Metallation of a Phenyl Group Induced by Oxidation: Carbene Complexes of Platinum(IV)

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The reactions of dichlorine with the complexes *cis*-$[PtCl_2\{C(NHR^1)(NHR^2)\}(PEt_3)]$, *cis*-$[PtCl_2\{C(OR^3)(NHR^2)\}(PR^4{}_3)]$ and *trans*-$[PtCl\{C(NHR^1)(NHR^2)\}(PEt_3)_2][ClO_4]$ (R^{12} = Me or Et; R^{12} = Me, Ph, 2,4-$Cl_2C_6H_3$, 2,6-$Cl_2C_6H_3$, 2-ClC_6H_4, or 4-ClC_6H_4; R^3 = Me or Et; $PR^4{}_3$ = PEt_3 or PPh_3) have been examined. Where $R^1 = R^2$ = Me, the platinum(IV)–carbene complexes $[PtCl_4\{C(NHMe)_2\}(PEt_3)]$ and $[PtCl_3\{C(NHMe)_2\}(PEt_3)_2][ClO_4]$ result, but where R^1 = Me or Et and R^2 = Ph, 2-ClC_6H_4, or 4-ClC_6H_4; 2-metallation (and chlorine substitution in some cases) of the phenyl group occurs, giving the complexes $[PtCl_3\{C(OR^3)(NHC_6H_3Cl\text{-}4)\}(PR^4{}_3)]$, $[PtCl_2\{C(NHR^1)(NHC_6H_3Cl\text{-}4)\}(PEt_3)_2][ClO_4]$, and $[PtCl_2\{C(NHMe)(NHC_6H_3Cl\text{-}2)\}(PEt_3)_2][ClO_4]$. The i.r. and n.m.r. spectra of these complexes and possible reaction mechanisms are discussed. Treatment of *trans*-$[PtBr\{C(NHMe)_2\}(PEt_3)_2][ClO_4]$ and *trans*-$[PtBr\{C(NHEt)(NHPh)\}(PEt_3)_2][ClO_4]$ with dibromine gave *trans*-$[PtBr_4(PEt_3)_2]$ as the only isolable product.

THE metallation of suitably placed phenyl groups in ligating molecules is a common reaction of transition metals in their lower oxidation states and is often induced by reduction. Here we report the metallation of a phenylaminocarbene ligand which has been induced by oxidation.

In previous studies of aminocarbene complexes of platinum(II) we noted that there is little π-character in the metal–carbene bond and that this ligand has a σ-donor capacity close to that of tertiary phosphines.[1,2] We therefore expected that carbene complexes of platinum(IV) would be stable. Accordingly we investigated the oxidation of such complexes as *cis*-$[PtCl_2\{C(OEt)NHPh\}(PEt_3)]$ (which has essentially a Pt–C single bond[2]) and its analogues with dichlorine. We obtained simple platinum(IV)–carbene complexes when the carbene substituents were purely aliphatic, but when the carbene ligand carried a phenyl group, both its chlorination and metallation could also occur, as detailed below.

Platinum(IV)–*Carbene Complexes*.—The yellow complex salts $[PtCl_3\{C(NHEt)(NHPh)\}(PEt_3)_2][ClO_4]$ and $[PtCl_3\{C(NHMe)_2\}(PEt_3)_2][ClO_4]$ and yellow uncharged complex $[PtCl_4\{C(NHMe)_2\}(PEt_3)]$ (see Tables for analytical and spectral data *etc.*) were obtained by the addition of dichlorine to the corresponding platinum(II) complexes in chloroform at room temperature [*e.g.* equation (1)].

TABLE 1

Analytical data *etc.* for platinum(II) and platinum(IV) complexes

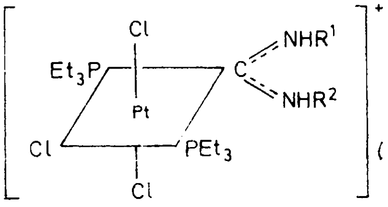
Complex [a]	M.p. (θ_c/°C)	Yield (%)	Analyses (%) [b] C	H	N	Cl	Molar conductivity [c] $\Lambda_m/\Omega^{-1}\,cm^2\,mol^{-1}$
$[PtCl(4\text{-}ClC_6H_4NC)(PEt_3)_2]^+$	147—149	85	32.6 (32.4)	5.2 (4.9)	2.1 (2.0)		
$[PtCl(2\text{-}ClC_6H_4NC)(PEt_3)_2]^+$	138—146	65	32.6 (32.4)	5.1 (4.9)	2.1 (2.0)		
$[PtCl_2(2,4\text{-}Cl_2C_6H_3NC)(PEt_3)]$	155—158	40	28.1 (28.9)	3.4 (3.3)	2.6 (2.5)		
$[PtCl_2(2,6\text{-}Cl_2C_6H_3NC)(PEt_3)]$	190—192	85	28.1 (28.1)	3.2 (3.2)	2.5 (2.5)		
$[PtCl(2,6\text{-}Cl_2C_6H_3NC)(PEt_3)_2]^+$	178—180	85	31.2 (30.9)	4.5 (4.5)	2.1 (1.9)	19.0 (19.2)	
$[PtCl\{C(NHMe)(NHC_6H_4Cl\text{-}4)\}(PEt_3)_2]^+$	148—153	90	32.5 (32.7)	5.6 (5.3)	3.8 (3.8)		28
$[PtCl\{C(NHMe)(NHC_6H_4Cl\text{-}2)\}(PEt_3)_2]^+$	322—324	80	32.6 (32.7)	5.5 (5.3)	3.8 (3.8)		
$[PtCl_2\{C(OEt)(NHC_6H_3Cl_2\text{-}2,4)\}(PEt_3)]$	173—175	40	29.6 (29.8)	4.1 (4.3)	2.3 (2.3)		
$[PtCl\{C(NHMe)(NHC_6H_3Cl_2\text{-}2,4)\}(PEt_3)_2]^+$	193—196	60	29.7 (31.2)	4.8 (5.0)	3.5 (3.6)		
$[PtCl_2\{C(OEt)(NHC_6H_3Cl_2\text{-}2,6)\}(PEt_3)]$	184—189	75	30.0 (29.8)	4.1 (4.3)	2.2 (2.3)		31
$[PtCl\{C(NHMe)(NHC_6H_3Cl_2\text{-}2,6)\}(PEt_3)_2]^+$	200—203	85	31.6 (31.2)	5.5 (5.0)	3.4 (3.6)		
$[PtCl_4\{C(NHMe)_2\}(PEt_3)]$ [d]	157—160	90	20.9 (20.5)	4.5 (4.4)	5.3 (5.3)	26.7 (26.9)	
$[PtCl_3\{(NHMe)_2\}(PEt_3)_2]^+$ [d]	156—160	85	25.7 (25.4)	5.5 (5.4)	4.0 (4.0)	20.0 (20.0)	15
$[PtCl_3\{C(NHEt)(NHC_6H_4)\}(PEt_3)_2]^+$ [d]	Decomp.	25	32.0 (32.1)	5.2 (5.4)	3.6 (3.6)		
$[PtCl_2\{C(NHMe)(NHC_6H_3Cl\text{-}2)\}(PEt_3)_2]^+$	226—237	50	31.3 (31.2)	5.0 (5.0)	3.6 (3.6)	18.7 (18.4)	15
$[PtCl_2\{C(NHMe)(NHC_6H_3Cl\text{-}4)\}(PEt_3)_2]^+$	254—285	50	31.4 (31.2)	5.2 (5.0)	3.7 (3.6)	18.6 (18.4)	15
$[PtCl_2\{C(NHEt)(NHC_6H_3Cl\text{-}4)\}(PEt_3)_2]^+$	203—206	40	32.3 (32.1)	5.3 (5.4)	3.5 (3.6)	19.0 (18.0)	13
$[PtCl_3\{C(OEt)(NHC_6H_3Cl\text{-}4)\}(PEt_3)]$	181—182	55	29.7 (29.8)	4.0 (4.3)	2.3 (2.3)	23.6 (23.5)	
$[PtCl_3\{C(OMe)(NHC_6H_3Cl\text{-}4)\}(PEt_3)]$	168—172	40	28.0 (28.5)	3.8 (4.1)	2.4 (2.4)	23.7 (24.0)	
$[PtCl_3\{C(OEt)(NHC_6H_5Cl\text{-}4)\}(PPh_3)]$	162—175	35	43.0 (43.3)	3.8 (3.5)	1.7 (1.9)		

[a] Complexes colourless unless otherwise stated, with $[ClO_4]^-$ as anion when cationic. [b] Required values in parentheses. [c] At *circa* 3×10^{-3}M in $PhNO_2$. [d] Yellow complex; decomp. = decomposed.

$$trans\text{-}[PtCl\{C(NHMe)_2\}(PEt_3)_2]^+ + Cl_2 \xrightarrow{CHCl_3} [PtCl_3\{C(NHMe)_2\}(PEt_3)_2]^+ \quad (1)$$

A similar oxidation of some platinum(II) complexes having aliphatic chelate-carbene ligands has been previously reported.[3] The (NH) and (NC) bands in the i.r. spectra of these compounds are little changed from those of the starting materials (Table 2), consistent with the low π-bonding character of the Pt–carbene bond in both series.

The cationic compounds have configuration (A) because they have two (Pt–Cl) i.r. bands at appropriate frequencies for platinum(IV) compounds[4] and their n.m.r spectra show the quintet pattern typical of methyl groups of *trans*-PEt_3 ligands (Table 3).[5] Only one set of carbene–methyl resonances occurs in the n.m.r. spectrum of $[PtCl_3\{C(NHMe)_2\}(PEt_3)_2][ClO_4]$ whereas the platinum(II) parent complex shows three resonances, due to three isomeric forms of the carbene ligand, the *amphi*-configuration being predominant.[6] Although it is not clear which carbene-configuration is adopted in the platinum(IV) compound, the occurrence of only one isomer seems general for octahedral complexes[7,8] and is probably a consequence of their greater steric crowding compared to the square planar situation of platinum(II) compounds.



(A)

On the basis of its three ν(Pt–Cl) i.r. bands, the poorly soluble yellow uncharged complex is assigned configuration (B).

Platinum(IV) *Compounds with Metallated Phenyl Groups*.—These compounds, obtained by chlorination of the phenylaminocarbene complexes under the conditions

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[2] E. M. Badley, J. Chatt, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 21.

[3] A. L. Balch, *J. Organometallic Chem.*, 1972, **37**, C19.

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[6] B. Crociani and R. L. Richards, *J.C.S. Dalton*, **1974**, **693**.

[7] J. Chatt, R. L. Richards, and G. H. D. Royston, *J.C.S. Dalton*, 1973, 1433.

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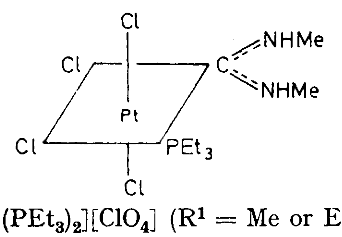
TABLE 2

I.r. data [a] for platinum complexes

Compound [b]	ν(NH)	ν(N–C)/(NH) [c]	ν(Pt–Cl)
$[PtCl_2\{C(OEt)(NHPh)\}(PEt_3)]$	3 150m 3 110s	1 590s 1 540vs	284s 306s
$[PtCl_2\{C(OEt)(NHPh)\}(PPh_3)]$	3 180mw, br	1 590m 1 540s	286m 318ms
$[PtCl_2\{C(NHMe)_2\}(PEt_3)]$	3 350m 3 275s	1 575s 1 515m	276s 297s
$[PtCl\{C(NHMe)(NHPh)\}(PEt_3)_2]^+$	3 350m 3 290m	1 600m, 1 560s 1 500m	305s
$[PtCl\{C(NHEt)(NHPh)\}(PEt_3)_2]^+$	3 300s 3 210w	1 610m, 1 595m 1 560s, 1 500s	306s
$[PtCl\{C(NHMe)_2\}(PEt_2)_3]^+$	3 320s	1 590vs 1 520s	293vs
$[PtCl\{C(NHMe)(NHC_6H_4Cl\text{-}4)\}(PEt_3)_2]^+$	3 320m 3 250m	1 590m 1 555ms	303s
$[PtCl\{(NHMe)(NHC_6H_4Cl\text{-}2)\}(PEt_3)_2]^+$	3 350m 3 300m	1 585m 1 550ms 1 510w	316s
$[PtCl_2\{C(OEt)(NHC_6H_3Cl_2\text{-}2,4)\}(PEt_3)]$	3 180m, br	1 545mw 1 525ms	280s 314ms
$[PtCl\{C(NHMe)(NHC_6H_3Cl_2\text{-}2,4)\}(PEt_3)_2]^+$	3 360m 3 320m	1 580m, 1 545ms 1 505w	312s
$[PtCl_2\{C(OEt)(NHC_6H_3Cl_2\text{-}2,6)\}(PEt_3)]$	3 140m, br	1 570w 1 525ms	
$[PtCl\{C(NHMe)(NHC_6H_3Cl_2\text{-}2,6)\}(PEt_3)_2]^+$	3 290mw 3 240m	1 565ms	305vs
$[PtCl_4\{C(NHMe)_2\}(PEt_3)]$	3 310s	1 605s 1 565s	342s 297s 263s
$[PtCl_3\{C(NHMe)_2\}(PEt_3)_2]^+$	3 305ms	1 595s 1 560m	346ms 302ms
$[PtCl_3\{C(NHEt)(NHC_6H_4)\}(PEt_3)_2]^+$	3 285m	1 575m 1 545s	347s 305ms
$[PtCl_2\{C(NHMe)(NHC_6H_3Cl\text{-}2)\}(PEt_3)_2]^+$	3 250br	1 610s	310s 298m 270ms
$[PtCl_2\{C(NHMe)(NHC_6H_3Cl\text{-}4)\}(PEt_3)_2]^+$	3265ms 3 200m, sh	1 615s	323s 308ms 278s
$[PtCl_3\{C(NHEt)(NHC_6H_3Cl\text{-}4)\}(PEt_3)_2]^+$	3 260m 3 200m, sh	1 615vs	316s 299s 274s
$[PtCl_3\{C(OEt)(NHC_6H_3Cl\text{-}4)\}(PEt_3)]$	3 200w 3 160w	1 595m, 1 580m 1 560m	315s 282br
$[PtCl_3\{C(OMe)(NHC_6H_3Cl\text{-}4)\}(PEt_3)]$	3 185m 3 145m	1 600m, 1 580m 1 650m	318s 285br
$[PtCl_3\{C(OEt)(NHC_6H_3Cl\text{-}4)\}(PPh_3)]$	3 190w 3 150w	1 595m, 1 580m 1 555s	

[a] Nujol mull spectra in cm^{-1}. [b] Compounds white unless otherwise stated, cationic complexes have $[ClO_4]^-$ anion and show its characteristic bands. [c] Tentative assignment, (N=C) band probably strongest. m = medium, s = strong, w = weak, br = broad, v = very.

of reaction (1), are colourless and are spectroscopically distinct from the yellow platinum(IV) carbene complexes. Thus the two complexes of composition $[PtCl_3\{C(NHR^1)(NHPh)\}(PEt_3)_2][ClO_4]$ (R^1 = Me or Et) have mutually similar (NH) i.r. bands, a lone intense (NC) band at *ca.* 1 615 cm^{-1} and three (PtCl) bands, a pattern contrasting with that of both the starting materials and the yellow platinum(IV)–carbene complexes (Table 2).



(B)

Their ^1H n.m.r. spectra (Table 3) show a *trans*-PEt_3 quintet P-*Me* resonance and also carbene-N*H* and -NH*R* resonances in most cases, but the resonance pattern in the phenyl region is of particular significance. It is almost identical when R = Me or Et but more complex than those of the starting materials or of the yellow platinum(IV)–carbene complexes. Moreover, these resonances integrate for only three protons, thus the phenyl group has been disubstituted.

It was thought at first that the phenyl rings had been modified by chlorine substitution only, but the preparation of complexes of phenyl isonitrile and derived carbene ligands substituted by one or more chlorine atoms (Table 1) showed that a more complex substitution had taken place. These chlorophenyl compounds are

TABLE 3

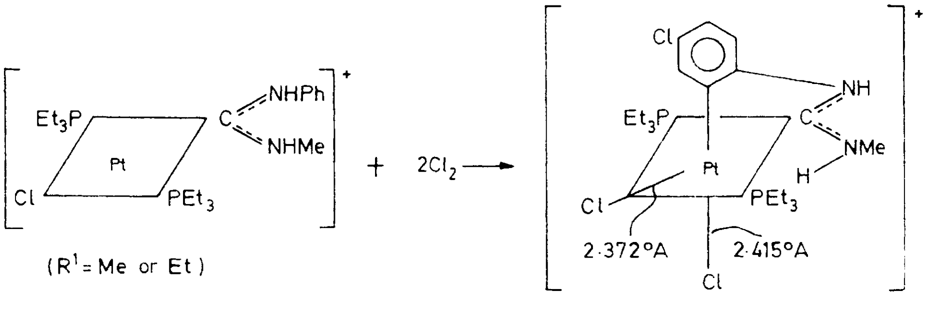
^{1}H N.m.r. data for platinum complexes [a]

Compound	Resonance (τ ±0.01)	Integration	J Value (Hz ±0.3)	Assignment
$[PtCl\{C(NHMe)(NHC_6H_4Cl\text{-}4)\}(PEt_3)_2]^+$	0.45t	0.5(1)	40 [b]	NHPh [c]
	1.46t			NHPh [c]
	2.33br	0.5(1)		NHMe
	1.8—2.7m	4(4)		NHPh
	6.53dt	3(3)	4.0 [d]	NHMe
	6.73dt		4.3 [d]	NHMe
	8.12m	12(12)	3.6 [e]	PCH_2CH$_3$ [f]
	8.89q	18(18)	8.0 [e]	PCH_2CH_3 [f]
$[PtCl\{C(NHMe)(NC_6H_4Cl\text{-}2)\}(PEt_3)_2]^+$	0.83t?	0.8(1)		NHPh [c]
	1.74t?			NHPh [c]
	2.3—2.9m			NHPh
	6.52dt	3(3)	4.2 [d]	NHMe
	6.71dt		4.7 [d]	NHMe
	8.10m	12(12)	3.8 [e]	PCH_2CH$_3$
	8.91q	18(18)	8.5 [e]	PCH$_2$$CH_3$
$[PtCl\{C(NHMe)(NHC_6H_3Cl_2\text{-}2,6)\}(PEt_3)_2]^+$	2.27t?	0.6(1)		NHPh [b]
	2.3—2.7m	3.5(3)		NHPh
	6.57dt	3(3)	4.5 [d]	NHMe
	7.90m	12(12)	3.5 [e]	PCH_2CH$_3$
	8.77q	18(18)	7.7 [e]	PCH$_2$$CH_3$
$[PtCl_3\{C(NHMe)_2\}(PEt_3)_2]^+$	2.06br	1.5(2)		NHMe
	6.53dt	6(6)	5.0 [d]	NHMe
	7.75m	12(12)	3.6 [e]	PCH_2CH$_3$
	8.74q	18(18)	8.0 [e]	PCH$_2$$CH_3$
$[PtCl_3\{C(NHEt)(NHPh)\}(PEt_3)_2]^+$	0.48t	0.5(1)	40 [b]	NHPh [e]
	1.95br	1(1)		NHEt [c]
	2.4—2.9m	4.5(5)		NHPh
	7.00m	2(2)		NHCH_2CH$_3$
	7.66m	12(12)	3.6 [e]	PCH_2CH$_3$
	8.4—9.1m	21(21)	8.5 [e]	PCH$_2$$CH_3$ + NHCH$_2$$CH_3$
$[PtCl_2\{C(NHMe)(NHC_6H_3Cl\text{-}4)\}(PEt_3)_2]^+$	−0.66t	1(1)	40 [b]	NHPh [c]
	1.50br	1(1)		NHMe [c]
	2.0—2.8m	3(3)		NHPh
	6.48dt	3(3)	4.5 [d]	NHMe
	7.98m	12(12)	3.5 [e]	PCH_2CH$_3$
	8.97q	18(18)	8.5 [e]	PCH$_2$$CH_3$
$[PtCl_2\{C(NHMe)(NHC_6H_3Cl\text{-}2)\}(PEt_3)_2]^+$	0.48t	0.7(1)	40 [b]	NHPh [c]
	1.23br	0.7(1)		NHMe [c]
	2.0—3.1m	2(3)		NHPh
	6.38dt	2.5(3)	4.5 [d]	NHMe
	7.94m	12(12)	3.5 [e]	PCH_2CH$_3$
	8.95q	18(18)	8.0 [e]	PCH$_2$$CH_3$
$[PtCl_2\{C(NHEt)(NHC_6H_3Cl\text{-}4)\}(PEt_3)_2]^+$	1.7br	1(1)		NHEt [c]
	2.1—2.7m	2.5(3)		NHPh
	6.14m	2(2)		NHCH_2CH$_3$
	8.00m	12(12)	3.5 [e]	PCH_2CH$_3$
	8.56t	3(3)	7.0 [g]	NHCH$_2$$CH_3$
	8.96q	18(18)	8.5 [e]	PCH$_2$$CH_3$

[a] In $CDCl_3$ solution, re-run in CD_2Cl_2 when integration of phenyl region required. [b] ^3J(Pt–H). [c] Disappears on addition of D_2O. [d] ^3J(HNCH), Pt–H coupling apparent on D_2O addition but ^4J(Pt–H) not measured. [e] Separation of adjacent resonances. [f] Presence of two isomers causes splitting of these resonances. [g] ^3J(HCCH).

t = triplet, m = multiplet, q = quintet, br = broad, dt = doublet of triplets.

clearly different in physical properties from the products of chlorination (Tables 2 and 3). Moreover, the complex *trans*-$[PtCl\{C(NHMe)(NHC_6H_4Cl\text{-}4)\}(PEt_3)_2][ClO_4]$, on chlorination, took up only one half as much chlorine as its phenyl analogue and the white product was identical with that obtained by the reaction of dichlorine with *trans*-$[PtCl\{C(NHMe)(NHPh)\}(PEt_3)_2][ClO_4]$. Thus the phenyl ring of the product from both the 4-chlorophenyl-



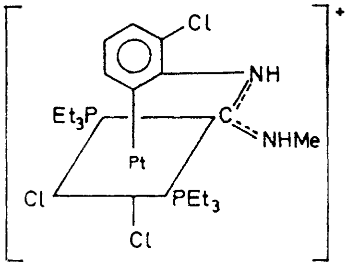
(2)

(C)

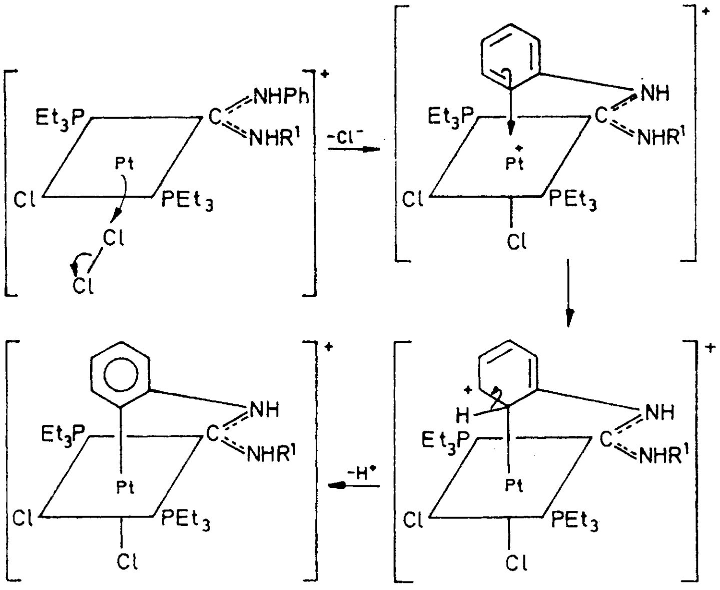
aminocarbene- and phenylaminocarbene-platinum(IV) compounds must have chlorine in the 4-position. Consistent with this conclusion, both compounds have a strong, very sharp, i.r. band at 820 cm^{-1}, a feature shared by all the 2,4- and 4-ring-chlorinated carbene complexes prepared, but no others.

It was then suspected that another ring position of the chlorinated product must have been metallated by the platinum and this was confirmed by the *X*-ray determination of the structure of $[PtCl_2\{C(NHMe)(NHC_6H_3Cl\text{-}4)\}(PEt_3)_2][ClO_4]$, (C) [9] which is formulated $[PtCl_2\{C(NHMe)(NHC_6H_3Cl\text{-}4)\}(PEt_3)_2][ClO_4]$ as shown in equation (2).

The ethyl analogue of the methyl complex (C) can be safely assigned the analogous structure in view of its very similar i.r. and ^1H n.m.r. parameters. Similarly the white complex derived from the chlorination of *trans*-$[PtCl\{C(NHMe)(NHC_6H_4Cl\text{-}2)\}(PEt_3)_2][ClO_4]$ can be formulated as (D), since, although its n.m.r. spectrum shows clearly that the ring is metallated and disubstituted, it does not have the 820 cm^{-1} i.r. band.

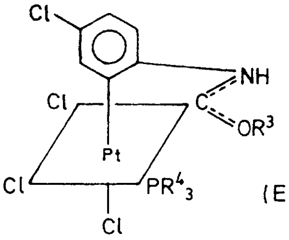


(D)



SCHEME 1

The compounds derived from chlorination of the complexes *cis*-$[PtCl_2\{C(OR^3)(NHPh)\}(PR^4{}_3)]$ (R = Me or Et; $PR^4{}_3$ = PEt_3 or PPh_3) are very insoluble and n.m.r. data could not be obtained for them. They show two bands assigned to ν(Pt–Cl), one of which is rather broad (Table 2) and a likely structure for them, by analogy with compound (C), is (E).



(E)

Isomeric forms of the metallated complexes involving co-ordination isomerisation (*cis* or *trans*) or isomerisation of the carbene ligands [6] are possible. The complex $[PtCl_2\{C(NHMe)(NHC_6H_3Cl\text{-}4)\}(PEt_3)_2][ClO_4]$ has been obtained exclusively in form (C) except on one occasion when it was obtained mixed with an isomer having different P-*Me* n.m.r. and ν(Pt-Cl) patterns, but the mixture could not be separated. Only one form of the carbene ligands with an –NHMe side-chain has been observed in these complexes, probably because the *amphi*-configuration [6] is sterically preferred.

Mechanism of the Reaction.—The metallation of phenyl groups of co-ordinated ligands generally occurs in complexes of transition metals in their lower oxidation states and is sometimes induced by reduction.[10] The metallation reported here is unusual since it is induced by oxidation. It resembles most closely the reactions of halogens with metal complexes of ligands having an olefinic side-chain, when addition of the halogen and the

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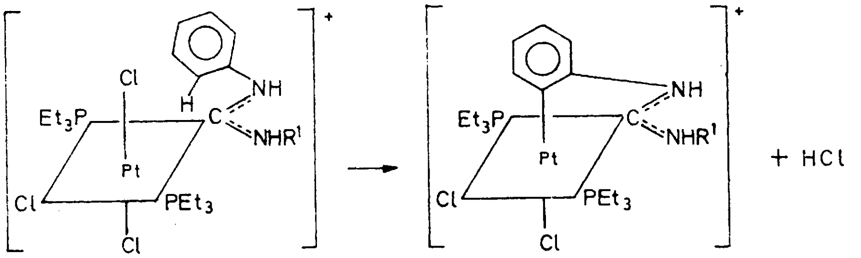
[9] J. Chatt, K. W. Muir, R. L. Richards, G. H. D. Royston, and R. Walker, *J. Organometallic Chem.*, 1973, **56**, C30; K. W. Muir and R. Walker, *J.C.S. Dalton*, 1975, 272.

[10] M. G. Clerici, B. L. Shaw, and B. Weaks, *J.C.S. Chem. Comm.*, 1973, 576, and references therein.

metal to the unsaturated group occurs.[11] For these reactions, a concerted mechanism has been proposed involving attack on the metal complex by a polarised halogen molecule.[12] Adaption of this mechanism to the present system gives the Scheme 1 for the metallation step, which would probably be a concerted process.

A more likely mechanism is as follows. In the reactions involving metallation of olefinic groups,[11] no intermediate platinum(IV) compounds could be isolated, hence the suggestion of a concerted mechanism.[12] All our metallation reactions passed through a yellow stage, corresponding to a platinum(IV) complex and platinum(IV) complexes have been isolated where the carbene ligand has no phenyl substituent. We have also isolated the yellow compound $[\text{PtCl}_3\{\text{C(NHEt)(NHPh)}\}(\text{PEt}_3)_2][\text{ClO}_4]$ which tends to lose dichlorine and metallates slowly in the solid state on storage, but more rapidly in presence of chlorine in solution. These observations suggest that the first step in the metallation of the carbene complexes is a rapid oxidative addition of dichlorine to the metal, followed by an electrophilic attack by the oxidised metal at the aromatic ring [equation (3)].



(3)

In the absence of kinetic data it is difficult to distinguish the above two mechanisms.

A third possibility, that insertion of platinum into a preformed carbon–chlorine bond occurs, has been eliminated on the following evidence. The complexes *trans*-$[\text{PtCl}\{\text{C(NHMe)(NHR}^2)\}(\text{PEt}_3)_2][\text{ClO}_4]$ (R^2 = 2-chloro-, 2,4- and 2,6-dichloro-phenyl) were not converted into metallated products, even when heated under reflux in 2-methoxyethanol solution. The attempted conversion of the 2,6-dichlorophenyl complex resulted in the loss of methylamine and formation of the isonitrile complex, probably because of steric crowding by the *ortho*-substituents. Its chlorination gave only *trans*-$[\text{PtCl}_4(\text{PEt}_3)_2]$. Moreover, the product obtained from chlorination of *trans*-$[\text{PtCl}\{\text{C(NHMe)(NHC}_6\text{H}_4\text{Cl-2)}\}(\text{PEt}_3)_2][\text{ClO}_4]$, (D) differs from that of the chlorination of the substituted complex (C). Thus it is clear that insertion into a preformed carbon–chlorine bond is not the metallation step but it is not certain whether metallation precedes ring chlorination in the 4-position or *vice-versa*.

In all these reactions, it is a necessary requirement for metallation that the phenyl ring be *cis* to the metal about the $\text{C}\overset{\cdots}{-}\text{M}$ bond. Most of the platinum(II) compounds examined so far exist in the solution as mixtures of isomers with this group in the *cis*- or *trans*-position.[6] The variation of isomer ratio probably accounts for the variation in yield of metallated products (Table 1). Further experiments are planned to elucidate this point.

The Bonding of the Carbene Ligand in Platinum(IV) *Complexes*.—The bonding is electronically closely similar to that in the platinum(II) complexes. The evidence is two-fold. Firstly the i.r. data for the carbene ligands of platinum(II) and corresponding platinum(IV) complexes (Table 2) are very similar. Secondly the platinum–carbene-carbon [1.973 Å] and mean carbene-carbon–nitrogen [1.337 Å] bond distance found for $[\overline{\text{PtCl}_2\{\text{C(ClC}}_6\text{H}_3\text{NH)(NHMe)}\}(\text{PEt}_3)_2][\text{ClO}_4]$[9] are very close to the lengths of such bonds in platinum(II) complexes, *e.g.* Pt–C = 2.01 Å in *cis*-$[\text{PtCl}_2\{\text{C(PhNCH}_2\text{CH}_2\text{NPh)}\}(\text{PEt}_3)]$ and 1.98 Å in *cis*-$[\text{PtCl}_2\{\text{C(OEt)(NHPh)}\}(\text{PEt}_3)]$; C–N = 1.33 Å in *cis*-$[\text{PtCl}_2\{\text{C(OEt)(NHPh)}\}(\text{PEt}_3)]$ and 1.33 Å in *cis*-$[\text{PtCl}_2\{\text{C(PhNCH}_2\text{CH}_2\text{NPh}\}(\text{PEt}_3)]$.[1] Thus, as has been suggested,[2] the platinum–carbene bond has little, if any, double-bond character and π-interaction is mainly between the carbon and nitrogen atoms of the carbene ligand. The carbene ligand is therefore principally a σ-donor and the Pt–Cl distances obtained[9] for the platinum(IV) metallated complex (C), [see equation (2)], together with those of 2.332 Å in *trans*-$[\text{PtCl}_4(\text{PEt}_3)_2]$[13] indicate the order of *trans*-influences $\text{Ph}^- >$ carbene $> \text{Cl}^-$ for platinum(IV) complexes. This accords with the order established by a variety of techniques for platinum(II) complexes, where carbene lies very close to PEt_3, between σ-alkyl and chloride.[2,14]

Bromination Reactions.—The reactions of dibromine with *trans*-$[\text{PtBr}\{\text{C(NHMe)}_2\}(\text{PEt}_3)_2][\text{ClO}_4]$ and *trans*-$[\text{PtBr}\{\text{C(NHEt)(NHPh)}\}(\text{PEt}_3)_2][\text{ClO}_4]$ were investigated in dilute chloroform solution but the only product which could be isolated was *trans*-$[\text{PtBr}_4(\text{PEt}_3)_2]$ in both cases, even from the reaction of 1 mole equivalent of dibromine.

EXPERIMENTAL

Instrumental Measurements.—I.r. spectra were measured on a Perkin-Elmer 457 grating spectrophotometer (250—4 000 cm^{-1}) using KBr plates. Polystyrene film was used

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[11] B. T. Heaton and D. J. A. McCaffrey, *J.C.S. Chem. Comm.*, 1973, 817, and references therein.

[12] M. A. Bennett, K. Hoskins, P. Hitchcock, W. R. Kneen, R. Mason, R. S. Nyholm, G. B. Robertson, and A. D. C. Towl, *J. Amer. Chem. Soc.*, 1971, **93**, 293.

[13] L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *J.C.S. Chem. Comm.*, 1970, 30.

[14] R. L. Richards, Section Lecture, Proceedings of the XIII International Co-ordination Chemistry Conference, Poland, 1970.

for calibration. Far-i.r. spectra were measured as Nujol mulls between strips of Polythene sheeting on the above instrument or, using rather thicker mulls, between Polythene discs, on a Grubb–Parsons DM4 (200—500 cm^{-1}) instrument.

^{1}H N.m.r. spectra were recorded on Varian Associates A60 and HA-100 spectrometers at *ca.* 30 °C with Me_4Si as an internal standard.

Molecular weights were determined with a Hitachi-Perkin-Elmer Model 116 molecular-weight apparatus, in 1,2-dichloroethane solution.

Conductivities were measured in nitrobenzene using a Portland Electronics conductivity bridge.

Melting points were determined in air on a Köfler hot-stage microscope or, for air-sensitive compounds, in sealed evacuated tubes with an Electrothermal melting-point apparatus. They are uncorrected.

Elemental microanalyses were carried out either by Mr. and Mrs. A. G. Olney of the Microanalytical Laboratories at the School of Molecular Sciences, University of Sussex, or by Dr. A. Bernhardt, Hohenweg 17, West Germany. Compounds were heated to 80 or 100 °C *in vacuo* for 4 h before analysis. Those insufficiently stable for this treatment were dried at 10^{-4} mmHg and 20 °C for several hours.

General Procedure.—Reactions were carried out in air unless otherwise stated. Schlenk-tube techniques were used when working with air-sensitive compounds. Reagent grade solvents were employed unless otherwise stated. Pure, dry solvents were obtained by standard methods.

Isonitriles were prepared by the method of Ugi,[15] except for methyl isonitrile.[16]

Platinum(II) *Isonitrile and Carbene Complexes*.—Known complexes were prepared by established methods,[2,17,18] and the new chlorophenyl complexes were prepared analogously. It was found however that 2,4-dichlorophenyl isonitrile could not be isolated without decomposition, and its dilute solution, as obtained from its preparation, was used to prepare its complexes.

Analytical data *etc.* for new complexes are in Table 1. For the purposes of nomenclature, we have given no number to the carbene carbon and the carbon atoms of the phenyl groups are numbered 2—6 in the usual way.

Reactions of Platinum(II) *Carbene Complexes with Dichlorine*.—The method was general so only a few representative examples are given here. Analytical data *etc.* are in Table 1.

Preparation of Trichloro[(*ethoxy*)(4-*chlorophenylamino*)*carbene*-CC^{2}]*triethylphosphineplatinum*(IV), $[PtCl_3\{C(OEt)(NHC_6H_3Cl\text{-}p)\}(PEt_3)]$ (*Tentative Formulation*).—Dichlorine was slowly bubbled into a solution of *cis*-$[PtCl_2\{C(OEt)(NHPh)\}(PEt_3)]$ (0.19 g) in chloroform (50 cm^3) for 1 min. The solution became bright yellow immediately on addition of dichlorine and deposited a white flocculent precipitate after a few minutes. This extremely insoluble solid was removed and washed with chloroform and ethanol to give the analytically pure *product* (0.11 g, 55%).

Preparation of Tetrachloro[*bis*(*methylamino*)*carbene*-C]*triethylphosphineplatinum*(IV), $[PtCl_4\{C(NHMe)_2\}(PEt_3)]$.—Dichlorine was passed into a chloroform (60 cm^3) suspension of *cis*-$[PtCl_2\{C(NHMe)_2\}(PEt_3)]$ (0.50 g) and the resultant yellow solution was stirred for 2 h. The bright yellow insoluble *product* was filtered off and found to be analytically pure (0.47 g, 90%).

Preparation of Dichloro[(*methylamino*)(4-*chlorophenylamino*)*carbene*-CC^{2}]*bis*(*triethylphosphine*)*platinum*(IV) *Perchlorate*, $[PtCl_2\{C(NHMe)(NHC_6H_3Cl\text{-}4)\}(PEt_3)_2][ClO_4]$.—Dichlorine was slowly bubbled into a solution of *trans*-$[PtCl\{C(NHMe)(NHPh)\}(PEt_3)_2][ClO_4]$ (0.40 g) in chloroform (10 cm^3) for $\frac{1}{2}$ min. The solution immediately turned bright yellow. After 5 min the solvent was removed under vacuum and the off-white solid recrystallised (methanol–ether) as white *crystals* (0.22 g, 50%). A few larger yellow crystals, identified as *trans*-$[PtCl_4(PEt_3)_2]$,[13] were easily removed by hand.

Preparation of Dichloro[(*ethylamino*)(4-*chlorophenylamino*)*carbene*-CC^{2}]*bis*(*triethylphosphine*)*platinum*(IV) *Perchlorate*, $[PtCl_2\{(NHEt)(NHC_6H_3Cl\text{-}4)\}(PEt_3)_2][ClO_4]$ (F) and trans-*trichloro*[(*ethylamino*)(*phenylamino*)*carbene*-C]*bis*(*triethylphosphine*)*platinum*(IV) *Perchlorate*, *trans*-$[PtCl_3\{C(NHEt)(NHPh)\}(PEt_3)_2][ClO_4]$ (G).—A chloroform solution of *trans*-$[PtCl\{C(NHEt)(NHPh)\}(PEt_3)_2][ClO_4]$ (0.40 g) was treated with dichlorine as above, to yield a yellow oil on removal of solvent under vacuum. This, dissolved in ethanol and cooled, gave a white *precipitate* of (F) (recryst. ethanol, 0.18 g, 40%). The filtrate, on further cooling, gave yellow crystals of (G) (0.11 g, 25%).

Compound (G), which smelled of dichlorine, turned white when set aside under nitrogen for 2 months. The white solid thus obtained had bands in its i.r. spectrum corresponding to the starting platinum(II) complex, but additional bands at 3 260 and 1 610 cm^{-1}. Its n.m.r. spectrum in $CDCl_3$ solution had a phenyl pattern containing a component typical of a metallated-phenyl group.

Preparation of trans-*Trichloro*[*bis*(*methylamino*)*carbene*-C]*bis*(*triethylphosphine*)*platinum*(IV) *Perchlorate*, trans-$[PtCl_3\{C(NHMe)_2\}(PEt_3)_2][ClO_4]$.—A chloroform solution of *trans*-$[PtCl_2\{C(NHMe)_2\}(PEt_3)_2][ClO_4]$ (0.40 g) was treated with dichlorine as above and solvent removed under vacuum to yield a bright yellow solid. This was dissolved in ethanol containing a little chloroform and on cooling gave bright yellow *crystals* (0.37 g, 85%).

Reaction of trans-$[PtBr\{C(NHMe)_2\}(PEt_3)_2][ClO_4]$, and trans-$[PtBr\{C(NHEt)(NHPh)\}(PEt_3)_2][ClO_4]$ *with Dibromine*.—To the complex (*ca.* 0.15 g) was added a solution of bromine, either an excess or 1 mol equivalent in chloroform (*ca.* 15 cm^3 solution), and the mixture was set aside for 1—2 h when a red colour developed. Removal of solvent (10^{-3} mmHg) then gave a red oil which solidified to an orange powder on addition of methanol. Recrystallisation from ethanol then gave $[PtBr_4(PEt_3)_2]$ identified by its m.p. and i.r. spectrum (yield 30—80% in repeated experiments). No other products of the reaction could be identified.

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