

Platinum(IV) Isocyanide Complexes

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Neutral and cationic platinum(IV) isocyanide complexes of the type $[\text{PtCl}_4(\text{CNR})_2]$, $[\text{PtCl}_4(\text{CNR})(\text{PMe}_2\text{Ph})]$, $[\text{PtCl}_3(\text{CNR})(\text{PMe}_2\text{Ph})_2]^+$, $[\text{PtCl}_2(\text{CNR})_2(\text{PMe}_2\text{Ph})_2]^{2+}$, where R = methyl, *t*-butyl, cyclohexyl, *p*-tolyl, have been prepared by chlorine addition to the corresponding platinum(II) derivatives. The complexes $[\text{PtCl}_2(\text{CN})_2(\text{CNR})_2]$ and $[\text{PtCl}_2(\text{CN})(\text{CNR})(\text{PMe}_2\text{Ph})_2]^+$ (R = *t*-butyl), are also reported. The cationic *t*-butylisocyanide derivatives are noteworthy in the way they readily lose the *t*-butyl cation at room temperature to give the corresponding cyano complexes. The compounds have been characterized by elemental analysis, molecular weights and conductivity measurements, and their i.r. and n.m.r. data are discussed in relation to structures and to the nature of the platinum–isocyanide bond.

Introduction

We have previously found that isocyanides react with chlorides of transition metals in high oxidation state, such as NbCl_5 , TaCl_5 ¹ and TiCl_4 ², to give insertion into the metal–chlorine bonds.

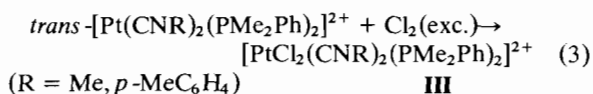
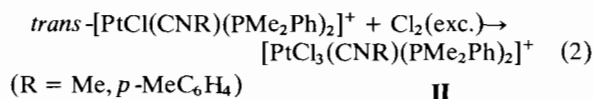
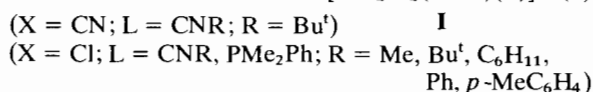
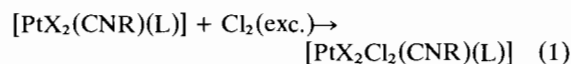
In order to get a better understanding of this reaction, we have studied the oxidative addition of chlorine to a variety of neutral and cationic platinum(II) isocyanide complexes which has given a series of platinum(IV) isocyanide compounds. Although these complexes showed no tendency to give insertion into the platinum–chloride bond, nevertheless there is a strong activation of the coordinate isocyanides, revealed by the extremely high values of the $\text{C}\equiv\text{N}$ stretching frequencies. For some cationic *t*-butyl isocyanide derivatives a dealkylation reaction occurred under very mild conditions yielding the corresponding cyano complexes. In this paper we describe the preparation of these compounds and their properties are discussed in the light of the platinum(IV) isocyanide compounds containing two or three σ bonded methyl groups, which have been recently published.^{3–5}

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Results and Discussion

The platinum(IV) isocyanide complexes can be easily obtained by chlorine additions to the corresponding platinum(II) derivatives [equations (1–3)]:



The reaction can be followed by i.r. spectroscopy because the CN stretching bands of the coordinated isocyanides are shifted to higher frequencies (30–60 cm^{-1}) on passing from Pt(II) to Pt(IV) complexes. In general the reactions are not influenced by the nature of the isocyanides nor by the presence of positive charges on the complexes and go to completion in a few minutes. Only in the case of reaction (1) (complexes of the type $[\text{PtCl}_2(\text{CNR})_2]$, R = Ph and *p*-MeC₆H₄) is the addition of chlorine not complete, even with a large excess of Cl₂ and after longer reaction times. When the excess of chlorine is removed during the working up of the reaction mixture the starting Pt(II) complexes are reformed (completely for R = Ph, partially for R = *p*-MeC₆H₄). This indicates that in this particular case an equilibrium is set up, the position of which depends on the nature of the group R. In fact, when R = alkyl the equilibrium is completely shifted to the right. This is related to the different bond properties of aryl isocyanides compared to those of alkyl isocyanides, the former being better π -accepting ligands and thus stabilising the lower oxidation state of the central metal.

The analytical, physical and i.r. data of all Pt(IV) complexes are reported in Table I and Table II respectively.

TABLE I. Analytical and Physical Data.

Complex	Colour	Melting point (°C) ^a	C		H		N		X		Λ^b (ohm ⁻¹ cm ² mol ⁻¹)
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
[PtCl ₄ (MeNC) ₂]	greenish yellow	165–175 dec. ^c	11.47	11.5	1.44	1.5	6.69	6.6	33.84	34.1	–
[PtCl ₄ (C ₆ H ₁₁ NC) ₂]	greenish yellow	153	30.28	30.5	3.99	4.0	5.05	5.0	25.54	25.4	–
[PtCl ₂ (CN) ₂ (<i>t</i> -C ₄ H ₉ NC) ₂]	pale–yellow	160–170 dec. ^c	29.76	29.6	3.75	3.7	11.57	11.6	14.64	14.8	–
[PtCl ₄ (<i>p</i> -MeC ₆ H ₄ NC) ₂]	yellow	160–170 dec.	33.64	33.4	2.47	2.6	4.90	4.8	24.82	24.5	–
[PtCl ₄ (PMe ₂ Ph)(MeNC)]	yellow	130–135 dec.	23.27	23.4	2.73	2.8	2.71	2.6	27.48	27.6	–
[PtCl ₄ (PMe ₂ Ph)(<i>i</i> -C ₄ H ₉ NC)]	yellow	175–180 dec. ^c	27.97	27.7	3.61	3.5	2.51	2.4	25.40	25.6	–
[PtCl ₄ (PMe ₂ Ph)(<i>p</i> -MeC ₆ H ₄ NC)]	yellow	163 dec.	32.45	32.3	3.06	3.0	2.37	2.3	23.94	24.1	–
[PtCl ₃ (PMe ₂ Ph) ₂ (MeNC)]ClO ₄	deep–yellow	133–138	30.14	30.1	3.37	3.3	1.95	1.9	19.77	20.1	79
[PtCl ₃ (PMe ₂ Ph) ₂ (<i>p</i> -MeC ₆ H ₄ NC)]ClO ₄	deep–yellow	155–160 dec.	36.29	35.3	3.68	3.6	1.76	1.7	17.85	17.9	81
[PtCl ₂ (PMe ₂ Ph) ₂ (MeNC) ₂](PF ₆) ₂	yellow	125–130 dec.	26.27	26.2	3.09	3.0	3.06	3.1	7.75	7.9	152
[PtCl ₂ (PMe ₂ Ph) ₂ (<i>p</i> -MeC ₆ H ₄ NC) ₂](BF ₄) ₂	yellow	153 dec.	40.45	40.1	3.82	3.8	2.95	2.9	7.46	7.5	167
[PtCl ₃ (CN)(PMe ₂ Ph) ₂]	yellow	190–200 dec.	33.82	33.7	3.67	3.5	2.32	2.3	17.61	17.9	–
[PtCl ₂ (CN) ₂ PMe ₂ Ph ₂]	pale–yellow	165 dec.	36.37	36.1	3.73	3.8	4.71	4.7	11.93	12.1	–
[PtCl ₂ (CN)(PMe ₂ Ph) ₂ (<i>t</i> -C ₄ H ₉ NC)]PF ₆	yellow	185 dec.	33.18	33.1	3.92	3.8	3.52	3.5	8.90	9.0	86

^aUncorrected values. ^b10⁻³ M Methanolic solutions at 25° C. ^cDecomposition without melting.

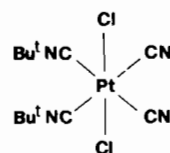
TABLE II. Characteristic I.R. Absorptions (cm^{-1}).^a

Complex	$\nu(\text{CN})_{\text{isocyanide}}$	$\nu(\text{Pt}-\text{Cl})$	Other Bands	$\Delta\nu^b$
$[\text{PtCl}_4(\text{CNMe})_2]$	2320 ms	350 vs		147
$[\text{PtCl}_4(\text{CNC}_6\text{H}_{11})_2]$	2296 s, 2285 s (2281 s)	349 vs, 337 s, 325 sh		138
$[\text{PtCl}_4(\text{CN}p\text{-C}_6\text{H}_4\text{Me})_2]$	2275 sh, 2265 m (2263 m)	353 sh, 343 s, 322 m		131
$[\text{PtCl}_4(\text{CNPh})_2]^f$	(2265 ms)			133
$[\text{PtCl}_2(\text{CN})_2(\text{CNBu}^t)_2]$	2295 s, 2283 s (2275 s)	353 s	2193 m, 2185 mw } $\nu(\text{CN})_{\text{cyanide}}$ (2190 w)	134
$[\text{PtCl}_4(\text{CNMe})(\text{PMe}_2\text{Ph})]$	2288 m (2287 m)	346 vs		114
$[\text{PtCl}_4(\text{CNBu}^t)(\text{PMe}_2\text{Ph})]$	2276 s (2280 s)	343 vs, 323 m, 292 vs		139
$[\text{PtCl}_4(\text{CN}p\text{-C}_6\text{H}_4\text{Me})(\text{PMe}_2\text{Ph})]$	2268 ms (2270 ms)	348 s, 340 m, 328 ms, 280 s		138
$[\text{PtCl}_3(\text{CNMe})(\text{PMe}_2\text{Ph})_2]\text{ClO}_4$	2310 ms (2300 ms)	352 s, 338 ms	1090 vs, br ($\nu(\text{ClO})$) 622 vs ($\delta(\text{ClO})$)	127
$[\text{PtCl}_3(\text{CNBu}^t)(\text{PMe}_2\text{Ph})_2]\text{ClO}_4^c$	(2270 ms)			129
$[\text{PtCl}_3(\text{CN}p\text{-C}_6\text{H}_4\text{Me})(\text{PMe}_2\text{Ph})_2]\text{ClO}_4$	2260 ms (2264 ms)	348 ms, 333 ms	1080 vs, br ($\nu(\text{ClO})$) 622 vs ($\delta(\text{ClO})$)	132
$[\text{PtCl}_2(\text{CNMe})_2(\text{PMe}_2\text{Ph})_2](\text{PF}_6)_2$	2315 s	361 ms	840 vs, br ($\nu(\text{PF})$); 561 vs ($\delta(\text{PF})$)	142
$[\text{PtCl}_2(\text{CN}p\text{-C}_6\text{H}_4\text{Me})(\text{PMe}_2\text{Ph})_2](\text{BF}_4)_2$	2268 m	360 m	1065 s, br ($\nu(\text{BF})$); 540 ms or 530 s ($\delta(\text{BF})$)	136
$[\text{PtCl}_2(\text{CN})(\text{CNBu}^t)(\text{PMe}_2\text{Ph})_2]\text{PF}_6$	2280 s	353 ms	2180 m ($\nu(\text{CN})_{\text{cyanide}}$), 840 vs, br ($\nu(\text{PF})$); 560 vs ($\delta(\text{PF})$)	139
$[\text{PtCl}_3(\text{CN})(\text{PMe}_2\text{Ph})_2]$		346 s, 318 ms	2170 mw ($\nu(\text{CN})_{\text{cyanide}}$)	
$[\text{PtCl}_2(\text{CN})_2(\text{PMe}_2\text{Ph})_2]$		347 s	2160 ms ($\nu(\text{CN})_{\text{cyanide}}$)	

^a Value in parentheses refer to CH_2Cl_2 solutions. ^b $\Delta\nu = \nu(\text{CN})_{\text{complex}} - \nu(\text{CN})_{\text{free isocyanide}}$; where possible, it refers to CH_2Cl_2 solution spectra. ^c The complexes were not isolated, their presence being assumed from the spectra of the reaction mixture after addition of Cl_2 to the corresponding Pt(II) derivatives.

The Pt(IV) complexes are more deeply coloured than the corresponding Pt(II) derivatives, and have a comparable thermal stability.⁶⁻⁸ Complexes of the type II and III are uni-univalent and bi-univalent electrolytes respectively in methanolic solution. Complexes I appear to be monomers as shown by the molecular weight of $[\text{PtCl}_4(\text{C}_6\text{H}_{11}\text{NC})_2]$ in 1,2-dichloroethane. The assignment of the structures in the solid and in solution is based on the i.r. and ^1H n.m.r. spectra (Table III).

In the solid state the complex $[\text{PtCl}_4(\text{CNMe})_2]$ shows a *trans* configuration, while the corresponding cyclohexyl and *p*-tolyl isocyanide derivatives have spectra which are better interpreted on the basis of a *cis* structure (two $\nu(\text{CN})$ and three $\nu(\text{PtCl})$ bands have been observed in agreement with a C_{2v} symmetry)*. With the same arguments the following structure:



has been assigned to $[\text{PtCl}_2(\text{CN})_2(\text{CNBu}^t)_2]$. However, although the complexes appear to have two *cis* isocyanides in the solid, they show only one C-N stretching frequency in solution [and one $\nu(\text{CN})$ band of the cyano groups for the above mentioned dicyano derivative]. This may be due either to an accidental degeneracy or to the *trans* isomer being present in solution.

The mixed derivatives $[\text{PtCl}_4(\text{CNR})(\text{PMe}_2\text{Ph})]$, have a *cis* configuration for $\text{R} = \text{Bu}^t$ and *p*- MeC_6H_4 , but when $\text{R} = \text{Me}$ the configuration is *trans*, as is found also for $[\text{PtCl}_4(\text{CNMe})_2]$. These structures are probably retained in CDCl_3 solution, as indicated by their ^1H n.m.r. spectra (see later). The cationic compounds II and III have been assigned the following structures:

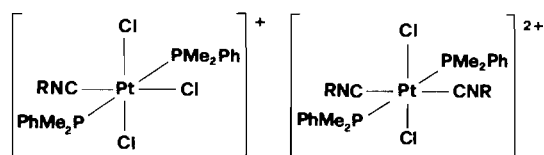
* According to theory four infrared active Pt-Cl stretching vibrations would be expected, but one of these, i.e. the symmetric stretch of the *trans* chlorines is very likely of low intensity.

TABLE III. ^1H N.m.r. Spectra.^a

Complex	δ Values and Coupling Constants	Assignment	Solvent
[PtCl ₄ (CNC ₆ H ₁₁) ₂]	4.49 [1] ^b 1.98 } [10] ^b 1.56 }	CN-CH \equiv -CH ₂ -	CDCl ₃
[PtCl ₄ (CN <i>p</i> -C ₆ H ₄ Me) ₂]	7.34 Q [4] ^c 2.42 S [3]	-C ₆ H ₄ - C ₆ H ₄ -CH ₃	CDCl ₃
[PtCl ₄ (CNMe)(PMe ₂ Ph)]	8.1-7.3 [5] ^b 3.70 [3] ^d 2.16 T _D [6], ² J _{P-CH} = 13.3, ³ J _{Pt-PCH} = 16	P-C ₆ H ₅ CN-CH ₃ P-CH ₃	CDCl ₃
[PtCl ₄ (CNBu ^t)(PMe ₂ Ph)]	8.2-7.4 [5] ^b 2.38 T _D [6], ² J _{P-CH} = 13.6, ³ J _{Pt-PCH} = 20 1.22 S [9] 8.1-7.4 ^b 2.24 T _D , ² J _{P-CH} = 13.6, ³ J _{Pt-PCH} = 21.5 1.49 S	P-C ₆ H ₅ P-CH ₃ C(CH ₃) ₃ P-C ₆ H ₅ P-CH ₃ C(CH ₃) ₃	CDCl ₃ (CD ₃) ₂ SO ^e
[PtCl ₄ (CN <i>p</i> -C ₆ H ₄ Me)(PMe ₂ Ph)]	8.0-6.8 [1] ^b 2.43 T _D } [1], ² J _{P-CH} = 13.1, ³ J _{Pt-PCH} = 19.4 2.41 S }	P-C ₆ H ₅ + -C ₆ H ₄ - P-CH ₃ C ₆ H ₄ -CH ₃	CDCl ₃
[PtCl ₃ (CNMe)(PMe ₂ Ph) ₂]ClO ₄	7.66 [10] ^b 2.91 T [3], ⁴ J _{Pt-CNCH} = 15 2.23 T _T [12], ³ J _{Pt-PCH} = 12.4	P-C ₆ H ₅ CN-CH ₃ P-CH ₃	CDCl ₃
[PtCl ₃ (CN <i>p</i> -C ₆ H ₄ Me)(PMe ₂ Ph) ₂]ClO ₄	8.0-7.3 [10] ^b 6.76 Q [4] ^c 2.36 S } [15], ³ J _{Pt-PCH} = 12.2 2.26 T _T }	P-C ₆ H ₅ -C ₆ H ₄ - C ₆ H ₄ -CH ₃ P-CH ₃	CDCl ₃
[PtCl ₂ (CN)(CNBu ^t)(PMe ₂ Ph) ₂]PF ₆	8.0-7.4 ^b 2.26 T _T , ³ J _{Pt-PCH} = 12.5 1.48 S	P-C ₆ H ₅ P-CH ₃ C(CH ₃) ₃	(CD ₃) ₂ SO ^e
[PtCl ₃ (CN)(PMe ₂ Ph) ₂]	n.r. ^f 2.20 T _T , ³ J _{Pt-PCH} = 14.8	P-CH ₃	CDCl ₃

^a δ Values in p.p.m. relative to tetramethylsilane as internal standard, coupling constants in Hz. δ Values are considered accurate to ± 0.02 and coupling constants to ± 0.2 Hz. ^b Unresolved multiplet. ^c AB Quartet. ^d Unresolved triplet.

^e Some decomposition occurs in this solvent. ^f The spectrum of this compound was recorded only in the PMe region.



Solid state and CDCl₃ solution Solid state
R = Me, *p*-MeC₆H₄

The i.r. spectra of complexes **II** are characterized by two $\nu(\text{Pt}-\text{Cl})$ bands, the higher frequency probably arises from the asymmetric stretch of the *trans* chlorines. Complexes **III** show only one CN and one Pt-Cl stretching frequency as expected from the highest symmetry possible, D_{2h}.

The configurations of the products of the reactions (1) (X = CN) and (3) shows that a *trans* addition has occurred. This may not be the initial step, however.

In general the Pt(IV) complexes show very high CN stretching frequencies of the coordinated isocyanides. The $\Delta\nu$ shifts from the free ligands range 114 to 147 cm⁻¹. This indicates a high effective nuclear charge

on the central metal and, accordingly, a reduced π -bonding contribution to the platinum-isocyanide bond. It is to be noted that the lowest $\Delta\nu$ value, 114 cm⁻¹, was observed for [PtCl₄(CNMe)(PMe₂Ph)] and is probably related to the *trans* configuration of this complex, if compared to the $\Delta\nu$ values, 139 and 138 cm⁻¹, found in the corresponding CNBu^t and CN*p*-C₆H₄Me *cis* derivatives.

The Pt(IV)-isocyanide complexes previously reported contain two or three methyl groups linked to platinum and show lower $\Delta\nu$ values than our chloro derivatives.³⁻⁵

This is probably related to a higher electron density on the central metal caused by the good electron-donating properties of the methyl group.

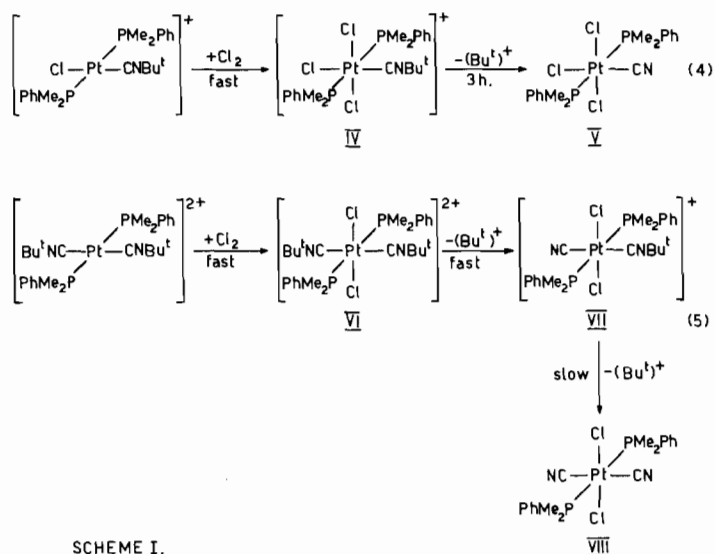
We have found that chlorides of transition metals in high oxidation state, such as NbCl₅, TaCl₅¹ and TiCl₄², readily insert the methyl and/or *ter*-butyl isocyanide into the metal-chlorine bond. However, no insertion reaction into the Pt-Cl bond was observed for the Pt(IV) complexes, although the coordinated isocyanides appear to be strongly activated, this being

probably due to the different strength of the metal-chlorine bonds.

The ^1H n.m.r. spectra, reported in Table III, are in good agreement with the proposed formulations. The coupling constants with the ^{195}Pt isotope show a marked decrease if compared with those of the Pt(II) complexes^{6,8-10}. This parallels the decreased s character of the bonds from square-planar to octahedral complexes. In the complexes $[\text{PtCl}_4(\text{CNR})(\text{PMe}_2\text{Ph})]$ the coupling constants between platinum and the phosphine methyls vary from 16 ($\text{R} = \text{Me}$) to 20 and 19.4 Hz ($\text{R} = \text{Bu}^t$ and $p\text{-C}_6\text{H}_4\text{Me}$ respectively). On the basis of *trans* influence arguments^{10,11} the lower value for the methyl isocyanide derivative supports a *trans* arrangement $\text{MeNC-Pt-PMe}_2\text{Ph}$ rather than $\text{Cl-Pt-PMe}_2\text{Ph}$, (CNMe has a higher *trans* influence than Cl^- and gives a lower $^3J_{\text{Pt-PMe}}$).

In the compounds **II** the phosphine-methyl signals appear as 1:3:1 triplets due to strong phosphorus-phosphorus coupling of the *trans* phosphines¹², flanked by ^{195}Pt satellites of one-fourth intensity. The four phosphine methyl groups are all equivalent. All this supports the configuration previously proposed on the basis of the i.r. spectra with two *trans* phosphines and three chlorines in meridionale positions.

The cationic Pt(II)-*ter*-butyl isocyanide complexes rapidly react with chlorine and then decompose with dealkylation of the coordinated isocyanide according to the scheme:



SCHEME I.

Reactions (4) and (5) proceed smoothly at room temperature. The complex **IV** was not isolated, but its presence was assumed from the appearance of a band at 2270 cm^{-1} , assigned to $\nu(\text{CN})$ of **IV**, the intensity of which decreased progressively while a weak band at

2170 cm^{-1} appeared, assigned to the cyano-group stretch of complex **V**.

Compounds **VI** was not observed in the reaction mixture. Its formation is only postulated as the transient product of chlorine addition, which is the first step of reaction (5). This is not unreasonable if we consider the course of reaction (3) previously discussed. Only the products **VII** and **VIII** could be detected and isolated from the reaction mixture, the complex **VII** being the major product. We have tried to rationalise all these facts by assuming a step-wise dealkylation of **VI**, the first step being so fast as to prevent the experimental observation of **VI**. The second step, *i.e.* the dealkylation of **VII** to produce **VIII**, occurs so slowly (as seen from the i.r. spectra of the reaction mixture taken at various times) that it was possible to isolate both complexes and even characterise the compound **VII** in solution by conductivity and ^1H n.m.r. measurements.

These results are reminiscent of those reported by Treichel and Hess for the dealkylation of coordinated methyl isocyanide in complexes of the type $[\text{PtX}(\text{CNMe})(\text{PR}_3)_2]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}; \text{R} = \text{Et}, \text{Ph}$) under reflux in benzene.¹³ The same reaction with $[\text{PtI}(\text{CNMe})_2(\text{PPh}_3)_2]^+$ gave $[\text{PtI}(\text{CN})(\text{CNMe})(\text{PPh}_3)_2]$ together with a small amount of $[\text{Pt}(\text{CN})_2(\text{PPh}_3)_2]$. A mechanism involving a five-coordinate intermediate was proposed. This was later criticised by Clark and Manzer who proposed an alternative mechanism in-

volving some concentration of the positive charge on nitrogen, which promotes elimination of methyl halide.⁸

We have tried to promote the dealkylation reaction on the complex $[\text{PtCl}_3(\text{CNMe})(\text{PMe}_2\text{Ph})_2]\text{ClO}_4$ by refluxing it in 1,2-dichloroethane for several hours,

but observed only reduction to $[\text{PtCl}(\text{CNMe})(\text{PMe}_2\text{Ph})_2]\text{ClO}_4$.

The failure to get dealkylation with the methyl isocyanide derivative indicates that the nature of the isocyanide also plays an important role in the sense that it may affect the polarization of the $\text{CN} \leftarrow \text{R}$ bond.

The structures of complexes **V**, **VII** and **VIII** derive from their i.r. and ^1H n.m.r. spectra. Compounds **V** has two *trans* chlorines, $\nu(\text{Pt}-\text{Cl}) = 346 \text{ cm}^{-1}$, and one chlorine *trans* to CN, $\nu(\text{Pt}-\text{Cl}) = 318 \text{ cm}^{-1}$. The triplet pattern of the phosphine methyls in the n.m.r. spectrum confirms the *trans* position of the PMe_2Ph ligands.¹²

Complex **VII** is a uni-univalent electrolyte in methanolic solution. Its i.r. spectrum shows only one $\nu(\text{Pt}-\text{Cl})$ band at 353 cm^{-1} , assigned to the *trans* chlorine asymmetric stretch. The ^1H n.m.r. spectrum in dimethylsulphoxide- d_6 shows that some decomposition occurs (probably dealkylation to **VIII**). However, it is possible to observe the typical signals of the complex, which show in the phosphine-methyl region only one 1/3/1 triplet (*trans* phosphines) with its ^{195}Pt satellites. The equivalence of all four methyl groups derives from the presence of two planes of symmetry, one passing through the P, Pt and C atoms, and the other through the Cl, Pt and C atoms.

The complex **VIII** is characterized by its i.r. spectrum showing one $\nu(\text{CN})$ band at 2160 cm^{-1} and one $\nu(\text{Pt}-\text{Cl})$ band at 347 cm^{-1} .

Experimental

Infrared spectra were recorded on a Perkin-Elmer Mod. 457 grating spectrometer using Hexachlorobutadiene mulls and KBr plates in the range $4000\text{--}1200 \text{ cm}^{-1}$, and Nujol mulls and CsI plates in the range $1700\text{--}250 \text{ cm}^{-1}$. Polystyrene was used for calibration. ^1H n.m.r. spectra were recorded on a Bruker 90 with TMS as internal standard. Molecular weights were measured with a Mechrolab Osmometer at 37°C . Conductivity data were obtained on a LKB 8300 B conductivity bridge at 25°C . Analyses were made by Mr. A. Berton of the Microanalytical Laboratory, Laboratorio Radioelementi C.N.R., Padova (Italy). We thank Mr. R. Salmaso for recording the ^1H n.m.r. spectra.

The isocyanides were prepared by known methods.¹⁴⁻¹⁶ The platinum(II) complexes *cis*- $[\text{PtCl}_2(\text{CNR})_2]$,¹⁷ *cis*- $[\text{Pt}(\text{CN})_2(\text{CNBu}^t)_2]$,¹⁷ *cis*- $[\text{PtCl}_2(\text{CNR})(\text{PMe}_2\text{Ph})_2]$,⁶ *trans*- $[\text{PtCl}(\text{CNR})(\text{PMe}_2\text{Ph})_2]^+$ ¹⁸ and *trans*- $[\text{Pt}(\text{CNR})_2(\text{PMe}_2\text{Ph})_2]^{2+}$ ⁸ were also prepared by published methods.

* Solution spectra were recorded with NaCl cells of 1 mm thickness.

Reactions with Chlorine

Reactions of *cis*- $[\text{PtCl}_2(\text{CNR})_2]$ ($R = \text{Me}, \text{C}_6\text{H}_{11}$), *cis*- $[\text{Pt}(\text{CN})_2(\text{CNBu}^t)_2]$, *cis*- $[\text{PtCl}_2(\text{CNR})(\text{PMe}_2\text{Ph})_2]$ ($R = \text{Me}, \text{Bu}^t, p\text{-MeC}_6\text{H}_4$), *trans*- $[\text{PtCl}(\text{CNR})(\text{PMe}_2\text{Ph})_2]$ and *trans*- $[\text{Pt}(\text{CNR})_2(\text{PMe}_2\text{Ph})_2]^{2+}$ ($R = \text{Me}, p\text{-MeC}_6\text{H}_4$).

Chlorine was slowly bubbled through a solution of the Pt(II) complex ($\sim 1 \text{ mmol}$) in CH_2Cl_2 (50 ml) under stirring. The almost colourless or slightly yellow solution rapidly became deep yellow. The end of the reactions was checked by i.r. spectroscopy. After 10-15 minutes nitrogen was vigorously bubbled in order to remove most of the excess chlorine. The remaining Cl_2 was eliminated by taking the solution to dryness at reduced pressure. The solid residue was dissolved again in CH_2Cl_2 treated with charcoal and filtered. The product was precipitated from the resulting solution by addition of diethyl ether. In most cases the Pt(IV) complexes were obtained analytically pure, but, if necessary, they were further purified by reprecipitation from the same solvents.

In the case of *trans*- $[\text{Pt}(\text{CNMe})_2(\text{PMe}_2\text{Ph})_2](\text{PF}_6)_2$ the reaction was carried out in the heterogeneous phase by bubbling Cl_2 through a suspension of this compound in CH_2Cl_2 for 90 min. The resulting Pt(IV) complex is itself insoluble in CH_2Cl_2 and can be recovered satisfactorily pure after filtration.

In the reaction of *trans*- $[\text{Pt}(p\text{-MeC}_6\text{H}_4\text{NC})_2(\text{PMe}_2\text{Ph})_2](\text{BF}_4)_2$ an immediate precipitation of the yellow Pt(IV) derivative occurred. After 10 min the product was filtered off, washed with CH_2Cl_2 and ethyl ether and dried *in vacuo*. No further purification is required. The yields vary in the range 70-90%.

The molecular weight of $[\text{PtCl}_4(\text{C}_6\text{H}_{11}\text{NC})_2]$ measured in 1,2-dichloroethane at 37°C gave a value of 540 (Calcd. = 555).

Reactions of *cis*- $[\text{PtCl}_2(\text{CNR})_2]$ ($R = \text{Ph}, p\text{-MeC}_6\text{H}_4$)

These reactions were carried out as previously described. Chlorine was bubbled for *ca.* 2 hours, but even after this time the addition was not complete. During the working up of the reaction mixture the starting Pt(II) complexes were reformed. When $R = \text{Ph}$ the only product isolated was the initial material; when $R = p\text{-MeC}_6\text{H}_4$ a mixture of the Pt(II) and Pt(IV) compounds was recovered, from which $[\text{PtCl}_4(p\text{-MeC}_6\text{H}_4\text{NC})_2]$ could be isolated satisfactorily pure by fractional precipitation from CH_2Cl_2 /diethyl ether. This complex is the first to precipitate by careful addition of ether.

Reactions of *trans*- $[\text{PtCl}(\text{CNBu}^t)(\text{PMe}_2\text{Ph})_2]\text{ClO}_4$ and *trans*- $[\text{Pt}(\text{CNBu}^t)_2(\text{PMe}_2\text{Ph})_2](\text{PF}_6)_2$

(a) The complex, *trans*- $[\text{PtCl}(\text{CNBu}^t)(\text{PMe}_2\text{Ph})_2]\text{ClO}_4$ (0.5 mmol), was treated with Cl_2 for 5 min. The corresponding Pt(IV) compound was formed first and progressively decomposed to give the cyano derivative $[\text{PtCl}_3(\text{CN})(\text{PMe}_2\text{Ph})_2]$. The course of the reac-

tions was followed by i.r. spectroscopy and was almost complete after 3 hours. The reaction mixture was stirred overnight and worked up in the usual way. The cyano complex was obtained as yellow crystals in ca. 90% yield.

(b) The complex, *trans*-[Pt(CNBu^t)₂(PMe₂Ph)₂](PF₆)₂ (0.454 g), was dissolved in a MeNO₂/CH₂Cl₂ mixture (10 ml MeNO₂/25 ml CH₂Cl₂) and treated with Cl₂ for 5 min. The reaction mixture was stirred for 1 hour. During this time the course of the reaction was followed by i.r. spectra. After bubbling nitrogen for 5 min and concentrating to small volume, addition of diethyl ether precipitated a solid which is a mixture of two compounds, [PtCl₂(CN)(CNBu^t)(PMe₂Ph)₂](PF₆)₂ present in larger amount, and [PtCl₂(CN)₂(PMe₂Ph)₂]. The latter complex could be isolated by chromatography on a Fluorosil column (15 cm) with CH₂Cl₂/Et₂O (1/1), while the former was purified by washing the mixture on the filter 10 times with CH₂Cl₂/Et₂O (3/7, 10 ml each time).

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