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REACTIONS OF *trans*-HYDRIDOCYANOALKYLPLATINUM(II) COMPLEXES WITH ISOCYANIDES. PREPARATION OF NOVEL PLATINUM(II) COMPOUNDS WITH ADJACENT Pt—H AND Pt—C BONDS

RENZO ROS *,
Facoltà di Chimica Industriale, The University, Venice (Italy)
RINO A. MICHELIN, GIOVANNI CARTURAN and UMBERTO BELLUCO
Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione C.N.R., c/o Istitutio di Chimica Industriale, The University, Padova (Italy)
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Summary

The hydridocyanopropyl complex of platinum(II) *trans*-[$PtH(CH_2CH_2CH_2CN)(PPh_3)_2$] reacts with an excess of isocyanide RNC (R = t-Bu or 2,6-$Me_2C_6H_3$) to yield platinum(0) isocyanide complexes of the type [$Pt(CNR)_2(PPh_3)_2$] through reductive elimination of 1-cyanopropane. In contrast the cyanomethyl complex *trans*-[$PtH(CH_2CN)(PPh_3)_2$] reacts with RNC to give the novel platinum(II) complexes [$PtH(CH_2CN)(CNR)(PPh_3)$] (R = CH_3; t-Bu; 2,6-$Me_2C_6H_3$; *p*-$MeOC_6H_4$) by displacement of one phosphine ligand.

Spectroscopic evidence shows these complexes to contain the cyanoalkyl group adjacent to the hydride and opposite to the phosphine. Heating of these complexes in the presence of equimolar amounts of PPh_3 and RNC gives the corresponding platinum(0) species [$Pt(CNR)_2(PPh_3)_2$].

Introduction

Whereas stable *cis*-dialkyl complexes of platinum(II) such as *cis*-[PtR_2L_2] are easily prepared, their *trans* counterparts are rather rare because of their lower stability [1]. Dihydridoplatinum(II) species of the type [PtH_2L_2] are even less common, and can only be obtained as the *trans* isomers with the bulkiest tertiary phosphines [2—4]. Only one example of a *cis*-dihydridoplatinum(II) complex has been described [5]. The preparation of the alkylhydrido derivatives *trans*-{$PtH[(CH_2)_nCN](PPh_3)_2$}, (Ia, $n = 1$; Ib, $n = 3$) was recently reported [6].

The present work was directed to investigate the relative reactivities of the hydride and cyanoalkyl groups attached to the metal atom in these complexes. In particular, since both the Pt—H and the Pt—C bonds easily undergo insertion reactions, we focused on the possible occurrence of such processes in reactions of isocyanides with complexes of type I. Insertion of isocyanides into both platinum—carbon [7] and platinum—hydride [8] bonds has been extensively studied.

Results and discussion

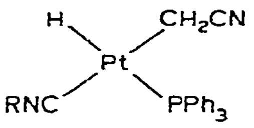
The white suspension of *trans*-$[PtH(CH_2CH_2CH_2CN)(PPh_3)_2]$ (Ib) in ether, when treated under mild conditions with a threefold excess of isocyanide (RNC; R = t-butyl; 2,6-dimethylphenyl) turns slowly yellow. The products are identified as the bis(isocyanide)platinum(0) species $[Pt(CNR)_2(PPh_3)_2]$ (II) on the basis of analytical data and spectroscopic properties. The ^1H NMR and IR data for $[Pt(t\text{-}BuNC)_2(PPh_3)_2]$ (IIb) are identical with those in the literature [9]. The complex $[Pt(2,6\text{-}Me_2C_6H_3NC)_2(PPh_3)_2]$ (IIa) shows $\nu(C{\equiv}N)$ at 1995 cm^{-1} which is typical of an isocyanide group coordinated to a platinum(0) atom, and the ^1H NMR spectrum displays absorbtions at 7.7—8.6 ppm (36H) and at 2.02 ppm (12H) which are consistent with this formulation.

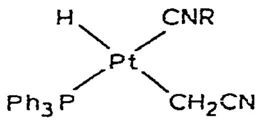
GLC analysis of the mother liquid after separation of the products shows the presence of $CH_3CH_2CH_2CN$ in virtually quantitative yield, in agreement with eq. 1.

$$\textit{trans-}[PtH(CH_2CH_2CH_2CN)(PPh_3)_2] + 2\ CNR \rightarrow \underset{(II)}{[Pt(CNR)_2(PPh_3)_2]} + CH_3CH_2CH_2CN \qquad (1)$$

Clearly the isocyanides do not end up inserted into the Pt—H and Pt—C bonds in the substrates Ib. However, the reaction might take place by prior insertion followed by reductive elimination.

The complex *trans*-$[PtH(CH_2CN)(PPh_3)_2]$ (Ia) reacts with isocyanides under similar conditions to yield white products which have analytical and spectral characteristics indicating them to be hydrides $[PtH(CH_2CN)(CNR)(PPh_3)]$ (IIIa, R = 2,6-dimethylphenyl; IIIb, R = *p*-methoxyphenyl; IIIc, R = t-butyl; IIId, R = methyl) (see Table 1 and Experimental). The IR spectrum of III shows the strong absorption typical of $\nu(C{\equiv}N)$ of platinum(II)-bound isocyanides in the range 2225—2170 cm^{-1}; the medium band at 2200 ± 5 cm^{-1} is assigned to the $\nu(C{\equiv}N)$ of the cyanomethyl moiety. The Pt—H stretching frequency appears as a weak absorption at 2090 and 2100 cm^{-1} for IIIb and IIId, respectively, but was not observed for IIIa and IIIc. This behaviour is usual for platinum(II) hydrides [10]. In all cases a weak band appears in the 865—880 cm^{-1} region, which is attributed to δ(Pt—H). These data suggested the possible structures A, B and C for the products.


(A)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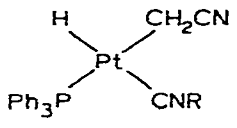

(C)

Structures A and B are ruled out by the ^1H NMR data based on the coupling

TABLE 1

^{1}H NMR DATA FOR COMPOUNDS [PtH(CH$_2$CN)(CNR)PPh$_3$]

Compound	R	δ(Pt—H) (ppm)	^1J(PtH) (^2J(PPtH)) {^3J(HCPtH)} (Hz)	δ(Pt—CH$_2$) (ppm)	^2J(PtCH) (^3J(PPtCH)) {^3J(HPtCH)} (Hz)	δ(CH$_3$ of RCN) (ppm)
IIIa	2,6-Me$_2$C$_6$H$_3$ [a]	—5.26dt	980 (19) {≈0.8}	2.48dd	95 (9.5) {≈0.8}	2.19s
IIIb	*p*-MeOC$_6$H$_4$ [b]	—5.61dt	975 (18) {≈0.8}	2.24dd	95 (8.5) {≈0.8}	3.82s
IIIc	Me$_3$C [a]	—5.57dt	976 (18) {≈1}	2.68dd	96 (10) {≈1}	1.52s
IIId	Me [b]	—6.30dt	985 (18) {≈0.7}	2.06dd	94 (10) {≈0.7}	2.93s [c]

[a] In C$_6$D$_6$/CH$_2$Cl$_2$ + TMS. [b] In CD$_2$Cl$_2$/CH$_2$Cl$_2$ + TMS. [c] ^4J(PtCNCH) 11.5 Hz.

constants of the hydrido proton with either ^{31}P or the cyanomethyl protons, and on the coupling constants of the latter with ^{31}P. The ^{1}H NMR spectrum of [PtH(CH$_2$CN)(t-BuNC)(PPh$_3$)] (IIIc) is shown in Fig. 1. Analogous patterns and signals were observed for all other complexes of type III. IIIc shows the hydride resonance at —5.57 ppm (doublet of triplets; ^1J(PtH) 976 Hz, ^2J(PPtH) 18 Hz,

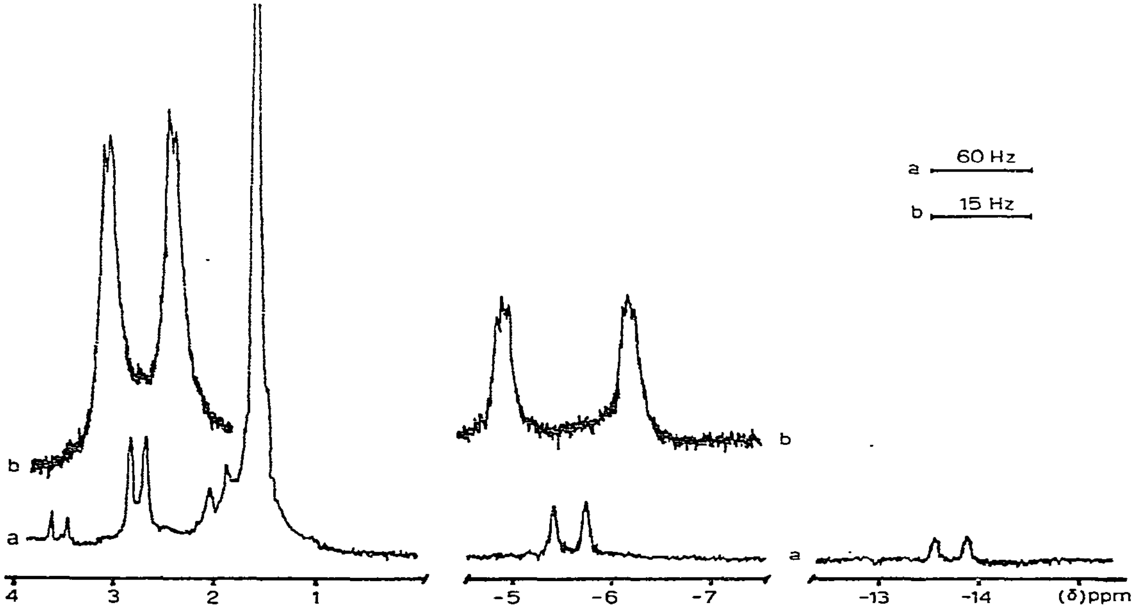
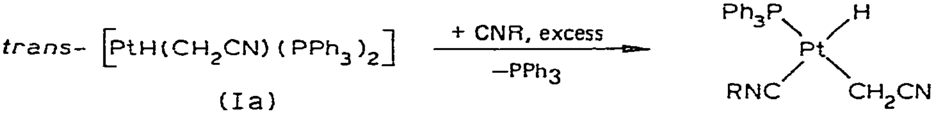


Fig. 1. ^{1}H NMR spectrum (60 MHz) of [PtH(CH$_2$CN)(t-BuNC)(PPh$_3$)].

^3J(HCPtH) ≃ 1 Hz) and the CH_2CN resonance at 2.68 ppm (doublet of doublets; ^2J(PtCH) 96 Hz, ^3J(PPtCH) 10 Hz, ^3J(HPtCH) ≃ 1 Hz). The t-butyl resonances appear at 1.52 ppm (singlet). This spectrum is consistent with structure C. In fact, the ^2J(PPtH) value for a *trans*-hydridophosphine arrangement of type A should be in the range 60—180 Hz [10]. On the other hand, structure B must also be ruled out, because: (i) ^3J(HCPtH) is smaller by about 3 Hz than in *trans*-hydridocyanomethyl complexes of type B and (ii) ^3J(PPtCH) is consistent with the values for a *trans*-cyanomethyltriphenylphosphine configuration [11], while being larger than those associated with *cis*-arrangements of type B [6]. Interestingly, the value of ^1J(PtH) (976 Hz) is higher than those found for *trans*-$[PtH(CH_2CN)(PPh_3)_2]$ (746 Hz) [6] and *trans*-$[PtH_2(PCy_3)_2]$ (794 Hz) [4], indicating a *trans* influence in the order R ≃ H > PPh_3 > RNC > X.

These findings indicate that reaction 2, unlike reaction 1 leads eventually to displacement of one coordinated phosphine with concomitant *trans*-to-*cis* isomerization of the hydride and cyanomethyl ligands. Under different experimental conditions the reaction of Ia with isocyanides also leads to platinum(0) complexes. Thus, Ia reacts with an excess 2,6-$Me_2C_6H_3NC$ in boiling ether during 24 h to give a yellow solid that is identified as $[Pt(2,6\text{-}Me_2C_6H_3NC)_2(PPh_3)_2]$, while CH_3CN can be detected in the mother solution.



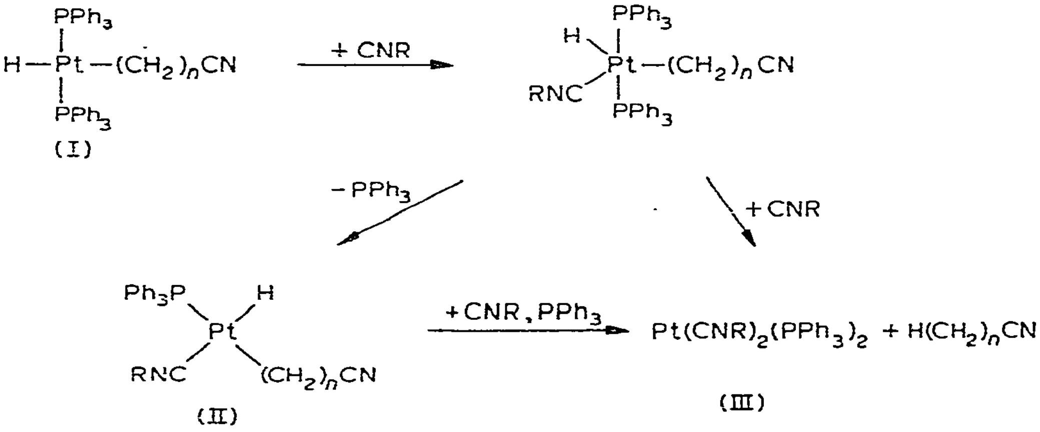
(Ia)

(III)

(2)

The fact that no isocyanide insertion was observed in either reaction 1 or 2 is noteworthy. As was pointed out earlier, isocyanide insertion requires an intermediate in which the entering isocyanide is adjacent to the alkyl (hydride) moiety, in order to allow an easy alkyl (hydride) migration [12]. In reactions 1 and 2, such an intermediate (which was isolated in the case of reaction 2, i.e., III) has the cyanoalkyl group in a position adjacent to both the hydride and the isocyanide, whereby reductive elimination of $H(CH_2)_nCN$ is also possible. The

SCHEME 1



likelihood of elimination is enhanced in our case by the presence of free neutral ligands in solution which are known to promote reductive elimination of saturated hydrocarbons under the experimental conditions [13].

Therefore, reactions 1 and 2 can be looked upon as occurring as shown in Scheme 1.

In cases in which no evidence for intermediates of type III was obtained, the reductive elimination may be thought of as involving the five-coordinate intermediate directly.

The differing behaviour of the hydridocyanoalkyl species Ia and Ib under the same experimental conditions is related to the different Pt—C σ bond strengths of the platinum—cyanoalkyl bonds involved.

Experimental

^{1}H NMR spectra were recorded on a Varian NV-14 60 MHz spectrometer. IR spectra were recorded on a Perkin—Elmer 457 spectrophotometer in Nujol mulls and were calibrated with a polystyrene film. Melting points were taken on a hot plate apparatus, and are uncorrected.

Chromatographic analyses were carried out on a Hewlett—Packard 7620A gas chromatograph. All manipulations were carried out under nitrogen or argon.

Preparation of complexes of type [PtH(CH$_2$CN)(isocyanide)(PPh$_3$)]

[PtH(CH$_2$CN)(2,6-Me$_2$C$_6$H$_3$NC)PPh$_3$] (IIIa). A suspension of *trans*-[PtH(CH$_2$CN)(PPh$_3$)$_2$] (Ia) (0.31 g, 0.40 mmol) in n-heptane (15 ml) was treated with 2,6-dimethylphenylisocyanide (0.157 g, 1.2 mmol) under nitrogen with stirring for 2 h at 25°C. The white product was filtered off and washed with n-heptane (0.209 g, yield 83%). m.p. 132—133°C. Analysis: Found, C, 55.64; H, 4.71; N, 4.37. $C_{29}H_{27}N_2PPt$ calcd.: C, 55.32; H, 4.32; N, 4.45%. IR: $\nu(C{\equiv}N)$ of the isocyanide 2170vs cm^{-1} (2177 cm^{-1} in CH$_2$Cl$_2$) $\nu(C{\equiv}N)$ of CH$_2$CN 2200s cm^{-1} (2205 cm^{-1} in CH$_2$Cl$_2$); ν(Pt—H) not observed; δ(Pt—H) 877w cm^{-1}.

The following compounds were obtained analogously:

[PtH(CH$_2$CN)(p-MeOC$_6$H$_4$NC)(PPh$_3$)] (IIIb). (4 h stirring; washed with ethyl ether, yield 85%). M.p. 130—131°C. Analysis: Found: C, 53.08; H, 4.12; N, 4.41. $C_{28}H_{25}N_2OPPt$ calcd.: C, 53.25; H, 3.99; N, 4.43%. IR: $\nu(C{\equiv}N)$ of the isocyanide 2190vs cm^{-1} (2190 cm^{-1} in C$_6$H$_6$); $\nu(C{\equiv}N)$ of CH$_2$CN 2203s cm^{-1} (2207 cm^{-1} in C$_6$H$_5$); ν(Pt—H) 2090w cm^{-1}; δ(Pt—H) 870w cm^{-1}.

[PtH(CH$_2$CN)(t-BuNC)(PPh$_3$)] (IIIc). (3 h stirring; washed with heptane, yield 80%). M.p. 129—130°C. Analysis: Found: C, 51.02; H, 4.74; N, 4.78. $C_{25}H_{27}N_2PPt$ calcd.: C, 51.63; H, 4.68; N, 4.82%. IR: $\nu(C{\equiv}N)$ of the isocyanide 2210vs cm^{-1} (2210 cm^{-1} in C$_6$H$_6$); $\nu(C{\equiv}N)$ of CH$_2$CN 2200m cm^{-1} (2198 cm^{-1} in C$_6$H$_6$); ν(Pt—H) not observed; δ(Pt—H) 870w cm^{-1}.

[PtH(CH$_2$CN)(CH$_3$NC)(PPh$_3$)] (IIId). (2 h stirring; washed with heptane, yield 90%). M.p. 129—132°C. Analysis: Found: C, 48.71; H, 3.96; N, 5.01. $C_{22}H_{21}N_2PPt$ calcd.: C, 48.98; H, 3.92; N, 5.19%. IR: $\nu(C{\equiv}N)$ of the isocyanide 2222vs cm^{-1} (2225 cm^{-1} in CH$_2$Cl$_2$); $\nu(C{\equiv}N)$ of CH$_2$CN 2195m cm^{-1} (2203 cm^{-1} in CH$_2$Cl$_2$); ν(Pt—H) 2100w cm^{-1}, δ(Pt—H) 866w cm^{-1}.

Preparation of complexes of type [Pt(CNR)$_2$(PPh$_3$)$_2$].

[Pt(2,6-Me$_2$C$_6$H$_3$NC)$_2$(PPh$_3$)$_2$] (IIa). 2,6-Dimethylphenylisocyanide (0.203 g,

1.55 mmol) was added to a suspension of *trans*-[PtH($CH_2CH_2CH_2CN$)(PPh_3)$_2$] (0.402 g, 0.51 mmol) in diethyl ether (20 ml). The suspension was stirred under nitrogen at 25°C for 3 h. The yellow solid was filtered off and washed with n-heptane. (0.325 g, yield 65%). M.p. 104—109°C. Analysis: Found: C, 65.73; H, 5.15; N, 2.80. $C_{54}H_{48}N_2P_2Pt$ calcd.: C, 66.05; H, 4.93; N, 2.85%. IR: $\nu(C\equiv N)$ 1995vs cm^{-1}. ^1H NMR: 7.7—8.6 ppm (broad multiplet, 36H); 2.02 ppm (singlet, 12H).

This compound was also obtained on refluxing for 24 h under nitrogen a mixture of *trans*-[PtH(CH_2CN)(PPh_3)$_2$] and 2,6-$Me_2C_6H_3NC$ (molar ratio 1/3) in ethyl ether.

[Pt(t-BuNC)$_2$(PPh$_3$)$_2$] (IIb). Compound IIb was prepared by the method used for IIa; its IR and PMR spectra were identical with published data [9].

GLC analysis of the mother solutions of the reaction mixtures showed the presence of 1-cyanopropane and acetonitrile respectively. These products were determined quantitatively by comparison with standard solutions in ethyl ether.

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