhCH{=}C(CN)_2$ (0.112 g), benzene (30 cm$^3$) was added. After 5 h the solution was evaporated to *ca.* half the volume and n-hexane was added. The pale yellow precipitate was filtered off, washed with n-hexane, crystallized from benzene–n-hexane, and dried *in vacuo* (86% yield). I.r. (Nujol): $\nu_{max.}$ at 2 210 cm$^{-1}$ (CN). Hydrogen-1 n.m.r. spectrum ($CD_2Cl_2$): δ($R^1$ = H) 4.7; $J(P^1{-}H)$ = 2.0, $J(P^2{-}H)$ = 3.6, $J(Pt{-}H)$ = 41.3 Hz. Phosphorus-31 n.m.r. spectrum ($CDCl_3$): δ($P^1$) 7.81, δ($P^2$) 20.46; $J(P^1{-}P^2)$ = 20.1, $J(Pt{-}P^1)$ = 3 365, $J(Pt{-}P^2)$ = 2 855 Hz.

*Reaction between* (1) *and* $NCCH{=}CHCN$.—To $[Pt(PPh_3)_2(PhNO)]$ (1) (0.25 g) and $NCCH{=}CHCN$ (0.024 g), n-hexane (30 cm$^3$) was added. After 72 h the yellow precipitate was filtered off and washed with n-hexane and diethyl ether (85% yield), m.p. 140 °C (Found: C, 59.6; H, 4.15; N, 4.7. $C_{46}H_{37}N_3OP_2Pt$ requires C, 61.1; H, 4.1; N, 4.7). I.r. (Nujol): $\nu_{max.}$ at 2 220 cm$^{-1}$ (CN). This compound was contaminated by $[Pt(PPh_3)_2(NCCH{=}CHCN)]$, as indicated by the $^1H$ and $^{31}P$ n.m.r. spectra (see text).

$[Pt\{ONH(Ph)C(CO_2Me){=}C(CO_2Me)\}(PPh_3)_2]BF_4$ (5).—To compound (2) (0.13 g) suspended in ethanol (20 cm$^3$) was added 15 drops of $HBF_4$ (40% in water). From the yellow solution a white compound precipitated in a few minutes. After 1 h it was filtered off, washed with water, n-hexane, and repeatedly with diethyl ether and dried *in vacuo*. I.r. (Nujol): $\nu_{max.}$ at 1 745 (C=O), 1 705 (C=C), 1 263 (C–O), and 1 063 cm$^{-1}$ ($BF_4$). When compound (5) (0.15 g) suspended in ethanol (20 cm$^3$) was treated drop by drop with $NEt_3$, a yellow solution was obtained. From this solution a yellow compound precipitated. After 1 h it was filtered off, washed with n-hexane and dried *in vacuo*. Its i.r. spectrum was identical to that of (2a).

*Reaction between* (2a) *and* HCl.—Hydrochloric acid was bubbled through benzene (100 cm$^3$). Compound (2a) (1.47 g) was added. The bubbling of HCl was continued for 1 h. The white-green precipitate was filtered off and extracted with chloroform (3 × 20 cm$^3$) at 50 °C. From the chloroform solutions, by evaporation and by addition of n-hexane, a white compound was obtained. It was determined to be *cis*-$[Pt(PPh_3)_2Cl_2]$ by its m.p. (310 °C) and i.r. spectrum, identical to those of an authentic sample. The green residue which was insoluble in chloroform showed a significant nitrogen content (Found: C, 53.5; H, 4.8; N,10.0%). The mother-liquor of the reaction with hydrochloric acid was evaporated to dryness and extracted with diethyl ether (50 cm$^3$). The ether was evaporated to dryness and the residue was crystallized from di-isopropyl ether–n-hexane, producing a pink precipitate (m.p. 60 °C). Its elemental analyses were close to those of $MeO_2C-C(O)-CH_2-CO_2Me$ (Found: C, 45.1; H, 4.1; N, 0.0. Calc. for $C_6H_8O_5$: C, 45.0; H, 5.0%).

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