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# HYDRIDO- AND HYDROXO-CYANOALKYL COMPLEXES OF PLATINUM(II). REACTIVITY OF THE Pt—H AND Pt—OH BONDS TOWARDS NUCLEOPHILES AND ELECTROPHILES

RENZO ROS,

*Facoltà di Chimica Industriale, University of Venice (Italy)*

RINO A. MICHELIN,

*Centro di Chimica e Tecnologia Composti Metallorganici Elementi Transizione, Facoltà di Ingegneria, University of Padua (Italy)*

RAYMOND BATAILLARD and RAYMOND ROULET

*Institut de chimie minérale et analytique de l'Université, Place du Château 3, CH-1005 Lausanne (Switzerland)*

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## Summary

Reactions of the Pt—H and/or Pt—C bonds of the hydridocyanoalkyl complexes *cis*- or *trans*-$PtH[(CH_2)_nCN]L_2$ ($n = 1, 3$; $L_2$ = 2 $PPh_3$, $Ph_2PCH{=}CHPPh_2$) are described, viz. reductive elimination induced by CO, $PhC{\equiv}CPh$, $PEt_3$, $PPhMe_2$, *cis*-$Ph_2PCH{=}CHPPh_2$ to give $Pt(CO)_2L_2$, $PtL_2(PhC{\equiv}CPh)$, $PtL_2$, $PtL(PPhMe_2)_3$, $PtL_2(Ph_2PCH{=}CHPPh_2)$ (L = $PPh_3$), respectively, and cleavages by acids, halogens and alkyl halides.

The monomeric hydroxo complexes *cis*-$Pt(OH)[(CH_2)_nCN]L_2$ were shown to be intermediates in the synthesis of $PtH[(CH_2)_nCN]L_2$ from cationic cyanoalkyl complexes in alcoholic NaOH. Their characterisation and the reactions of the Pt—OH bond with activated methyl groups are reported.

## Introduction

The role of platinum in organometallic chemistry has been of major importance [1—4]. Studies on novel alkyl and hydrido complexes have shed light on some basic aspects of oxidative addition [5—11], reductive elimination [11—14], $\beta$-hydrogen abstraction [15—18], $\pi$-complex formation [19—22] and insertion or de-insertion reactions of ligands [6,19,23—30]. A particularly interesting class of compounds contains a hydrido and a $\sigma$-alkyl ligand, of type $PtH(R)L_2$, and can be considered as intermediates in catalytic activation of the C—H bond

[31]. Such complexes are generally both thermodynamically and kinetically unstable, and only a few have been prepared: viz. $PtH(R)L_2$ with R = $CH_2SiMe_3$, L = $PEt_3$ [32]; R = $C(CN)_3$, L = $PPh_3$ [33], R = $(CH_2)_nCN$, $n$ = 1, 2, 3, $o$-$CH_2$-$C_6H_4CN$, L = $PPh_3$, $L_2$ = diphosphine, diarsine [34,35]; R = $CF_3$, L = $PPh_3$, $L_2$ = diphosphine [36]. The strengthening of the Pt—C bond by electronegative groups in the alkyl chain appears to prevent the reductive elimination of HR.

The present paper describes some reactions of cyanoalkyl hydrides of the type *trans*-$PtH[(CH_2)_nCN](PPh_3)_2$ and *cis*-$PtH[(CH_2)_nCN]$(diphos) with nucleophiles and electrophiles, with the aim of comparing the reactivity and the mutual influence of hydride and cyanoalkyl groups in both *cis*- and *trans*-positions. Monomeric hydroxo complexes $Pt(OH)(C_3H_6CN)L_2$ were isolated in the course of the synthesis of the hydrido complexes $PtH(C_3H_6CN)L_2$ from cationic cyanoalkylplatinum(II) complexes in alcoholic NaOH. Their characterisation and their reactions with activated methyl groups are also described.

## Results and discussion

### *1. Reactions of the hydrido complexes*

Of the various hydridocyanoalkyl complexes of platinum(II) we prepared previously [34,35], we chose to examine the reactions of cyanomethyl and cyanopropyl species, viz.: $PtH[(CH_2)_nCN]L_2$ (L = $PPh_3$: Ia, $n$ = 1; Ib, $n$ = 3; $L_2$ = $Ph_2PC_2H_4PPh_2$: IIa, $n$ = 1; IIb, $n$ = 3; $L_2$ = *cis*-$Ph_2PCH{=}CHPPh_2$: IIIa, $n$ = 1; IIIb, $n$ = 3), the cyanomethyl complexes have the stronger Pt—C bond, and the weaker bonds in the cyanopropyl complexes are almost similar to those in unsubstituted Pt—alkyl complexes.

The several organic and inorganic reagents examined give rise either to reductive elimination of HR or cleavage of Pt—H and Pt—C bonds, in some cases selectively. We did not get any evidence for intermediates or products of association and/or insertion of reactants, except for the insertion of olefins, as reported elsewhere [34,35].

*(a) Reductive elimination*

The complexes *trans*-$PtH(n\text{-}C_3H_6CN)(PPh_3)_2$ (Ib) and *cis*-$PtH(n\text{-}C_3H_6CN)$-$(Ph_2PC_2H_4PPh_2)$ (IIb) are stable indefinitely in toluene, but react with CO (1 atm, 25—30°C) with reductive elimination of 1-cyanopropane (93%) to give a dicarbonylplatinum(0) species:

$$PtH(n\text{-}C_3H_6CN)L_2 \xrightarrow{CO} \begin{cases} \xrightarrow[\text{Ib, 1h; IIb, 12h}]{\text{1 atm}} Pt(CO)_2L_2 + n\text{-}C_3H_7CN \\ \xrightarrow[\text{Ib, 6h}]{\text{80 atm}} Pt_3(CO)_3L_4 + n\text{-}C_3H_7CN \end{cases} \quad (1)$$

The corresponding cyanomethyl derivatives, *trans*-$PtH(CH_2CN)(PPh_3)_2$ (Ia) and *cis*-$PtH(CH_2CN)(Ph_2PC_2H_4PPh_2)$ (IIa) under similar experimental conditions do not undergo any reaction even during several days.

Insertions into Pt—H or Pt—C bonds seem not to occur since during the reac-

tion no $\nu$(C=O) IR bands characteristic of acyl species of type PtCOH and Pt-COR were observed, and also because 1-cyanopropane can be determined quantitatively by GLC and is shown to be the sole final product (eq. 1).

The hydridocyanoalkyl complexes Ia, Ib, IIa and IIb, when treated with a three-fold excess of diphenylacetylene in toluene at ca. 100°C undergo complete reductive elimination of cyanoalkane with formation of two platinum(0) complexes, after significantly different reaction times:

$$PtH[(CH_2)_nCN]L_2 \xrightarrow[-H(CH_2)_nCN]{+PhC\equiv CPh} \begin{cases} \xrightarrow[Ib,25min]{Ia,115min} Pt(PPh_3)_2(PhC\equiv CPh) \\ \xrightarrow[IIb,35min]{IIa,420min} Pt(Ph_2PC_2H_4PPh_2)(PhC\equiv CPh) \end{cases} \quad (2)$$

$L_2$ = 2 $PPh_3$: Ia, $n$ = 1; Ib, $n$ = 3, $L_2$ = $Ph_2PC_2H_4PPh_2$: IIa, $n$ = 1; IIb, $n$ = 3.

It is noteworthy that these reactions with diphenylacetylene also gave no evidence for insertion products, indicating that these reductive eliminations (eq. 1,2) are kinetically more favoured over any competing insertion reactions. The majority of insertions of unsaturated molecules such as CO, olefins or alkynes into Pt—H or $\sigma$-Pt—C bonds do not usually involve experimental conditions too different from those in reactions 1 and 2. In particular, we have described the insertion of olefin into the Pt—H bond of complexes Ia and Ib [34,35] and the insertion of CO into the Pt—C bond of cyanoalkyl complexes *trans*-$PtBr[(CH_2)_nCN](PPh_3)_2$ ($n$ = 2,3) [37].

The reaction times for eq. 1 and 2 clearly indicate that the rate of reductive elimination of cyanoalkane is higher for cyanopropyl than for cyanomethyl complexes of the same configuration, and also higher for tri- than for di-phenylphosphine derivatives with the same cyanoalkyl group. The former finding can be explained by the greater strength of the $\sigma$-Pt—C bond of cyanomethyl, in which the coordinated carbon atom is more electronegative. As for the latter observation, it is hard to find an explanation for a slower elimination of cyanoalkane from complexes already having a *cis*-configuration of Pt—H and Pt—C bonds relative to their *trans* analogs, since intermediates which favour intramolecular *cis*-elimination are generally required in reductive elimination from organocomplexes of platinum(II) [4].

A possible path would require displacement of a phosphine from Ib by L = CO or PhC≡CPh forming $PtHR(PPh_3)L$ and isomerisation of the latter catalysed by the liberated $PPh_3$. It should be noted that a fast exchange of phosphine on the $^{31}P$ NMR time scale is observed between Ib and free $PPh_3$ at room temperature [35]. The formation of the four-coordinate intermediate $PtHR(PPh_3)L$ is supported by the isolation of the comparatively stable $PtH(CH_2CN)(PPh_3)(CNR)$ (with H *cis* to $CH_2CN$) by reaction of *trans*-$PtH(CH_2CN)(PPh_3)_2$ (Ia) with isocyanides [38] under comparable conditions, and *cis/trans* isomerisation catalysed by $PPh_3$ was observed in the case of $PtCl(CH_2CN)(PPh_3)_2$ [37]. If such a mechanism operates for Ib, the greater difficulty of reductive elimination from the diphosphine complexes IIa and IIb relative to their triphenylphosphine analogs Ia and Ib could be due to IIa and IIb being kinetically unfavoured in

forming four-coordinated species, since one tooth of the bidentate diphosphine has to become loose. However, other factors cannot be disregarded, such as the greater bulkiness of $PPh_3$ over $Ph_2PCH_2$; bulky ligands are known to promote reductive elimination [4] *.

Facile reductive elimination was brought about by treating Ib with an excess of $PEt_3$, $PPhMe_2$ or *cis*-$Ph_2PCH{=}CHPPh_2$ under similar experimental conditions (eq. 3–5).

$$\textit{trans}\text{-}PtH(n\text{-}C_3H_6CN)(PPh_3)_2 \xrightarrow{PEt_3} Pt(PPh_3)_2 \quad (3)$$

$$\textit{trans}\text{-}PtH(n\text{-}C_3H_6CN)(PPh_3)_2 \xrightarrow[-PPh_3]{PPhMe_2} Pt(PPh_3)(PPhMe_2)_3 \quad (4)$$

$$\textit{trans}\text{-}PtH(n\text{-}C_3H_6CN)(PPh_3)_2 \xrightarrow{Ph_2PCH=CHPPh_2} Pt(Ph_2PCH{=}CHPPh_2)(PPh_3)_2 \quad (5)$$

In reaction 3 the more basic phosphine $PEt_3$ is the sole reducing species, and promotes elimination of 1-cyanopropane without incorporation of extra phosphine molecules in the final platinum(0) complex. The elemental analysis, the melting point, and the pale yellow colour correspond to the "elusive" $Pt(PPh_3)_2$ [39], rather than to the deeply coloured polynuclear species $[Pt(PPh_3)_2]_n$ ($n$ = 2, 3) [40]. Reactions 4 and 5 also involve ready reductive elimination, leading to $Pt(PPh_3)(PPhMe_2)_3$ and $Pt(Ph_2PCH{=}CHPPh_2)(PPh_3)_2$, respectively. The identity of the latter platinum(0) complex was ascertained from its $^{31}P\text{-}\{^1H\}$ NMR spectrum, since its elemental analysis is similar to that of the known complex

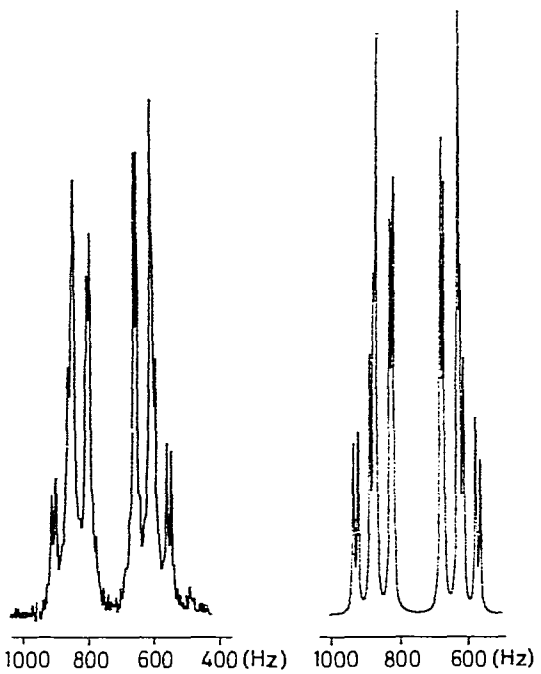


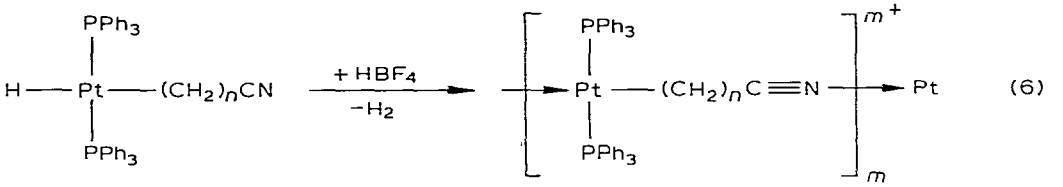

Fig. 1. $^{31}P\text{-}\{^1H\}$ NMR spectrum of $Pt(Ph_2PCH{=}CHPPh_2)(PPh_3)_2$ in $CD_2Cl_2$ at −40°C and calculated $A_2B_2$ spectrum.

* See Note added in proof on p. 90.

$Pt(Ph_2PCH{=}CHPPh_2)_2$ [41] (Fig. 1; the satellites due to $^{195}Pt$ are not shown). The calculated spectrum ($A_2B_2$ system, program LAOCN 4 [42]) gave the following coupling constants: diphosphine, $\delta$(P) 17.0 ppm, $^1J$(PtP) 4133 Hz; $PPh_3$, $\delta$(P) 24.0 ppm, $^1J$(PtP) 3471 Hz, $^2J$(PPtP) 52 Hz.

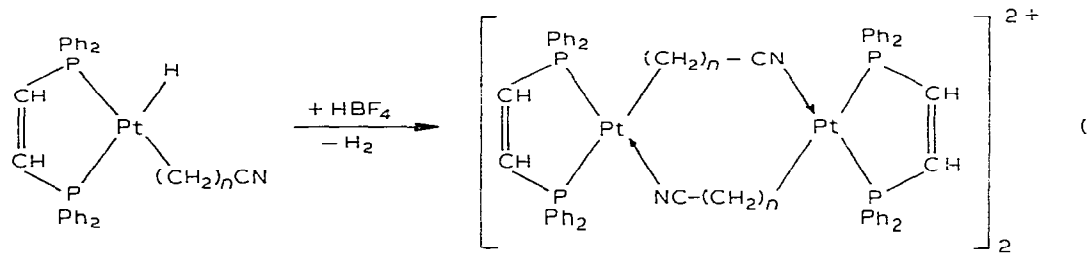
*(b) Cleavage reactions by acids*

When treated with excess fluoboric acid the hydrido complexes *trans* Ia, Ib and *cis* IIIa, IIIb suspended in ethyl ether liberate hydrogen to give the cationic complexes *trans*-$\{Pt[(CH_2)_nCN](PPh_3)_2\}_m(BF_4)_m$ (IVa, $n$ = 1, IVb, $n$ = 3 [37]) and *cis*-$\{Pt[(CH_2)_nCN](Ph_2PCH{=}CHPPh_2)\}_2(BF_4)_2$ (Va, $n$ = 1; Vb, $n$ = 3), respectively, in which the cyano group is linked by a $\sigma$-N—Pt bond to another platinum atom (eq. 6,7).



(6)

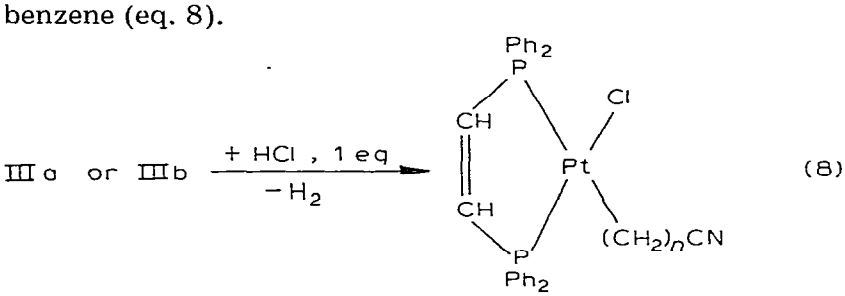
(Ia, $n$ = 1 ; Ib, $n$ = 3) (IVa, $n$ = 1, IVb, $n$ = 3)



(7)

(IIIa, $n$ = 1 ; IIIb, $n$ = 3) (Va, $n$ = 1 ; Vb, $n$ = 3)

These cationic complexes can also be prepared by chloride abstraction with $AgBF_4$ from the corresponding chloro derivatives (see Experimental and ref. 37). A similar electrophilic cleavage of the Pt—H bond occurs in the reaction of stoichiometric amounts of HCl with complexes IIIa and IIIb in diethyl ether/benzene (eq. 8).



(8)

(VIa, $n$ = 1 ; VIb, $n$ = 3)

These reactions take place with high selectivity (>90%), as shown by the absence of secondary products indicated by IR and $^1$H NMR analysis of the final products. It is noteworthy that whereas excess of $HBF_4$ does not cause cleavage of the Pt—C bond, excess of HCl selectively breaks first the Pt—H bond in IIIa and IIIb and then, slowly, the Pt—C bond, giving the corresponding cyanoalkane and the complex $PtCl_2(Ph_2PCH{=}CHPPh_2)$ [41]. The ratio of $^1J$(PtP) coupling constants (P *trans* to H/P, *trans* to C) is smaller than in IIIa but greater than in IIIb [35], thus, there is apparently no relation between the relative *trans* influence of H and C and the fact that the Pt—H bond breaks prior to the Pt—C bond in both complexes.

In contrast with the above reactions, hydrochloric acid selectively breaks the Pt—C bond of Ia and Ib under similar experimental conditions (eq. 9). Reaction 9

$$\textit{trans}\text{-}PtH[(CH_2)_nCN](PPh_3)_2 \xrightarrow{+HCl,\,1\,eq} \textit{trans}\text{-}PtHCl(PPh_3)_2 + H(CH_2)_nCN \qquad (9)$$

(Ia, $n$ = 1; Ib, $n$ = 3)

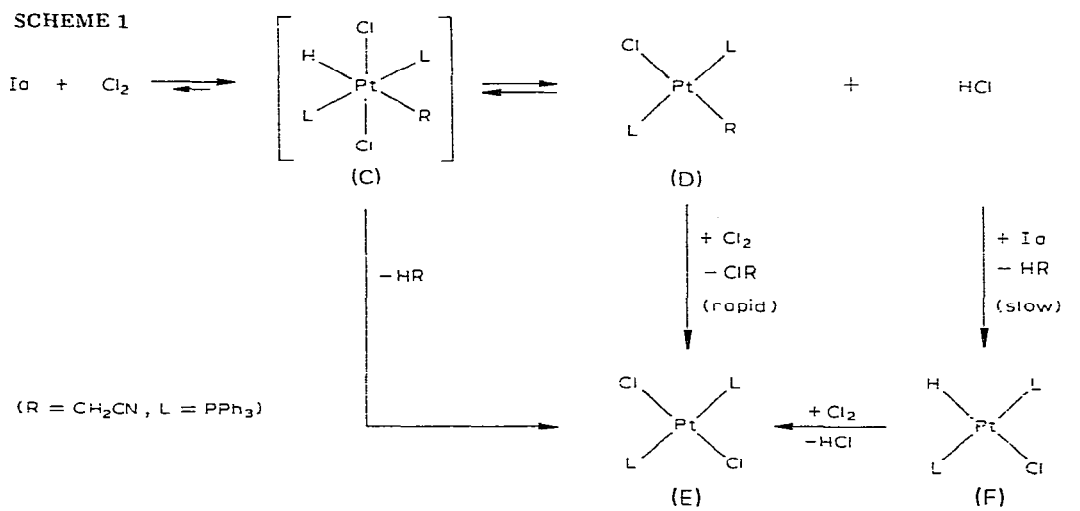
leads to quantitative formation of cyanoalkane and the platinum hydride *trans*-$PtHCl(PPh_3)_2$ [43], which is relatively weakly reactive towards HCl even in excess, and is slowly converted into $PtCl_2(PPh_3)_2$.

All these reactions with acids are likely to involve an oxidative addition-reductive elimination mechanism, analogous to the reactions of alkyl- and aryl-platinum compounds with acids [44—46].

*(c) Reactions with halogens and alkyl halides*

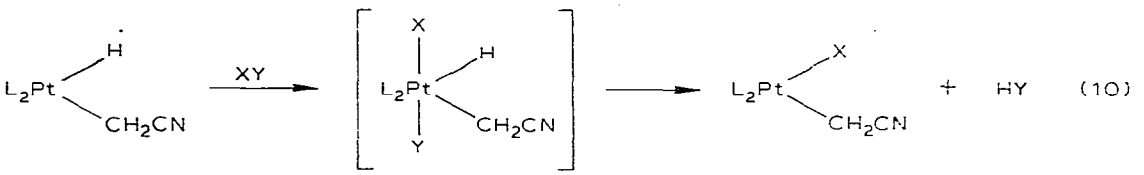
The complexes Ia and IIIa in toluene react vigorously with an excess of chlorine. The solution becomes strongly acidic and in a few minutes the dichloroderivatives *trans*-$PtCl_2(PPh_3)_2$ [47] and $PtCl_2(Ph_2PCH{=}CHPPh_2)$ [41] separate. The mother solution shows the presence of $ClCH_2CN$ in almost quantitative amount. These reactions, which involve the cleavage of both Pt—C and Pt—H bonds, were more complex when carried out with stoichiometric amounts of chlorine. The reactions of *trans*-$PtH(CH_2CN)(PPh_3)_2$ (Ia) are outlined in Scheme 1

SCHEME 1



Such a scheme can explain (i) the fact that the reaction with an excess of $Cl_2$ gives ClR and complex E in good yields, (ii) the finding that the reaction with stoichiometric $Cl_2$ leads to organic derivatives ClR and HR in ca. 1/2 molar ratio and to a mixture of mainly D, E and F complexes along with ca. 10% of unreacted starting material Ia.

The complexes Ia and IIa when dissolved in $CH_3I$ slowly liberate methane to give the corresponding iodo-complexes. Analogously, the complexes Ia dissolved in the halogenated solvents $CHCl_3$ or $ClCH_2CN$ yield *trans*-$PtCl(CH_2CN)(PPh_3)_2$ and $CH_2Cl_2$ or $CH_3CN$, respectively (eq. 10).




($L_2$ = $2PPh_3$, $Ph_2PC_2H_4PPh_2$ ; XY = $ICH_3$, $ClCH_2CN$, $ClCHCl_2$)

*2. Preparation and reactions of the hydroxo complexes*

Only a limited number of monomeric hydroxo complexes of platinum(II) have been prepared to date: $Pt(OH)(GePh_3)(PEt_3)_2$ [48], $Pt(OH)(C_6H_9)(Ph_2PCH_2CH_2PPh_2)$ [49], $Pt(OH)R(PPh_3)_2$ (R = Me, Ph, $C_6F_5$, $CCl{=}CCl_2$, $HC{=}CCl_2$) [50]. The hydrido complex Ib has been obtained by the reaction of the cationic complex *trans*-$[Pt(n\text{-}C_3H_6CN)(PPh_3)_2]_m(BF_4)_m$ (IVb) with NaOH in alcohol [34]. Monitoring of the IR spectrum of the mixture of complexes formed during the reaction (after removal of the excess of NaOH and ROH) indicated the fast

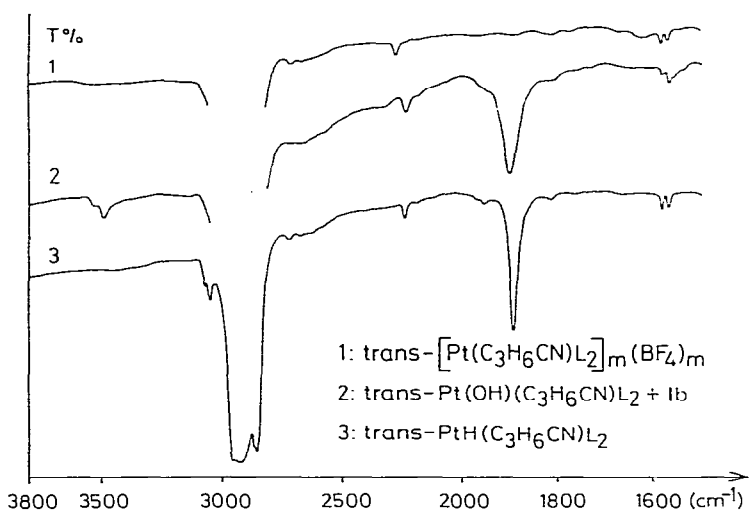



Fig. 2. IR spectra of the reaction of *trans*-$[Pt(C_3H_6CN)(PPh_3)_2]_m(BF_4)_m$ (IVb) with NaOH in alcohol. 1: starting complex IVb ($\nu$(CN) at 2282 $cm^{-1}$ is indicative of a CN group coordinated to Pt). 2: mixture of complexes isolated after ca. 60% of reaction. 3: final complex *trans*-$PtH(C_3H_6CN)(PPh_3)_2$ (Ib).

TABLE 1

IR, $^1$H AND $^{31}$P NMR SPECTRAL DATA FOR CYANOALKYL COMPLEXES OF PLATINUM(II)

| Complex [a] | | IR [b] ($\nu$ in cm$^{-1}$) | $\delta(CH_2)$ [d] (ppm) | $^2J$(PtCH) (Hz) | $^3J$(PPtCH) (Hz) | $\delta$(P) [l] (ppm) | $^1J$(PtP) (Hz) | $^2J$(PPtP) (Hz) |
|---|---|---|---|---|---|---|---|---|
| IVa | *trans*-$[Pt(CH_2CN)(PPh_3)_2]_m(BF_4)_m$ | 2225w $\nu$(CN)<br>1055vs $\nu(BF_4)$ [c] | 1.35 t | 105 | 8 | 32.7 s | 2989 | |
| Va | $[Pt(CH_2CN)(Ph_2PCH{=}CHPPh_2)]_2(BF_4)_2$ | 2250w $\nu$(CN)<br>1050vs $\nu(BF_4)$ [c] | 2.16 dd [e] | 65 | 4 (*cis*)<br>9 (*trans*) | 38.0 d<br>51.0 d | 3990<br>2380 [m] | 7 |
| Vb | $[Pt(n\text{-}C_3H_6CN)(Ph_2PCH{=}CHPPh_2)]_2(BF_4)_2$ | 2295w $\nu$(CN)<br>1055vs $\nu(BF_4)$ [c] | 1.2 m<br>1.7 m | [k] | [k] | | | |
| VIb | $PtCl(n\text{-}C_3H_6CN)(Ph_2PCH{=}CHPPh_2)$ | 2240w $\nu$(CN)<br>308m $\nu$(PtCl) | 1.5 m<br>2.0 m | [k] | [k] | 47.8 d<br>55.4 d | 4290<br>1709 [m] | 9 |
| VIIa | *cis*-$Pt(OH)(CH_2CN)(PPh_3)_2$ | 2202s $\nu$(CN)<br>3603m $\nu$(OH) | 1.48 dd | 79 | 5 (*cis*)<br>9 (*trans*) | 11.8 d<br>23.6 d | 3458<br>2225 [m] | 15 |
| VIIIa | $Pt(OH)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ | 2205s $\nu$(CN)<br>3600m $\nu$(OH) | 1.62 dd | 79 | 4 (*cis*)<br>10 (*trans*) | 39.4 d<br>49.8 d | 3239<br>2368 [m] | ~3 |
| IXa | $[Pt(CH_2CONH)(PPh_3)_2]_2$ | 3358w $\nu$(NH)<br>1640s $\nu$(C=O) | 1.03 dd | 52 | 4 (*cis*)<br>6 (*trans*) | 15.9 d<br>21.2 d | 3767<br>2118 [m] | 12 |
| Xa | *cis*-$Pt(CH_2CN)(CH_2NO_2)(PPh_3)_2$ | 2208s $\nu$(CN)<br>1498s $\nu(NO_2)$as<br>1358s $\nu(NO_2)$s | 1.58 t [f]<br>4.63 t [g] | 80<br>81 | 8<br>8 | 21.2 d<br>22.6 d | 2390<br>2335 | 14 |
| XIa | $Pt(CH_2CN)(CH_2NO_2)(Ph_2PCH{=}CHPPh_2)$ | 2212s $\nu$(CN)<br>1498s $\nu(NO_2)$as<br>1358s $\nu(NO_2)$s | 1.70 dd<br>5.01 dd [g,h] | 87<br>88 | 7 (*cis*)<br>9 (*trans*) | 54.9 d<br>56.6 d | 2359<br>2250 | ~3 |
| XIIa | $Pt(CH_2CN)(CH_2COPh)(Ph_2PCH{=}CHPPh_2)$ | 2203s $\nu$(CN)<br>1633s $\nu$(C=O) | 1.62 dd<br>3.22 dd [i] | 88<br>96 | 7 (*cis*)<br>9 (*trans*) | 48.5 d<br>49.4 d | 2274<br>2333 | 12 |
| XIIIa | *cis*-$Pt(OCH_3)(CH_2CN)(PPh_3)_2$ | 2202s $\nu$(CN)<br>2773s $\nu$(OC–H)<br>1069s $\nu$(C–O) | 1.56 dd<br>3.10 d [j] | 84 | 5 (*cis*)<br>10 (*trans*) | 11.0 d<br>22.2 d | 3340<br>2250 | 15 |

[a] IR and NMR data of the hydrido complexes: Ia, IIa, IIIa [35]; Ib, IIb, IIIb [34]; IVb [37] and VIa [35]. [b] In Nujol mulls. [c] Broad. [d] In $CD_2Cl_2$ at room temperature; TMS as internal standard; d, doublet; m, multiplet; t, triplet. The multiplicity indicated does not include coupling to $^{195}$Pt. [e] $\delta$(H–C=) ~7.0 (m) ppm. [f] We cannot explain this 1/3/1 triplet; the complex is, however, of *cis* configuration as shown by its $^{31}$P NMR data. [g] $\delta(CH_2NO_2)$. [h] $^3J$(PPtCH) 6 (*cis*) and 9 Hz (*trans*). [i] $\delta(CH_2COPh)$; $^3J$(PPtCH) 6 (*cis*) and 11 Hz (*trans*). [j] $\delta(CH_3)$; $^3J$(PtOCH) 45 Hz, $^4J$(PPtOCH) 6 Hz, strong coupling occurs only with the *trans*-phosphorus atom in this type of complexes [55,57]. [k] not observed. [l] In $CD_2Cl_2$ at room temperature; positive sign for a resonance at lower field than 85% $H_3PO_4$ (external reference). [m] P *trans* to C.

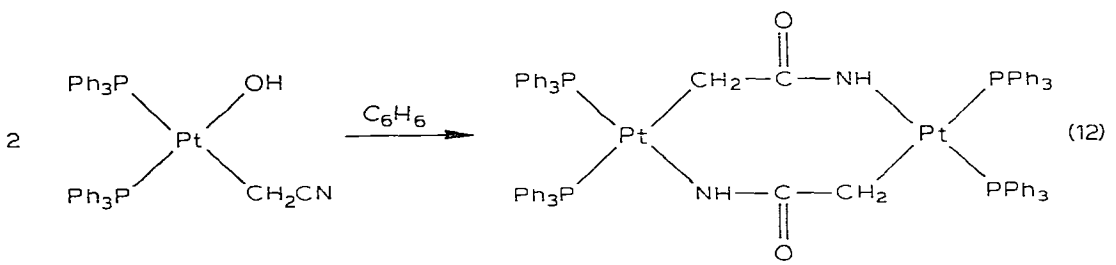
appearance of a band at 3600 $cm^{-1}$ whose intensity decreased progressively in favour of a new band at 1950 $cm^{-1}$ ($\nu$(PtH) of Ib). This suggested that an hydroxo complex was formed prior to the formation of the hydride (Fig. 2).

Pure monomeric hydroxo complexes were obtained in the case of R = $CH_2CN$ from reaction 11. Solutions of VIIa in THF or benzene are not stable on standing;

$$cis\text{-}[Pt(CH_2CN)L_2]_2(BF_4)_2 + 2\ NaOH \xrightarrow[40°C]{MeOH} 2\ cis\text{-}Pt(OH)(CH_2CN)L_2 + 2\ NaBF_4 \quad (11)$$

(VIIa, $L_2$ = 2 $PPh_3$, VIIIa, L = $Ph_2PCH{=}CHPPh_2$)

hydrolysis of the CN group occurs, to give the corresponding dimeric imido-complex IXa (eq. 12)




(12)

(IXa)

The hydrido complexes underwent condensation when treated with activated methyl groups (similar reactions were observed by Otsuka [50]) whenever such processes were faster than hydrolysis of the CN group (eq. 13).

$$cis\text{-}Pt(OH)(CH_2CN)L_2 \begin{cases} \xrightarrow[-H_2O]{+CH_3NO_2} cis\text{-}Pt(CH_2NO_2)(CH_2CN)L_2 \\ \quad (Xa,\ L_2 = 2\ PPh_3,\ XIa,\ L = Ph_2PCH{=}CHPPh_2) \\ \xrightarrow[-H_2O]{+CH_3(CO)Ph} cis\text{-}Pt(CH_2\overset{O}{\overset{\|}{C}}Ph)(CH_2CN)L_2 \\ \quad (XIIa,\ L_2 = Ph_2PCH{=}CHPPh_2) \end{cases} \quad (13)$$

Complex VIIa did not react with acetonitrile and acetylacetone, and the sole product formed in each case was IXa. The methoxo complex $Pt(OCH_3)(CH_2CN)(PPh_3)_2$ (XIIIa) was not obtained by treating VIIa with diazomethane, but was formed in quantitative yield in reaction 14. XIIIa is converted into the hydroxo

$$cis\text{-}PtCl(CH_2CN)(PPh_3)_2 + NaOCH_3 \xrightarrow[50°C]{toluene} cis\text{-}Pt(OCH_3)(CH_2CN)(PPh_3)_2 + NaCl \quad (14)$$

(XIIIa)

complex VIIIa in wet benzene or in suspensions containing 1 equivalent NaOH. All the complexes were characterized by elemental analysis, and IR, $^1H$ and $^{31}P$ NMR spectra (Table 1).

## Experimental

The spectroscopic techniques have been described previously [37]. Manser (Mikrolabor ETH, Zürich) and the Institute of Organic Chemistry (University of Padua) carried out the microanalyses. GLC was carried out on a Hewlett—Packard 5730A gas-chromatograph equipped with flame ionization detectors and with a Hewlett—Packard 3380A integrator. Solution samples were injected at 170°C (at this temperature no cyanoalkanes are generated by thermal decomposition of solutions of hydridocyanoalkylplatinum(II) complexes) in a column consisting of 5 ft 10% W UCC on Chromosorb WAW-DMCS thermostatted at 70—90°C, and comparisons were made with standard solutions. Gas samples were analyzed using a column of 3 ft Parapak Q at room temperature. These determinations are accurate to within 3%.

The preparation of the hydrido complexes is reported elsewhere: Ia, IIa, IIIa [35]; Ib, IIb, IIIb [34].

*Reductive elimination reactions of $PtH[(CH_2)_nCN]L_2$ ($n$ = 1, 3; $L_2$ = 2 $PPh_3$, $Ph_2PC_2H_4PPh_2$) with carbon monoxide*

A typical procedure is described for *trans*-$PtH(n\text{-}C_3H_6CN)(PPh_3)_2$. Ib (158 mg, 0.20 mmol) was dissolved in 5.0 ml of carbon monoxide-saturated toluene contained in a 15 ml two-necked flask fitted with a magnetic stirrer, a CO inlet and outlet, and a serum cap. The mixture was stirred under 1 atm of CO at 25—30°C. A small amount of solution was extracted periodically with a syringe and analyzed by gas chromatography, and its IR spectrum was recorded in the range 2300—1600 $cm^{-1}$. After 1 h, GLC analysis indicated that 0.192 mmol (96%) of 1-cyanopropane was obtained. The remaining yellow solution was treated with n-heptane under CO and on cooling pale-cream crystals, separated. The elemental analysis and IR spectrum of the product agree with those of $Pt(CO)_2(PPh_3)_2$ [51]. M.p. 103—104°C (dec.). Analysis. Found: C, 58.51; H, 4.16. $C_{38}H_{30}O_2P_2Pt$ calcd.: C, 58.84; H, 3.90%. The same reaction with 80 atm CO in benzene for 6 h at room temperature yielded an orange-red compound, whose elemental analysis and IR spectrum agree with those of $Pt_3(CO)_3(PPh_3)_4$ [52] ($\nu$(CO) 1787s, 1802s, 1845w $cm^{-1}$).

Similar reaction of $PtH(n\text{-}C_3H_6CN)(Ph_2PC_2H_4PPh_2)$ (146 mg, 0.220 mmol) with 1 atm CO in toluene (6.0 ml) gave 1-cyanopropane (yield 0.204 mmol, 93%) after 12 h. The IR spectrum of the yellow solution showed two strong bands at 1990 and 1935 $cm^{-1}$ assigned to the $\nu$(C≡O) of the terminal carbonyl ligands in a platinum(0) complex formulated as $Pt(CO)_2(Ph_2PC_2H_4PPh_2)$. Several attempts to isolate it under a CO atomophere gave only a non-crystallizable yellow oil. The oil was treated with n-heptane under nitrogen to give a red-violet powder, which analyzed as $Pt_4(CO)_3(Ph_2PC_2H_4PPh_2)_3$. M.p. 155—160°C (dec.). The IR spectrum in nujol mulls showed three strong $\nu$(C≡O) bands at 1918, 1795 and 1770 $cm^{-1}$. Analysis. Found: C, 47.30; H, 3.76%. $C_{81}H_{72}O_3P_6Pt_4$ calcd.: C, 47.24; H, 3.52%.

Similar carbonylations carried out with *trans*-$PtH(CH_2CN)(PPh_3)_2$ and with *cis*-$PtH(CH_2CN)(Ph_2PC_2H_4PPh_2)$ in toluene for 15 and 20 days, respectively, showed no reductive elimination (less than 5% of the stoichiometric amount of $CH_3CN$ was formed; no $\nu$(C≡O) nor $\nu$(C=O) bands appeared in the 2300—1600 $cm^{-1}$ IR region).

*Reductive elimination reactions of PtH[$(CH_2)_nCN$]$L_2$ ($n$ = 1, 3; $L_2$ = 2 $PPh_3$, $Ph_2PC_2H_4PPh_2$) with diphenylacetylene*

A typical procedure is described for *trans*-PtH(n-$C_3H_6CN$)($PPh_3$)$_2$. Ib (166 mg, 0.21 mmol), PhC≡CPh (107 mg, 0.60 mmol) and toluene (3.0 ml) were placed in a 15 ml two necked flask fitted with a serum cap, a nitrogen inlet and outlet and a teflon-coated magnetic stirrer. The solution was degassed in vacuum. Nitrogen was introduced and the flask was placed in a thermostatted oil bath at ca. 100°C. A small sample of the solution was extracted periodically with a syringe and the amount of 1-cyanopropane determined by GLC, the same sample was used to follow the disappearance of the strong IR band at 1950 $cm^{-1}$ ($\nu$(PtH)). After 25 min, GLC analysis indicated that 0.202 mmol (96%) of 1-cyanopropane was obtained. The remaining yellow solution was concentrated in vacuo, and the solid product was crystallized from methanol/diethyl ether (yield 73 mg). The pale yellow crystals showed physical properties and an IR band at 1730 $cm^{-1}$ ($\nu$(C≡C)) corresponding to those of the well known $Pt(PPh_3)_2$(PhC≡CPh) [53].

The reaction of *trans*-PtH($CH_2CN$)($PPh_3$)$_2$ (175 mg, 0.20 mmol) with a threefold excess of PhC≡CPh in toluene (3.0 mol) for 115 min at ca. 100°C under nitrogen gave acetonitrile (0.217 mmol, 94%) and $Pt(PPh_3)_2$(PhC≡CPh) (148 mg). The same reaction with PtH(n-$C_3H_6CN$)($Ph_2PC_2H_4PPh_2$) or PtH($CH_2CN$)($Ph_2PC_2H_4PPh_2$) gave an almost quantitative reductive elimination, yielding 1-cyanopropane and acetonitrile after 35 and 420 min, respectively. The same complex was precipitated from both solutions by addition of n-heptane, and recrystallization from $CH_2Cl_2$/n-heptane yielding 60—75% of $Pt(Ph_2PC_2H_4PPh_2)$(PhC≡CPh). M.p. 225—228°C. Analysis. Found: C, 63.32; H, 4.69; Pt, 7.28. $C_{40}H_{34}P_2Pt$ calcd.: C, 62.25; H, 4.44; P, 8.03%. IR in nujol mulls: 1738 $cm^{-1}$ ($\nu$(C≡C)); $^{31}$P NMR (in $CD_2Cl_2$ at −40°C): $\delta$(P) 31.0 ppm, $^1J$(PtP) 2262 Hz.

*Reductive elimination reactions of trans-PtH(n-$C_3H_6CN$)($PPh_3$)$_2$*

*(a) With triethylphosphine.* Ib (521 mg, 0.66 mmol) was suspended in n-hexane (25 ml) at −50°C. Triethylphosphine (0.30 ml, 2.03 mmol) was introduced by syringe and the mixture stirred under nitrogen at room temperature. The suspended white solid slowly became pale yellow. After 35 h, it was filtered off, washed several times with n-heptane under nitrogen, and dried under vacuum (0.1 Torr). Yield 258 mg (54%) of [$Pt(PPh_3)_2$] [39]. M.p. 140—145°C. The IR spectrum showed no bands in the 2300—1700 $cm^{-1}$ region nor at ca. 730 $cm^{-1}$, $\nu$(CH) characteristic of *ortho*-metallated phenyl ring [56], and no nitrogen was detected by elemental analysis. Analysis. Found: C, 61.09; H, 4.48; P, 8.95. $C_{36}H_{30}P_2Pt$ calcd.: C, 60.08, H, 4.20; P, 8.61%. (The slightly higher values observed are probably due to the presence of a small amount of $Pt(PPh_3)_3$.)

*(b) With dimethylphenylphosphine.* Ib (403 mg, 0.51 mmol) was suspended in n-hexane (20 ml) at −50°C. $PPhMe_2$ (0.332 g, 2.40 mmol) was introduced by syringe and the mixture was stirred under nitrogen at room temperature for 45 h. GLC analysis of the filtered solution showed that 1-cyanopropane (0.480 mmol, 94%) had been formed. The pale-yellow solid was washed several times with n-hexane and dried under vacuum. Yield 284 mg (64%) of $Pt(PPh_3)$-$(PPhMe_2)_3$. M.p. 85—92°C. Analysis. Found: C, 57.41; H, 5.64. $C_{42}H_{48}P_4Pt$ calcd.: C, 57.86; H, 5.55%. $^1$H NMR in $CD_2Cl_2$ at 34°C: $\delta(CH_3)$ 2.1 ppm (18 H), $\delta(C_6H_5)$ 7.8 ppm (30 H).

*(c) With cis-bis(diphenylphosphino)ethylene.* Ib (254 mg, 0.32 mmol) was dissolved in toluene (5.0 ml) and mixed with $Ph_2PCH{=}CHPPh_2$ (163 mg, 0.41 mmol at room temperature under nitrogen. After 20 h the red-orange solution contained 1-cyanopropane in almost quantitative yield (GLC analysis). From this solution the orange complex $Pt(Ph_2PCH{=}CHPPh_2)(PPh_3)_2$ was precipitated by addition of n-heptane (40 ml), it was filtered off, washed with n-heptane then with methanol and dried under vacuum. Yield 305 mg (85%). M.p. 165—175°C. Analysis. Found: C, 65.57; H, 4.62; P, 11.12. $C_{62}H_{52}P_4Pt$ calcd.: C, 66.72; H, 4.70; P, 11.10%. $^{31}P$ NMR see part 1.a. The same reaction with $PtH(n\text{-}C_3H_6CN)(Ph_2PCH{=}CHPPh_2)$ (0.20 mmol) and $Ph_2PCH{=}CHPPh_2$ (0.25 mmol) afforded the known complex $Pt(Ph_2PCH{=}CHPPh_2)_2$ [41]. M.p. 240—245°C. Analysis. Found, C, 62.83; H, 4.76. $C_{52}H_{44}P_4Pt$ calcd.: C, 61.90; H, 4.37%.

*Cleavage of the Pt-H bond of $PtH[(CH_2)_nCN]L_2$ (n = 1, 3; $L_2$ = 2 $PPh_3$, $Ph_2PCH{=}CHPPh_2$) with tetrafluoboric acid*

A typical procedure is described for the reaction of *trans*-$PtH(CH_2CN)(PPh_3)_2$ with $HBF_4$. An ethereal solution (4.0 ml) of tetrafluoboric acid (0.71 *M*, 2.84 mmol) was added to a stirred suspension of Ia (305 mg; 0.40 mmol) in anhydrous diethyl ether (15 ml). The mixture was stirred under nitrogen for 18 h at room temperature. The white solid *trans*-$[Pt(CH_2CN)(PPh_3)_2]_m(BF_4)_m$ was filtered off, washed with ether, and recrystallized from $CH_2Cl_2$/diethyl ether. Yield 295 mg (87%). M.p. 145—148°C. Analysis. Found: C, 54.54; H, 4.32; N, 1.12. $C_{38}H_{32}NP_2PtBF_4$ calcd.: C, 53.92; H, 3.81; N, 1.65%. IR and NMR data see Table 1.

Similar cleavage reactions, carried out in diethyl ether using other hydridocyanoalkyl complexes and a large excess of $HBF_4$, always resulted in hydrogen elimination and formation of cationic cyanoalkylplatinum(II) complexes (yields 85—95%) in which the CN group is coordinated. In particular, *trans*-$PtH(n\text{-}C_3H_6CN)(PPh_3)_2$ after 5 h gave *trans*-$[Pt(n\text{-}C_3H_6CN)(PPh_3)_2]_m(BF_4)_m$ [37], $PtH(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ after 20 h gave $[Pt(CH_2CN)(Ph_2PCH{=}CHPPh_2)]_2(BF_4)_2$ [37], and $PtH(n\text{-}C_3H_6CN)(Ph_2PCH{=}CHPPh_2)$ after 22 h gave the new complex $[Pt(n\text{-}C_3H_6CN)(Ph_2PCH{=}CHPPh_2)]_2(BF_4)_2$; M.p. 185—190°C. Analysis. Found: C, 46.98; H, 3.81; N, 1.84. $C_{30}H_{28}NP_2PtBF_4$ calcd.: C, 48.27; H, 3.78; N, 1.88%. IR and NMR data see Table 1. This last complex was also prepared by abstraction of chloride from $PtCl(n\text{-}C_3H_6CN)(Ph_2PCH{=}CHPPh_2)$ with a stoichiometric amount of $AgBF_4$ in dichloromethane.

*Cleavage of the Pt-H bond of $PtH[(CH_2)_nCN](Ph_2PCH{=}CHPPh_2)$ (n = 1, 3) with hydrochloric acid*

A solution of HCl (2.0 ml) in diethyl ether (0.165 *M*, 0.330 mmol) was added to a solution of IIIa (203 mg, 0.320 mmol) or IIIb (211 mg, 0.320 mmol) in benzene (25 ml) and the mixture was stirred under nitrogen at room temperature. After 20 h the suspension was concentrated to 5 ml. Precipitation with diethyl ether followed by recrystallisation from $CH_2Cl_2$/ether yielded almost quantitative amounts of $PtCl(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ [54] and $PtCl(n\text{-}C_3H_6CN)(Ph_2PCH{=}CHPPh_2)$ (VIb), respectively. VIb: m.p. 205—208°C. Analysis. Found, C, 51.59; H, 4.13; N, 1.95; Cl, 5.27. $C_{30}H_{28}ClNP_2Pt$ calcd.: C, 51.84; H, 4.06; N, 2.02; Cl, 5.10%. IR and NMR data see Table 1.

*Cleavage of the Pt—C bond of trans-PtH[$(CH_2)_nCN$]$(PPh_3)_2$ (n = 1, 3) with hydrochloric acid*

1.0 ml of a solution of HCl in diethyl ether (0.165 *M*) was added to a solution of Ia (125 mg, 0.164 mmol) or Ib (128 mg, 0.162 mmol) in toluene (2.0 ml) and the mixture was stirred at room temperature. After 25 h GLC analysis of samples of the solutions showed acetonitrile or 1-cyanopropane to have been formed in almost quantitative yields. Diethyl ether (ca. 10 ml) was added to the solutions to ensure complete precipitation. In both cases the white crystalline complex *trans*-[$PtHCl(PPh_3)_2$] [43] was obtained (yields 85—90%), and identified by its physical and spectroscopic properties.

*Cleavage of both Pt—H and Pt—C bonds with excess hydrochloric acid*

*(a) On trans-PtH[$(CH_2)_nCN$]$(PPh_3)_2$ (n = 1, 3).* 2.0 ml of a solution of HCl in diethyl ether (0.82 *M*, 1.64 mmol) was added to a stirred solution of Ib (148 mg, 0.188 mmol) or Ia (135 mg, 0.177 mmol) in toluene (2.0 ml). After 2.5 and 7 h, the only intermediate identified in samples of both solutions was *trans*-$PtHCl(PPh_3)_2$. After ca. 30 h, GLC of the solutions showed quantitative amounts of 1-cyanopropane or acetonitrile to be present. Evaporation of the solutions to dryness yielded yellow crystals, which were filtered off, washed with ether and dried under vacuum. These yellow solids were identified as mixtures of ca. 20—35% *cis*- and ca. 65—80% *trans*-$PtCl_2(PPh_3)_2$ [47] on the basis of the relative intensity of the IR band at ca. 550 $cm^{-1}$, as proposed by Mastin [47] for bis(triphenylphosphine)platinum(II) complexes, and of the $\nu$(PtCl) bands (*trans* 342(m); *cis* 316(m) and 297(m) $cm^{-1}$).

*(b) On PtH[$(CH_2)_nCN$]$(Ph_2PCH{=}CHPPh_2)$ (n = 1, 3).* A suspension of IIIb (93 mg, 0.140 mmol) or IIIa (102 mg, 0.160 mmol) in diethyl ether (10 ml) was treated with 2.0 ml of a solution of HCl in diethyl ether (0.82 *M*, 1.64 mmol). The heterogenous mixture was vigorously stirred for 14 and 40 h, respectively. IR spectra in Nujol mulls of samples of the white products showed that the products were mainly $PtCl(n\text{-}C_3H_6CN)(Ph_2PCH{=}CHPPh_2)$ and $PtCl(CH_2CN)$-$(Ph_2PCH{=}CHPPh_2)$. Only after 3 and 10 days, respectively, were the suspended complexes fully transformed into the dichloro complex $PtCl_2(Ph_2PCH{=}CHPPh_2)$ [41].

*Cleavage of both Pt—H and Pt—C bonds of $PtH(CH_2CN)L_2$ ($L_2$ = 2 $PPh_3$, cis-$Ph_2CH{=}CHPPh_2$)*

*(a) With chlorine in excess.* Chlorine was bubbled at room temperature through a solution of Ia (183 mg, 0.240 mmol) or IIIa (136 mg, 0.215 mmol) in toluene (3.0 ml). The solution became strongly acidic and turbid after a few minutes; complete precipitation of the dichloroplatinum complexes occurred after 10 and 30 min, respectively. GLC analysis of degassed samples of both solutions showed chloroacetonitrile in almost quantitative yield. Methanol (10 ml) was added to the solutions to ensure complete precipitation of the complexes (yields 90—96%), which were identified as *trans*-$PtCl_2(PPh_3)_2$ [47] and $PtCl_2(Ph_2PCH{=}CHPPh_2)$ [41], respectively.

*(b) With stoichiometric chlorine.* A solution of Ia (167 mg, 0.220 mmol) in toluene (3.0 ml) was treated at room temperature with chlorine (5.0 ml, ca. 0.22 mmol). The solution immediately became strongly acidic. After 10 min,

GLC analysis of the solution showed acetonitrile (0.128 mmol, 58%) and chloroacetonitrile (0.053 mmol, 24%) to be present. Evaporation of the solution to dryness yielded a yellow product, which was washed with methanol. Its IR and $^1$H NMR spectra were consistent with those of a mixture of *trans*-$PtCl(CH_2CN)(PPh_3)_2$ (ca. 47%), *trans*-$PtHCl(PPh_3)_2$ (ca. 25%), *trans*-$PtCl_2(PPh_3)_2$ (ca. 20%) and unreacted starting complex Ia (ca. 10%).

*Cleavage of the Pt—H bond of $PtH(CH_2CN)L_2$ ($L_2$ = 2 $PPh_3$, $Ph_2PC_2H_4PPh_2$) with alkyl halogenides*

*(a) With methyl iodide.* Ia (309 mg, 0.406 mmol) or IIa (320 mg, 0.504 mmol) was placed under helium in a 100 ml flask equipped with a serum cap. $CH_3I$ (5 ml) was added with a syringe. After 15 h the evolution of gas was complete, and GLC analysis of samples of the gas showed methane to be present in 90% of the stoichiometric amount. Evaporation of the solutions to dryness gave quantitative yields of pale-yellow solids which, after recrystallisation from $CH_2Cl_2/Et_2O$, were characterized by IR and $^1$H NMR as *trans*-$PtI(CH_2CN)(PPh_3)_2$ and $PtI(CH_2CN)(Ph_2PC_2H_4PPh_2)$ [54], respectively.

*(b) With chloroform.* Ia (104 mg, 0.136 mmol) was stirred with $CHCl_3$ (2.0 ml) under nitrogen at room temperature. After 5 days GLC analysis of the solution showed $CH_2Cl_2$ (0.121 mmol, 89% of stoichiometric amount) to be present. The white complex *trans*-$PtCl(CH_2CN)(PPh_3)_2$ [37] (83 mg, 76%) was precipitated by adding ethanol.

*(c) With chloroacetonitrile.* Ia (152 mg, 0.200 mmol) was stirred with $ClCH_2CN$ (2.0 ml) under nitrogen at room temperature. After 16 days GLC analysis of the solution showed $CH_3CN$ (0.184 mmol, 92%) to be present. *trans*-$PtCl(CH_2CN)(PPh_3)_2$ [37] (137 mg, 86%) was precipitated by adding ethanol.

*Preparation of hydroxocyanoalkylplatinum(II) complexes and condensation reactions*

The IR and NMR data are listed in Table 1.

*cis-$Pt(OH)(CH_2CN)(PPh_3)_2$ (VIIa).* A solution of NaOH (0.3 g) in methanol (5 ml) was added to a suspension of *cis*-$[Pt(CH_2CN)(PPh_3)_2]_2(BF_4)_2$ (1.3 g) [37] in methanol (25 ml). A clear solution was obtained after heating at 40°C for 30 min. The white complex VIIa was precipitated by adding water, and recrystallized from $CH_2Cl_2/Et_2O$. Yield 98%. M.p. 151—161°C (dec.). Analysis. Found: C, 57.86; H, 4.26; N, 1.76; P, 7.62. $C_{38}H_{33}NOP_2Pt$ calcd.: C, 58.76; H, 4.28; N, 1.80; P, 7.97%.

*$Pt(OH)(CH_2CN)(Ph_2PCH{=}CHPPh_2)$ (VIIIa).* A solution of NaOH (0.56 g) in methanol (15 ml) was added to a suspension of $[Pt(CH_2CN)(Ph_2PCH{=}CHPPh_2)]_2(BF_4)_2$ (2.0 g) [37] in methanol (40 ml). The mixture was stirred for 30 min at room temperature and the resulting solution evaporated to 10 ml. The white complex VIIIa was precipitated by adding water, and recrystallized from $CH_2Cl_2/Et_2O$. Yield 94%. M.p. 213—214°C (dec.). Analysis. Found: C, 50.96; H, 4.06; N, 2.06; P, 9.57. $C_{28}H_{25}NOP_2Pt$ calcd.: C, 51.85; H, 3.89; N, 2.16; P, 9.55%.

*$[Pt(CH_2CONH)(PPh_3)_2]_2$ (IXa).* VIIa (0.3 g) was dissolved in THF or benzene (10 ml); after 6 h at room temperature, the solution was evaporated to 4 ml. IXa was precipitated by adding diethyl ether and recrystallized from $CH_2Cl_2/Et_2O$. Yield 98%. M.p. 195—196°C. Analysis. Found: C, 58.95; H, 4.25; N, 1.93; P,

7.62. $C_{38}H_{33}NOP_2Pt$ calcd.: C, 58.76; H, 4.28; N, 1.80; P, 7.97%. It should be noted that the direct nucleophilic attack by water of the coordinated group of *cis*-$[Pt(o\text{-}CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ giving the analogous dimeric amido complex $[Pt(o\text{-}CH_2C_6H_4CONH)(PPh_3)_2]_2$ [55] does not take place in the case of *cis*-$[Pt(CH_2CN)(PPh_3)_2]_2(BF_4)_2$.

*cis-Pt(CH₂CN)(CH₂NO₂)L₂ (Xa, L₂ = 2 PPh₃; XIa, L = Ph₂PCH=CHPPh₂).* VIIa (0.25 g) or VIIIa (0.3 g) and nitromethane (1.0 and 2.4 g, respectively) were dissolved in benzene (6 and 15 ml, respectively). The solutions were heated at 70°C for 6 h and then evaporated to a small volume. The complexes were precipitated by adding n-hexane and recrystallized from $CH_2Cl_2$/MeOH. Yields 70%. Xa: m.p. 220—221°C (dec.). Analysis. Found: C, 57.25; H, 4.26; N, 3.64; P, 7.71. $C_{39}H_{34}N_2O_2P_2Pt$ calcd.: C, 57.14; H, 4.18; N, 3.42; P, 7.56%. XIa: m.p. 207—209°C (dec.). Analysis. Found: C, 50.27; H, 3.80; N, 4.04; P, 8.86. $C_{29}H_{26}N_2O_2P_2Pt$ calcd.: C, 50.36; H, 3.79; N, 4.05; P, 8.96%.

*Pt(CH₂CN)(CH₂COPh)(Ph₂PCH=CHPPh₂) (XIIa).* A solution of VIIa (0.2 g) in acetophenone (10 ml) was stirred at room temperature for 30 h and then concentrated to 7 ml at 80°C/15 Torr. n-Hexane was added and the suspension stirred for 3 h. After filtration, the white complex was washed with n-hexane and recrystallized from THF/n-hexane. Yield 55%. M.p. 187—189°C (dec.). Analysis. Found: C, 56.29; H, 4.22; N, 1.87; P, 8.14. $C_{36}H_{31}NOP_2Pt$ calcd.: C, 57.60; H, 4.16; N, 1.87; P, 8.25%.

*cis-Pt(OCH₃)(CH₂CN)(PPh₃)₂ (XIIIa).* A solution of $NaOCH_3$ (0.125 g) in methanol (4 ml) was added to a suspension of *cis*-$PtCl(CH_2CN)(PPh_3)_2$ (0.5 g) in toluene (35 ml). The mixture was stirred for 2 h at 60°C. Excess $NaOCH_3$ and NaCl were filtered off and the filtrate was concentrated until precipitation occurred. The white complex *cis*-$Pt(OCH_3)(CH_2CN)(PPh_3)_2$ was recrystallized from $CH_2Cl_2$/MeOH. Yield 70%. M.p. 137—138°C. Analysis. Found: C, 60.45; H, 4.64; N, 1.72; P, 7.96. $C_{39}H_{35}NOP_2Pt$ calcd.: C, 61.00; H, 4.69; N, 1.67; P, 7.40%.

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## References

1 U. Belluco, Organometallic and Coordination Chemistry of Platinum, Academic Press, London 1974; F.R. Hartley, The Chemistry of Platinum and Palladium, Halsted Press, New York, 1973; D.M. Roundhill, Advan. Organometal. Chem., 13 (1975) 273.
2 R. Romeo, P. Uguagliati and U. Belluco, J. Molecular Catal., 1 (1975/76) 325.
3 M.H. Chisholm, Platinum Met. Rev., 19 (1975) 100.
4 P.J. Davidson, M.F. Lappert and R. Pearce, Chem. Rev., 76 (1976) 219.
5 J. Chatt and B.L. Shaw, J. Chem. Soc., (1959) 4020.
6 J. Chatt and B.L. Shaw, J. Chem. Soc., (1962) 5075.
7 H.C. Clark and J.D. Ruddick, Inorg. Chem., 9 (1970) 2556.
8 J.S. Bradley, A.V. Kramer, J.A. Labinger and J.A. Osborne, J. Amer. Chem. Soc., 96 (1974) 7145.
9 A.V. Kramer and J.A. Osborne, J. Amer. Chem. Soc., 96 (1974) 7832.
10 M.H. Chisholm and L.A. Rankel, Inorg. Chem., 16 (1977) 2177.
11 T.G. Appleton, H.C. Clark and L.E. Manzer, J. Organometal. Chem., 65 (1974) 275.
12 P.S. Braterman, R.J. Cross and G.B. Young, J. Chem. Soc. Dalton, (1976) 1310.

13 H.C. Clark and L.E. Manzer, Inorg. Chem., 12 (1973) 362.
14 M.P. Brown, R.J. Puddephatt, C.E. Upton and S.W. Lavington, J. Chem. Soc., Dalton Trans., (1974) 1613.
15 J. Chatt, R.S. Coffey, A. Gough and D.T. Thompson, J. Chem. Soc. A, (1968) 190.
16 G.M. Whitesides, J.F. Gaasch and E.R. Stedronsky, J. Amer. Chem. Soc., 94 (1972) 5258.
17 J.X. McDormott, J.F. White and G.M. Whitesides, J. Amer. Chem. Soc., 95 (1973) 4451.
18 J.X. McDormott, J.F. White and G.M. Whitesides, J. Amer. Chem. Soc., 98 (1976) 6521.
19 M.H. Chisholm and H.C. Clark, Accounts Chem. Res., 6 (1973) 202.
20 H.C. Clark and L.E. Manzer, J. Amer. Chem. Soc., 95 (1973) 3812.
21 H.C. Clark and L.E. Manzer, Inorg. Chem., 13 (1974) 1291, 1996.
22 L.E. Manzer, Inorg. Chem., 15 (1976) 2354.
23 R. Cramer and R.V. Lindsey, J. Amer. Chem. Soc., 88 (1966) 3534.
24 H.C. Clark and H. Kurosawa, Inorg. Chem., 11 (1972) 1275.
25 A.J. Deeming, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton, (1973) 1848.
26 H.C. Clark, C. Jablonski, H. Halpern, A. Mantovani and T.A. Weil, Inorg. Chem., 13 (1974) 1541.
27 M.H. Chisholm and W.S. Johns, Inorg. Chem., 14 (1975) 1189.
28 P.E. Garrou and R.G. Heck, J. Amer. Chem. Soc., 98 (1976) 4115.
29 Y. Yamamoto and H. Yamazaki, Coord. Chem. Rev., 8 (1972) 225.
30 D.F. Christian, H.C. Clark and R.F. Stepaniak, J. Organometal. Chem., 112 (1976) 209.
31 A. Nakamura and S. Otsuka, J. Amer. Chem. Soc., 95 (1973) 7262.
32 B. Worniak, J.D. Ruddick and G. Wilkinson, J. Chem. Soc. A, (1971) 3116.
33 W. Beck, K. Schropp, C. Oetker, R. Schlodder and H.S. Smedal, Chem. Ber., 106 (1973) 2144.
34 R. Ros, R. Bataillard and R. Roulet, J. Organometal. Chem., 118 (1976) C53, and results in press.
35 R. Ros, R.A. Michelin, R. Bataillard and R. Roulet, J. Organometal. Chem., 139 (1977) 355; idem, ibid., submitted.
36 R.A. Michelin, U. Belluco and R. Ros, Inorg. Chim. Acta, 24 (1977) L33.
37 R. Ros, J. Renaud and R. Roulet, Helv. Chim. Acta, 58 (1975) 133.
38 R. Ros, R.A. Michelin, G. Carturan and U. Belluco, J. Organometal. Chem., 133 (1977) 213.
39 R. Ugo, G. La Monica, F. Cariati, S. Cenini and F. Conti, Inorg. Chim. Acta, 4 (1970) 390.
40 R. Ugo, S. Cenini, M.F. Pilbrow, B. Deibl and G. Schneider, Inorg. Chim. Acta, 18 (1976) 113 and ref. therein.
41 R.B. King and Pramesh N. Kapoor, Inorg. Chem., 11 (1972) 1524.
42 J.A. Musso and A. Isaia, NMR-LAOCN-4A, QCPE Program, No. 232.
43 C. Eaborn, A. Pidcock and B.R. Steele, J. Chem. Soc. Dalton, (1976) 767, and ref. therein.
44 U. Belluco, M. Giustiniani and M. Graziani, J. Amer. Chem. Soc., 89 (1967) 6494.
45 U. Belluco, U. Croatto, P. Uguagliati and R. Pietropaolo, Inorg. Chem., 6 (1967) 718.
46 R. Romeo, D. Minniti, S. Lanza, P. Uguagliati and U. Belluco, Inorg. Chim. Acta, 19 (1976) L55.
47 S.H. Mastin, Inorg. Chem., 13 (1974) 1003.
48 R.J. Cross and F. Glockling, J. Chem. Soc., (1965) 5422.
49 T.G. Appleton and M.A. Bennett, J. Organometal. Chem., 55 (1973) C88; Inorg. Chem., 17 (1978) 738.
50 T. Yoshida, T. Okano and S. Otsuka, J. Chem. Soc. Dalton, (1976) 933.
51 P. Chini and G. Longoni, J. Chem. Soc. A, (1970) 1542.
52 J. Chatt and P. Chini, J. Chem. Soc. A, (1970) 1538.
53 L. Malatesta and S. Cenini, Zerovalent Compounds of Metals, Academic Press, London 1974, p. 181.
54 K. Suzuki, H. Yamamoto and S. Kanie, J. Organometal. Chem., 73 (1974) 131.
55 D. Schwarzenbach, A. Pinkerton, G. Chapuis, J. Wenger, R. Ros and R. Roulet, Inorg. Chim. Acta, 25 (1977) 255; R. Ros, J. Renaud and R. Roulet, J. Organometal. Chem., 104 (1976) 271.
56 S. Sostero, O. Traverso, M. Lenarda and M. Graziani, J. Organometal. Chem., 134 (1977) 259.
57 M.A. Bennett, G.B. Rovertson, P.O. Whimp and T. Yoshida, J. Amer. Chem. Soc., 95 (1973) 3028.
58 L. Abis, A. Sen and J. Halpern, J. Amer. Chem. Soc., 100 (1978) 2915.

*Note added in proof.* Halpern et al. [58] have reported recently that the reductive elimination of methane from *cis*-$PtH(CH_3)(PPh_3)_2$ is an intramolecular process. However, the hydridocyanoalkyl complexes reported here are thermally stable in hydrocarbon solutions (see Experimental and section 1.a.)