Facile P–C Bond Cleavage in the Reactions of Nitrile Oxides with Zerovalent Triphenylphosphine Platinum Complexes

By WOLFGANG BECK,* MICHAEL KEUBLER, ERICH LEIDL, ULRICH NAGEL, and MATHIAS SCHAAL
(*Institut für Anorganische Chemie, Universität München, Meiserstrasse* 1, 8000 *München* 2, *Germany*)

SERGIO CENINI, PAOLA DEL BUTTERO, EMANUELA LICANDRO, and STEFANO MAIORANA*
(*Istituto di Chimica Generale dell'Università, Via Venezian* 21, 20133 *Milano, and Istituto di Chimica Industriale dell'Università, Via Golgi* 19, 20133 *Milano, Italy*)

and ANGIOLA CHIESI VILLA*
(*Istituto di Strutturistica Chimica dell'Università, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via Massimo d'Azeglio* 85, 43100 *Parma, Italy*)

Summary Stable nitrile oxides react with $Pt(PPh_3)_2L$ ($L = PPh_3,C_2H_4$) to give 1:1 products; *X*-ray studies show that the nitrile oxide is deoxygenated by triphenylphosphine and that a phenyl group migrates to the platinum atom to give the complexes $[Pt(Ph)(OPPh_2)(RCN)(PPh_3)]$.

OUR interest in fulminate complexes[1] and in the behaviour of organic dipoles such as nitrile imines[2] or nitrile sulphides[3] towards transition-metal complexes has led us to examine the reaction of nitrile oxides[4] with zerovalent platinum compounds.†

The triphenylphosphine platinum complexes $(Ph_3P)_2PtL$ ($L = PPh_3,C_2H_4$) were treated with the stable nitrile oxides (**1a**)—(**1d**) to give the products (**2a**)—(**2d**) which were, by analysis, the expected 1:1 adducts between bis(triphenylphosphine)platinum and nitrile oxide. Also, from the reaction of $Pt(PPh_3)_3$ with nitrile oxides the corresponding nitriles and phosphine oxide have been obtained. Compound (**2a**) does not react with triphenylphosphine[5] or with *N*-morpholinocyclohexene[6] which shows that at least some aspects of the typical reactivity of nitrile oxides have been lost. Elementary analysis and spectroscopic data did not give an unequivocal structural assignment. So we undertook a single crystal *X*-ray diffraction study of the products from compounds (**1a**) and (**1b**) which established the molecular structure shown in the Figure.

The *X*-ray structures of compounds (**2a**) and (**2b**) show that a phenyl group from the triphenylphosphine has migrated to the platinum atom; the oxygen atom of the nitrile

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† This work has been carried out independently by both the groups in Milan and Munich.

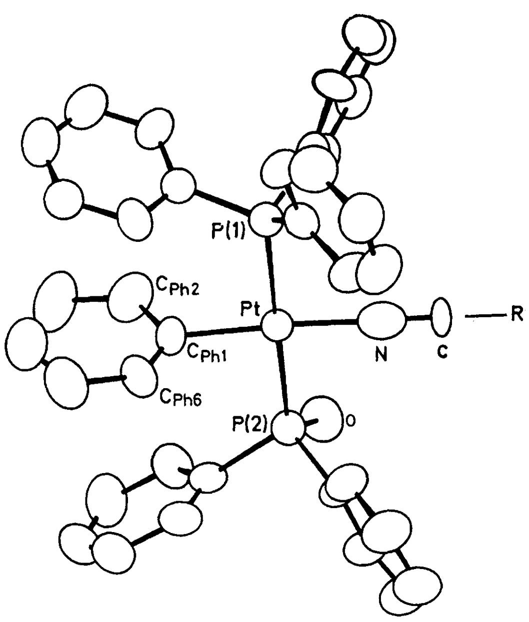


FIGURE. Molecular structure of compounds (**2a**) and (**2b**).

Distances (Å)	(**2a**)	(**2b**)
Pt–P(1)	2·347(6)	2·354(2)
Pt–P(2)	2·316(5)	2·324(2)
Pt–C	2·03(2)	2·05(1)
Pt–N	1·98(2)	2·01(1)
N≡C	1·17(2)	1·14(1)
P(2)=O	1·51(1)	1·51(1)
Angles (°)	(**2a**)	(**2b**)
P(1)–Pt–N	96·0(5)	93·9(3)
P(1)–Pt–C$_{\text{Ph1}}$	89·0(5)	89·4(3)
P(2)–Pt–N	85·8(6)	85·8(3)
P(2)–Pt–C$_{\text{Ph1}}$	89·8(5)	90·9(3)
Pt–C$_{\text{Ph1}}$–C$_{\text{Ph2}}$	127(1)	122·2(8)
Pt–C$_{\text{Ph1}}$–C$_{\text{Ph6}}$	117(1)	118·6(8)
C$_{\text{Ph2}}$–C$_{\text{Ph1}}$–C$_{\text{Ph6}}$	115(2)	119(1)

oxide is found at the phosphorus atom which gives a diphenylphosphinito–nitrile–phenyl–triphenylphosphine–platinum complex. The overall reaction is represented by equations (1) and (2).

$$\underset{(\mathbf{1\ a,d})}{2\text{R–CNO}} + \text{Pt(PPh}_3)_3 \xrightarrow[\text{ethanol–ether}]{} \underset{(\mathbf{2\ a,d})}{[\text{Pt(OPPh}_2)(\text{RCN})(\text{Ph})(\text{PPh}_3)]} + \text{RCN} + \text{OPPh}_3 \qquad (1)$$

$$\underset{(\mathbf{1\ b,c,d})}{\text{R–CNO}} + \text{Pt(PPh}_3)_2(\text{C}_2\text{H}_4) \xrightarrow[\text{toluene}]{} \underset{(\mathbf{2\ b,c,d})}{[\text{Pt(OPPh}_2)(\text{RCN})(\text{Ph})(\text{PPh}_3)]} + \text{C}_2\text{H}_4 \qquad (2)$$

R

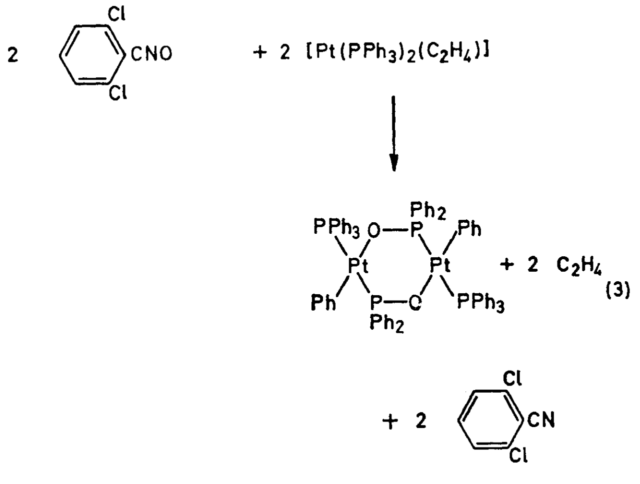
a; 3,5-dichloro-2,4,6-trimethylphenyl-
b; 9-anthracenyl-
c; 2,4,6-trimethoxyphenyl-
d; 2,4,6-trimethylphenyl-

The yields, based on the starting nitrile oxides, are *ca.* 50% [reaction (1)] and *ca.* 80% [reaction (2)]. The product (**2a**) is also obtained by the reaction of diphenylacetylenebis(triphenylphosphine)platinum with compound (**1a**) (83% yield). It is known that nitrile oxides are deoxygenated either by free or co-ordinated phosphine;[5] in the latter case this behaviour parallels the reduction of nitrile oxides by $\text{Co}_2(\text{CO})_8$.[7] The migration of a methyl group from a co-ordinated trimethylphosphite ligand to the metal atom has been observed by Neukomm and Werner.[8]

Crystal data: (**2a**) (crystals grown from ethanol) $\text{C}_{46}\text{H}_{39}\text{Cl}_2\text{NOP}_2\text{Pt}$, $M = 949{\cdot}8$; monoclinic $P2_1/c$, $a = 8{\cdot}715(1)$, $b = 18{\cdot}485(2)$, $c = 24{\cdot}948(3)$ Å, $\beta = 97{\cdot}03(1)^\circ$, $Z = 4$, $D_c = 1{\cdot}582\ \text{g cm}^{-3}$, $F(000) = 1888$, $\mu(\text{Mo-}K_\alpha) = 38{\cdot}0\ \text{cm}^{-1}$. The structure was refined to $R = 0{\cdot}056$, $R_W = 0{\cdot}056$ for 2879 independent reflections [$I \geqslant 2\sigma(I)$, $4 \leqslant 2\theta \leqslant 56^\circ$, Siemens AED diffractometer]; (**2b**) (crystals grown from chloroform–toluene) $\text{C}_{51}\text{H}_{39}\text{NOP}_2\text{Pt}$, $M = 938{\cdot}8$; monoclinic $P2_1/c$, $a = 19{\cdot}812(2)$, $b = 11{\cdot}743(5)$, $c = 21{\cdot}453(8)$ Å, $\beta = 125{\cdot}21(3)^\circ$, $Z = 4$, $D_c = 1{\cdot}53\ \text{g cm}^{-3}$, $F(000) = 1872$, $\mu(\text{Mo-}K_\alpha) = 37{\cdot}4\ \text{cm}^{-1}$. The structure was refined to $R = 0{\cdot}064$, $R_W = 0{\cdot}066$ for 7256 independent reflections [$I \geqslant 4\sigma(I)$, $5 \leqslant 2\theta \leqslant 58^\circ$, Syntex R3 diffractometer].‡

This co-ordination involves a diphenylphosphinito-ligand *cis* to the phenyl group and *cis* to the nitrile ligand. Probably the capture of the nitrile oxide oxygen atom by the phosphorus atom is accompanied, in a concerted way, by a facile migration of a phenyl group from the same phosphorus atom to the platinum atom. The lengthening of the Pt–P(1) distance with respect to the Pt–P(2) distance [2·27—2·32 Å observed in *trans*-[Pt$^{\text{II}}$(PPh$_3$)$_2$] complexes][9] could be attributed to a greater *trans* influence of the oxygenated ligand with respect to triphenylphosphine itself. The Pt–C$_{\text{Ph1}}$ bond length agrees well with those observed for Pt–phenyl bonds[10] and the Pt–C$_{\text{Ph1}}$–C$_{\text{Ph2}}$ angles are in agreement with the σ-character of the Pt–C$_{\text{Ph1}}$ bond. The Pt–N–CR angle and the N–C (nitrile) bond distance correspond to σ-co-ordination of the CN group and sp-hybridization of the nitrogen atom. The Pt–N bond distance is in the range found in other Pt$^{\text{II}}$ nitrile complexes.[11,12] The P–O bond distance is similar to the values reported for the P=O double bond.[13]

The complexes (**2a**)—(**2d**) show strong i.r. absorption at ν 2150—2180 (CN) and 1120—1125 cm^{-1} (P=O). The



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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

^{31}P n.m.r. spectra of complex (**2c**) show two signals for the two different phosphorus atoms at δ_P + 49·7 and +17·2 p.p.m. (relative to H_3PO_4). The large coupling constant, *J*[P(1)–P(2)] 398 Hz is consistent with two phosphorus atoms in the *trans*-position [*J*(Pt–P) 880 and 1590 Hz].[14]

From the reaction of the 2,6-dichlorophenylnitrile oxide with $[Pt(PPh_3)_2(C_2H_4)]$ a complex without the nitrile ligand has been isolated [equation (3)]. The ν(P=O) absorptions at 995, 1022, and 1035 cm^{-1} are characteristic of phosphinito-bridged compounds.[15] Similar phosphinito-bridged complexes have been obtained by different methods.[16,17]

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