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CATIONIC COMPLEXES OF PLATINUM AND PALLADIUM WITH *p*-TOLYL ISOCYANIDE

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Summary

Cationic complexes of platinum and palladium of the type $[MCl(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})\text{-L}_2]\text{ClO}_4$ ($M = \text{Pt, Pd}$; $L = p\text{-tolyl}_3\text{P, } o\text{-tolyl}_3\text{P, Cy}_3\text{P, Ph}_2\text{MeAs, Ph}_2\text{EtAs, Ph}_2\text{PrAs, Cy}_3\text{As}$; $\text{Cy} = \text{cyclohexyl}$) have been isolated. These show a $\nu(\text{CN})$ band at ca. 2200 cm^{-1} compared with 2130 cm^{-1} for the free isocyanide ligand, suggesting weak π -character in the metal–carbon bond. The PMR spectra of the cationic complexes indicate *trans* configurations for the complexes.

Introduction

Several cationic complexes of platinum(II) containing carbon monoxide and/or an isocyanide as a ligand have been isolated, and their properties have been extensively investigated [1–8]. Invariably such complexes are stabilised by tertiary phosphine or arsine ligands. Very few of the analogous complexes of palladium have been synthesised. In fact, the unstable compound *trans*- $[\text{PdCl}(\text{CO})(\text{Et}_3\text{P})_2]\text{BF}_4$ [2] seems to be the only cationic carbonyl species of palladium previously made. Clark and coworkers [6], however, have prepared several isocyanide complexes of palladium of the type *trans*- $[\text{PdCl}(\text{RNC})\text{L}_2]^+$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5, \text{OCH}_3\text{C}_6\text{H}_4, \text{CH}_3\text{C}_6\text{H}_4$; $\text{L} = \text{Ph}_3\text{As}$ or tertiary phosphine). Busetto et al. [9] have isolated two cations of the formulae *trans*- $[\text{PdCl}\{\text{C}(\text{NPh})\text{NHC}_7\text{H}_7\}(\text{PhNC})_2]^+$ and *trans*- $[\text{PdCl}\{\text{C}(\text{NH-}p\text{-NO}_2\text{C}_6\text{H}_4)\text{NHC}_7\text{H}_7\}(p\text{-NO}_2\text{C}_6\text{H}_4\text{NC})_2]^+$. They suggest that the presence of the carbene ligand helps to stabilise these compounds. These workers also reported that they were unable to isolate cationic palladium(II) isonitrile complexes analogous to platinum(II) complexes of the type *trans*- $[\text{PtX}(\text{RNC})(\text{Et}_3\text{P})_2]\text{ClO}_4$ ($\text{X} = \text{Cl, Br}$; $\text{R} = \text{Me, Ph}$) which they isolated.

We have previously described the synthesis of several complexes of platinum and palladium of the general formulae MX_2L_2 ($\text{M} = \text{Pd, Pt}$; $\text{X} = \text{halogen}$; $\text{L} = \text{tertiary arsine}$), PtX_4L_2 and *trans*- $[\text{PtCl}(\text{CO})\text{L}_2]\text{ClO}_4$ [8]. We have extended these studies, and have investigated the possibility of isolating new cationic carbonyl and isocyanide complexes of both platinum and palladium.

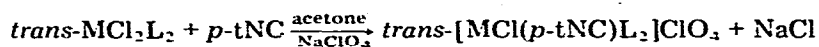
TABLE I
PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR CATIONIC COMPLEXES OF PALLADIUM AND PLATINUM

Compound ^a	M.p. or dec. p. (°C)	$\nu(\text{CN})^b$ (cm^{-1})	$\Delta \epsilon$	Analytical data (found (calcd.)) (%)						
				C	H	N	X	M		
$[\text{PdCl}(\text{p-tNC})(\text{Ph}_2\text{MeAs})_2]\text{ClO}_4$	98	2214	22.5	47.7 (48.2)	4.1 (3.9)	2.2 (1.5)	6.1 (8.3)	11.6 (12.6)		
$[\text{PtCl}(\text{p-tNC})(\text{Ph}_2\text{MeAs})_2]\text{ClO}_4$	100-101	2208	32.5	43.3 (43.6)	3.8 (3.5)	2.1 (1.5)	7.2 (7.6)	—		
$[\text{PdCl}(\text{p-tNC})(\text{Ph}_2\text{EtAs})_2]\text{ClO}_4$	80-83	2215	22.1	48.9 (49.4)	4.5 (4.3)	1.8 (1.6)	—	—		
$[\text{PtCl}(\text{p-tNC})(\text{Ph}_2\text{EtAs})_2]\text{ClO}_4$	95-100	2207	24.4	44.5 (44.5)	4.1 (3.9)	1.7 (1.4)	—	—		
$[\text{PdCl}(\text{p-tNC})(\text{Ph}_2\text{PrAs})_2]\text{ClO}_4$	79-81	2213	22.9	51.4 (50.6)	4.8 (4.6)	2.0 (1.6)	6.2 (7.3)	11.1 (11.8)		
$[\text{PtCl}(\text{p-tNC})(\text{Ph}_2\text{PrAs})_2]\text{ClO}_4$	74-76	2210	26.9	45.9 (46.0)	4.1 (4.2)	1.6 (1.4)	5.8 (7.1)	—		
$[\text{PdCl}(\text{p-tNC})(\text{C}_3\text{As})_2]\text{ClO}_4$	125	2200	21.4	52.3 (52.5)	7.5 (7.3)	1.3 (1.4)	7.6 (7.0)	10.3 (10.6)		
$[\text{PtCl}(\text{p-tNC})(\text{C}_3\text{As})_2]\text{ClO}_4$	217	2197	31.0	47.3 (48.2)	6.6 (6.7)	1.7 (1.3)	6.9 (6.5)	—		
$[\text{PdCl}(\text{p-tNC})(\text{C}_3\text{P})_2]\text{ClO}_4$	228-230	2200	27.6	57.3 (57.5)	7.9 (8.0)	1.6 (1.5)	—	—		
$[\text{PdCl}(\text{p-tNC})(\text{o-tolyl}_3\text{P})_2]\text{ClO}_4$	135	2204	22.7	61.4 (62.1)	5.2 (5.1)	3.5 (1.5)	6.2 (7.3)	10.2 (11.0)		
$[\text{PdCl}(\text{p-tNC})(\text{p-tolyl}_3\text{P})_2]\text{ClO}_4$	123-126	2213	26.1	60.2 (62.1)	4.8 (5.1)	1.2 (1.5)	—	11.2 (11.0)		
$[\text{PtCl}(\text{p-tNC})(\text{p-tolyl}_3\text{P})_2]\text{ClO}_4$	236-238	2210	25.0	56.1 (56.8)	4.6 (4.7)	1.6 (1.3)	—	—		

^a Compounds are white or pale yellow, ^b $\nu(\text{CN})$ (for *p-tNC*) 2130 cm^{-1} , ^c Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$) of ca. 10^{-3}M solutions in nitrobenzene (ca. 25°C).

Results and discussion

Cationic carbonyl complexes of platinum can be made by bubbling carbon monoxide through a solution of PtCl_2L_2 (L = tertiary phosphine or arsine) in a polar solvent such as acetone, in the presence of an anion such as ClO_4^- , BF_4^- or PF_6^- (as sodium salt) [1]. The corresponding isocyanide complexes may be made by using isocyanide in place of CO. Our attempts to prepare carbonyl complexes of palladium analogous to the platinum complexes we made earlier by this method were unsuccessful (the metal slowly separates out from the system). The method does, however, give four-coordinate cationic complexes of platinum and palladium of the composition $[\text{MCl}(p\text{-tNC})\text{L}_2]\text{ClO}_4$ (M = Pd, Pt; $p\text{-tNC} = p\text{-CH}_3\text{C}_6\text{H}_4\text{NC}$; L = tertiary arsine or phosphine):



The new isocyanide complexes behave as 1 : 1 electrolytes in nitrobenzene, and show a $\nu(\text{CN})$ band around 2200 cm^{-1} and a perchlorate stretch at ca. 1100 cm^{-1} in their infrared spectra. The analytical results support the proposed formulae (Table 1). Details of the PMR spectra of the cationic complexes containing the ligands Ph_2MeAs , Ph_2EtAs and $p\text{-tolyl}_3\text{P}$ are shown in Table 2. All the spectra show a singlet resonance due to the methyl of the $p\text{-tolyl}$ isocyanide ligand at τ ca. 7.7 ppm. Further the Ph_2EtAs -containing complexes show an additional single ethyl pattern suggesting that the two arsine ligands are located *trans* to each other. Similarly the complexes containing Ph_2MeAs and $p\text{-tolyl}_3\text{P}$ ligands show only a single resonance peak due to the methyl groups of these ligands. However, in these complexes there is a coincidental overlap of the resonance due to the methyl groups of the arsine (or phosphine) with that from the methyl group of the $p\text{-tolyl}$ isocyanide ligand. These results suggest a *trans* configuration for the cationic complexes.

As expected for cationic complexes of this type, the value of $\nu(\text{CN})$ for the coordinated isocyanide is higher than that of the free ligand, indicating an increase in the bond order of the CN group and hence a poorer π -character in the

TABLE 2
PMR DATA FOR LIGANDS AND COMPLEXES

Compound	chemical shift (τ , ppm) ^a			
	CH_3 ($p\text{-tNC}$)	CH_3	CH_2	C_6H_5
Ph_2MeAs		8.45s		2.9–2.4 cm
Ph_2EtAs		8.85t	7.99q	3.2–2.0 cm
$p\text{-Tolyl}_3\text{P}$		7.67s		2.9–2.2 cm
$p\text{-CH}_3\text{C}_6\text{H}_4\text{NC}$	7.24s			3.6–2.4 cm
$[\text{PdCl}(p\text{-tNC})(\text{Ph}_2\text{MeAs})_2]\text{ClO}_4$	7.70s	7.70s		3.6–2.0 cm
$[\text{PtCl}(p\text{-tNC})(\text{Ph}_2\text{MeAs})_2]\text{ClO}_4$	7.75s	7.68s		3.6–2.0 cm
$[\text{PdCl}(p\text{-tNC})(\text{Ph}_2\text{EtAs})_2]\text{ClO}_4$	7.72s	8.63t	7.08q	3.6–2.0 cm
$[\text{PtCl}(p\text{-tNC})(\text{Ph}_2\text{EtAs})_2]\text{ClO}_4$	7.70s	8.57t	7.03q	3.8–2.1 cm
$[\text{PdCl}(p\text{-tNC})(p\text{-tolyl}_3\text{P})_2]\text{ClO}_4$	7.64s	7.64s		3.8–2.4 cm
$[\text{PtCl}(p\text{-tNC})(p\text{-tolyl}_3\text{P})_2]\text{ClO}_4$	7.67s	7.67s		3.9–2.4 cm

^a s, singlet; t, triplet; q, quartet; cm, complex multiplet.

TABLE 3
 PHYSICAL PROPERTIES, ANALYTICAL AND FAR-INFRARED DATA FOR COMPLEXES OF PALLADIUM AND PLATINUM

Compound	Colour	M.p. or dec. p. (°C)	Analytical data (found (calct.)) (%)				Far-IR data ^a	
			C	H	X	M	$\nu(\text{M}-\text{X})$	Other bands
$\text{PdCl}_2(\text{Cy}_3\text{As})_2$	yellow	257	53.1 (52.4)	8.2 (8.1)	8.4 (8.4)	12.8 (12.9)	353vs	104m, 173w, 202s, 212(sh), 280w, 292(sh), 303m, 320(sh), 330s, 423(sh), 431w, 443s
$\text{PdBr}_2(\text{Cy}_3\text{As})_2$	orange	210	47.2 (47.3)	7.0 (7.3)	18.6 (17.5)	11.6 (11.6)	276s	82w, 194w, 212w, 292w, 303s, 331s, 347vs, 431s, 443vs
$\text{PtCl}_2(\text{Cy}_3\text{As})_2$	white	270-273	47.1 (47.3)	7.2 (7.3)	8.4 (7.8)	—	338vs(br)	100w(br), 168w, 280w, 292w, 308m, 351m, 432m, 443s
$\text{PtBr}_2(\text{Cy}_3\text{As})_2$	pale-yellow	260-265	42.6 (43.1)	6.2 (6.6)	20.3 (16.0)	—	248 vs	84w, 158w, 218w(br), 279m, 290m, 308s, 333s, 348vs, 431s, 443vs

^a w, weak; m, medium; s, strong; vs, very strong; (br), broad; (sh), shoulder.

metal-carbon bond of the complex [4,10,11]. In a series of analogous complexes of the type $[MCl(RNC)L_2]^+$ ($M = Ni, Pd, Pt$; $R = p-CH_3C_6H_4, p-OCH_3C_6H_4, Ph$; $L = Ph_2MeP, PhMe_2P$), Clark et al. [4,6] found that $\nu(CN)$ uniformly increases in the order $Ni < Pd < Pt$. In contrast, with our compounds the $\nu(CN)$ values of the cationic platinum complexes are a little lower than those of the corresponding palladium complexes. A similar trend is apparent in the neutral complexes $PtCl_2(RNC)_2$ and $PdCl_2(RNC)_2$ ($R = C_6H_5, C_6H_{11}$) [12-14]. These results suggest that the antibonding orbitals of carbon of the CN group have a higher electron density in the platinum complexes than in the palladium complexes probably due to greater back-bonding in the former. Similar results were noted with complexes of Ru and Os of the type $MCl_2(RNC)_2(Ph-n-Bu_2P)_2$ ($M = Ru, Os$; $R = p-NO_2C_6H_4, p-OCH_3C_6H_4$) [15].

The compounds MX_2L_2 used for the preparation of cationic complexes were prepared by refluxing stoichiometric quantities of the metal halide and ligand in an alcoholic medium [8]. The Cy_3As -containing complexes ($Cy =$ cyclohexyl) have been made for the first time, and some of their properties are listed in Table 3. The far-infrared spectra of these compounds were recorded in the range 50 to 450 cm^{-1} , and show a single $\nu(M-X)$ band, suggesting a *trans* configuration for these compounds as expected [16-19].

Experimental

The platinum and palladium salts were supplied by Messrs. Johnson Matthey Chemicals Ltd, London. The tertiary arsines, phosphines and *p*-tolyl isocyanides were prepared as described elsewhere [20]. Microanalyses (C, H and N) were carried out at the Universities of Manchester and Surrey (England). Halogen was estimated by sodium hydroxide fusion and subsequent titration by the Vohlhard's method [21]. Palladium was determined gravimetrically (as palladium dimethyl glyoximate) as follows: a known amount of the complex was digested with conc. H_2SO_4 (Kjeldahl method) and was diluted with water. The metal was precipitated as sulphide and then taken up into nitric acid from which palladium dimethyl glyoximate was isolated according to the usual procedure [21,22]. Conductivity measurements were made with a Toshniwal conductivity bridge type Cl 01.02. Infrared spectra (in nujol mull) were recorded on a Carl Zeiss UR 10 spectrophotometer. Far-infrared spectra (in polyethylene powder) were recorded on a Polytec FIR 30 Fourier spectrometer. NMR spectra were recorded on a Varian T-60 instrument using $CDCl_3$ as solvent and $Si(CH_3)_4$ as internal standard.

trans-Chloro-p-tolyl isocyanide bis(tertiary arsine or phosphine)-palladium(II) or -platinum(II) perchlorate compounds, trans-[MCl(p-tNC)L₂]ClO₄ (M = Pd, Pt; L = Ph₂MeAs, Ph₂EtAs, Ph₂PrAs, Cy₃As, Cy₃P, p-tolyl₃P, o-tolyl₃P)

To an acetone solution (25 ml) (acetone/benzene mixture in the case of Cy_3As and Cy_3P) of MCl_2L_2 (0.2 mmol) and *p*-tNC (0.2 mmol), sodium perchlorate was added in excess. The mixture was stirred at room temperature for 6 h. The $NaCl$ was filtered off and the filtrate was concentrated to dryness under reduced pressure. The white or pale yellow pasty residue was washed successively with ether and water to give a solid, which was dried in vacuo.

Dihalo bis(tricyclohexyl arsine)-platinum(II) or -palladium(II) compounds, trans-MX₂(Cy₃As)₂ (M = Pd, Pt; X = Cl, Br; Cy = cyclohexyl)

The metal halide (PdCl₂ or K₂PtCl₄; 0.2 mmol) was treated with Cy₃As (0.4 mmol) in alcohol (25 ml) and hydrochloric or hydrobromic acid (2 ml). The mixture was refluxed for 5 h, and the solid which separated was washed with water and alcohol, and dried in vacuo.

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