Cationic Carbene Complexes of Palladium(II) and Platinum(II)

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A series of cationic carbene complexes *trans*-$[MX\{C(NHR)NR'R''\}(L)_2]ClO_4$ (M = Pd or Pt; X = H, Cl, or Br; R = Me, Ph, or *p*-$NO_2C_6H_4$; R' = H or Me; R'' = Me, Et, Ph, or *p*-$CH_3C_6H_4$; L = PEt_3, PBu^n_3, PPh_3, PhNC, or *p*-$NO_2C_6H_4NC$) have been prepared and characterised. Certain platinum compounds may be converted, by treatment with KOH in alcohol, to the neutral amidino-complexes *trans*-$[PtX\{C(NHR)=NR'\}(PEt_3)_2]$ (X = Cl or Br; R = Ph or *p*-$NO_2C_6H_4$; R' = Ph, Me, or Et). The i.r. and n.m.r. spectra of these compounds are recorded and used to assign configurations.

REACTION of isonitriles co-ordinated to Pd^{II} or Fe^{II} with nucleophilic reagents such as alcohols and primary amines to give carbene complexes is now well documented.[1-4] Here we describe the preparation by this route of cationic carbene complexes of Pt^{II} and Pd^{II} and also their conversion by base into complexes of the amidino-ligand [equations (1)—(3)].

$$\textit{trans}\text{-}[PtX(CNR)(PEt_3)_2]^+ + HNR'R'' \longrightarrow \textit{trans}\text{-}[PtX\{C(NHR)NR'R''\}(PEt_3)_2]^+ \quad (1)$$

(X = H, Cl, or Br; R = Ph, *p*-$NO_2C_6H_4$, or Me; R' = H or Me; R'' = Me, Ph, Et, or *p*-$CH_3C_6H_4$)

$$\textit{cis}\text{-}[PdCl_2\{C(NH\textit{p}\text{-}CH_3C_6H_4)NHR\}L] \xrightarrow[-NaCl]{L,NaClO_4} \textit{trans}\text{-}[PdCl\{C(NH\textit{p}\text{-}CH_3C_6H_4)NHR\}L_2]ClO_4 \quad (2)$$

(L = PBu^n_3, PPh_3, PhNC, or *p*-$NO_2C_6H_4NC$)

$$\textit{trans}\text{-}[PtX\{C(NHR)NR'R''\}(PEt_3)_2]^+ \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \textit{trans}\text{-}[PtX\{C(NR)NR'R''\}(PEt_3)_2] \quad (3)$$

(X = H, Cl, or Br; R = Me, Ph, or Et; R' = H; R'' = Ph or *p*-$NO_2C_6H_4$)

The cationic platinum(II) isonitrile starting complexes were prepared by the method of Church and Mays,[5] the physical data *etc.* of those which are new are shown in

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Tables 1—3. These compounds and the derived carbene and amidino-complexes are assigned the *trans*-configuration because of their **1 : 4 : 6 : 4 : 1** quintet pattern for the P–Me resonance of the $\mathrm{PEt_3}$ ligands.[5] Related compounds, where $\mathrm{PMe_2Ph}$ replaces $\mathrm{PEt_3}$ as ligand have recently been described by Clark and Manzer.[6]

The palladium(II) carbene complexes were prepared by the route shown [equation (2)] because we were unable to isolate cationic palladium(II) isonitrile complexes analogous to those of platinum(II). However, by means of reaction (2), stable cationic $\mathrm{Pd^{II}}$ isonitrile compounds have been isolated, to our knowledge the first to be reported. Presumably the presence of the carbene ligand helps to stabilise these compounds.

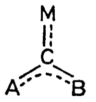
TABLE 1

Isonitrile, carbene, and amidino-complexes of $\mathrm{Pd^{II}}$ and $\mathrm{Pt^{II}}$

			Analyses [c]				Λ_M	I.r. spectra (Nujol mull, in $\mathrm{cm^{-1}}$)			
Compound [a]	Colour	M.p.[b]	C	H	N	Cl	$\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$	ν(N–H)	ν(N$\equiv$C)	ν(C$\cdots$N) [j]	ν(M–X) [k]
trans-$[\mathrm{PtCl(MeNC)(PEt_3)_2}]^+$	White	146—147	27·9(27·8)	5·8(5·5)	2·5(2·3)		20·5 [d]		2261s		334s
trans-$[\mathrm{PtCl(PhNC)(PEt_3)_2}]^+$	White	166—168	33·8(34·1)	5·3(5·2)	2·0(2·1)	10·1(10·6)	25·7 [d]		2208s		327s
trans-$[\mathrm{PtBr(MeNC)(PEt_3)_2}]^+$	White	140—143	25·6(25·8)	5·0(5·1)	2·1(2·2)		35·1 [d]		2265s		
trans-$[\mathrm{PtBr(PhNC)(PEt_3)_2}]^+$	White	155—159	32·1(32·0)	5·0(4·9)	2·1(2·0)		25·5 [d]		2215s		
trans-$[\mathrm{PtCl\{C(NHPh)NHMe\}(PEt_3)_2}]^+$	White	147—149	34·4(34·3)	5·9(5·7)	4·2(4·0)	10·2(10·1)	28·1 [d]	3346ms, 3292ms		1565s	305ms
trans-$[\mathrm{PtCl\{C(NHPh)NHEt\}(PEt_3)_2}]^+$	White	153—155	35·6(35·3)	5·9(5·9)	4·0(3·9)	10·1(9·9)	24·7 [d]	3328s, 3283w 3143m, 3178m		1562s	306ms
trans-$[\mathrm{PtBr\{C(NHPh)NHEt\}(PEt_3)_2}]^+$	White	137—142	32·9(33·2)	5·9(5·5)	3·5(3·7)		24·7 [d]	3294s, 3205w 3150m, 3105m		1567s	
trans-$[\mathrm{PtCl\{C(NHPh)NHC_7H_7\}(PEt_3)_2}]^+$	White	187	40·0(40·2)	5·9(5·7)	3·9(4·0)	9·8(10·1)	90 [e]	3260ms, 3203m		1528s	305ms
trans-$[\mathrm{PtCl\{C(NH}p\text{-}\mathrm{NO_2C_6H_4)NHC_7H_7\}\text{-}(PEt_3)_2}]^+$	Ivory	191	38·1(38·0)	5·3(5·3)	5·2(5·1)	8·7(8·6)	81 [e]	3254m, 3105m		1565s	306ms
trans-$[\mathrm{PtCl\{C(NH}p\text{-}\mathrm{NO_2C_6H_4)NHMe\}(PEt_3)_2}]^+$	Yellow	130	31·9(32·2)	5·4(5·3)	5·8(5·7)	9·5(9·5)	90 [e]	3362m, 3265m		1570s	303ms
trans-$[\mathrm{Pt\{C(NH}p\text{-}\mathrm{NO_2C_6H_4)NHMe\}(PEt_3)_2}]^+$	White	182	33·4(33·8)	5·6(5·7)	5·8(5·9)	4·8(5·0)	82 [e]	3371m, 3278m		1562s	2036s
trans-$[\mathrm{PtH\{C(NH}p\text{-}\mathrm{NO_2C_6H_4)N(Me)_2\}(PEt_3)_2}]^+$	White	180	34·9(34·8)	5·8(5·8)	5·7(5·8)	4·9(4·9)	85 [e]	3318m		1565s	2060s
trans-$[\mathrm{PtH\{C(NHPh)NHMe\}(PEt_3)_2}]^+$	White	168	35·6(36·1)	6·1(6·2)	4·1(4·2)	5·1(5·3)	147 [f]	3300m, 3235m		1540s	2050s
trans-$[\mathrm{PtH\{C(NHPh)N(Me)_2\})PEt_3)_2}]^+$	White	185	37·2(37·1)	6·4(6·4)	4·2(4·1)	5·1(5·2)	92 [e]	3280m		1545s	2050s
trans-$[\mathrm{PtCl\{C(NHPh)_2\}(PEt_3)_2}]^+$	White	164—165	39·4(39·4)	5·8(5·6)	3·5(3·5)		20·7 [d]	3255ms, 3205w 2368m [l]		1555s 1549s	310ms
trans-$[\mathrm{PtBr\{C(NHPh)_2\}(PEt_3)_2}]^+$	White	164—166	37·1(37·2)	5·4(5·2)	3·6(3·5)		25·5 [d]	3260ms, 3205m		1555s	
trans-$[\mathrm{PtCl\{C(NHMe)NHEt\}(PEt_3)_2}]^+$	White	160—164	29·6(29·5)	6·3(6·2)	4·6(4·3)		28·4 [d]	3350sh, 3320s		1592s	303ms
trans-$[\mathrm{PtCl\{C(NHMe)_2\}(PEt_3)_2}]^+$	White	171—175	28·5(28·4)	5·8(5·5)	4·5(4·6)		29·5 [d]	3315ms		1599s	295s
trans-$[\mathrm{PtBr\{C(NHMe)_2\}(PEt_3)_2}]^+$	White	193—194	26·6(26·4)	5·6(5·6)	3·9(4·1)		32·1 [d]	3420m, 3310ms 2543m,[e] 2440ms [l]		1581s 1543s [l]	
trans-$[\mathrm{PdCl\{C(NHPh)NHC_7H_7\}(PBu^n_3)_2}]^+$ [g]	Ivory	150	52·8(53·3)	8·0(8·0)	3·7(3·3)	8·7(8·3)	75 [e]	3280m, 32225m, 3160sh 3120m, 3070ms		1540s	305ms
trans-$[\mathrm{PdCl\{C(NHPh)NHC_7H_7\}(PPh_3)_2}]^+$ [g]	White	250	61·9(61·5)	4·7(4·5)	2·9(2·9)	7·2(7·3)	73 [e]	3250m, 3200m 3140sh, 3100sh, 2330m,[l] 2265w [l]		1541s 1541ms [l]	308ms 309ms [l]
trans-$[\mathrm{PdCl\{C(NHPh)NHC_7H_7\}(PhNC)_2}]^+$	Pale yellow	160	51·2(51·1)	3·6(3·7)	8·6(8·5)	10·2(10·3)	82 [e]	3240ms, 3060m	2214s	1550s	314ms or 303ms
trans-$[\mathrm{PdCl\{C(NH}p\text{-}\mathrm{NO_2C_6H_4)NHC_7H_7\}\text{-}(}p\mathrm{NO_2C_6H_4NC)_2}]^+$	Yellow	185	42·5(42·4)	2·8(2·7)	12·5(12·4)	9·0(8·9)	80 [e]	3225mbr, 3115m, 3080m	2209s	1552s	304ms or 292ms
trans-$[\mathrm{PdCl\{C(NHPh)NHMe\}(PPh_3)_2}]^+$ [g]	Yellow	228	58·5(58·7)	4·5(4·5)	3·2(3·7)	8·0(7·9)	83 [e]	3278mbr, 3120sh, 3150w		1570s	310m
							M [h]				
trans-$[\mathrm{PtCl\{C(NHPh)NMe\}(PEt_3)_2}]$ [i]	White	137—139	39·8(40·0)	6·7(6·5)	4·6(4·7)		650(600)	3435m 2540m [l]		1539m 1533m [l]	270s
trans-$[\mathrm{PtCl\{C(NHPh)NPh\}(PEt_3)_2}]$ [i]	White	139—141	45·6(45·4)	6·4(6·2)	4·3(4·2)		700(662)	3443m 2550m [l]		1571s 1565s [l]	278s
trans-$[\mathrm{PtBr\{C(NHPh)NPh\}(PEt_3)_2}]$ [i]	White	134—137	42·6(42·5)	6·0(5·8)	4·1(4·0)			3445m		1569s	
trans-$[\mathrm{PtCl\{C(NHPh)NEt\}(PEt_3)_2}]$ [i]	White	100—102	41·2(41·1)	6·9(6·7)	4·7(4·6)	5·6(5·8)	675(614)	3430ms 2540m [l]		1535s 1525s [l]	272ms
trans-$[\mathrm{PtCl\{C(NH}p\text{-}\mathrm{NO_2C_6H_4)NMe\}(PEt_3)_2}]$ [i]	Yellow	185	37·1(37·2)	5·8(5·9)	6·4(6·5)	5·4(5·5)		3344m		1564s	Not recorded
trans-$[\mathrm{PtBr\{C(NHPh)NEt\}(PEt_3)_2}]$ [i]	White	118—119	38·5(38·3)	6·4(6·2)	4·3(4·3)			3431m		1545s	
trans-$[\mathrm{PtH\{C(N}p\text{-}\mathrm{NO_2C_6H_4)NMe\}PEt_3)_2}]$										1560ms	1972s
trans-$[\mathrm{PtH\{C(NHPh)NMe\}(PEt_3)_2}]$								3330mbr		1565s	1953s

[a] Cationic compounds have $\mathrm{ClO_4^-}$ as counter-anion. [b] With decomposition, uncorrected. [c] Calculated values in parentheses. [d] In $\mathrm{PhNO_2}$ solution. [e] In $\mathrm{MeNO_2}$ solution. [f] In $\mathrm{Me_2CO}$ solution. [g] Configuration assumed, see text. [h] In $\mathrm{C_2H_4Cl_2}$ solution, calculated value in parentheses. [i] Location of N–H proton not certain, see text. [j] Tentative assignment, doubtless a coupled vibration, see text. [k] M = Pd or Pt; X = Cl or H. [l] ν(N–D) of corresponding deuterio-compound.

A number of limiting electronic structures for the carbene ligands may be drawn [1] including the amidinium-ion form [4] $\mathrm{Fe{-}[HRN{=}\overset{+}{C}{=}NHMe]}$. Since these are limiting forms, however, the electronic structure of the carbene ligand is probably best represented as (*a*), the polarisation of the π electron cloud depending on the nature of the substituents at carbon A and B and of the metal, M.



(*a*)

The deprotonation of the cationic carbene complexes [equation (3)] occurs when they are treated with strong base, such as alcoholic KOH.[7]

The starting complexes may be regenerated by treatment with acid. This deprotonation does not occur with mildly basic reagents such as the excess of amine used in reaction (1) and contrasts with the reactions of cationic carbonyl derivatives of Fe, Pt, and Ir [8-10] [equation (4)]

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[9] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *Chem. Comm.*, 1968, 548.

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TABLE 2

N.m.r. data for carbene complexes [a] (τ)

Compound	Phenyl	N–CH$_2$ or O–CH$_2$	N–CH$_3$ or Ph–CH$_3$	N–H	PEt$_3$
trans-$[PtCl\{C(NHPh)_2\}(PEt_3)_2]^+$	(1·8—1·95)m(4)(*o*) (2·6—2·9)m(6)(*mp*)			−0·24(∼1)	8·4m(12) 9·0q(18) *J*(ar)8·0
trans-$[PtBr\{C(NHPh)_2\}(PEt_3)_2]^+$	(1·7—1·9)m(4)(*o*) (2·6—2·9)m(6)(*mp*)			−0·22(∼1)	8·3m(12) 9·0q(18) *J*(ar)8·0
trans-$[PtCl\{C(NHPh)NHMe\}(PEt_3)_2]^+$	(1·75—2·0)m(2)(*o*) (2·6—2·9)m(3)(*mp*)		6·58(m)(2·7) ^3J(HNCH)4·8 ^4J(PtH)7·8 [b] 6·62(m)(0·3)	1·25(∼1) 0·4(∼1)	8·15m(12) 8·90q(18) (*J*ar)8·0
trans-$[PtCl\{C(NHPh)NHEt\}(PEt_3)_2]^+$	(1·9—2·1)m(2)(*o*) (2·6—3·0)m(3)(*mp*)	6·20m(2) ^3J(HCCH)7·0 ^3J(HNCH)5·0 [c] ^4J(PtH)8·0 [b, c]	8·64t(3) ^3J(HCCH)7·0	0·41(∼2)	8·15m(12) 8·90q(18) *J*(ar)8·0
trans-$[PtBr\{C(NHPh)NHEt\}(PEt_3)_2]^+$	(1·9—2·1)m(2)(*o*) (2·7—3·0)m(3)(*mp*)	6·18m(2) ^3J(HCCH)7·0 ^3J(HNCH)5·0 [c] ^4J(PtH)8·0 [b, c]	8·62t(3) ^3J(HCCH)7·0	0·42(∼2)	8·15m(12) 8·90q(18) *J*(ar)8·0
trans-$[PtCl\{C(NHMe)_2\}(PEt_3)_2]^+$			6·62m(∼2) ^3J(HNCH)4·8 ^4J(PtH)7·0 [b] 6·74m(∼2) ^3J(HNCH)4·8 ^4J(PtH)7·1 [b] 7·0m(2) ^3J(HNCH)4·8 ^4J(PtH)7·1 [b]	n.o.	8·1m(12) 8·85q(18) *J*(ar)8·0
trans-$[PtBr\{C(NHMe)_2\}(PEt_3)_2]^+$			6·5m(∼2) ^3J(HNCH)4·8 ^4J(PtH)7·0 [b] 6·85m(∼2) ^3J(NCNH)4·8 ^4J(PtH)7·0 [b] 6·95m(2) ^3J(NCNH)4·8 ^4J(PtH)7·1 [b]	n.o.	8·0m(12) 8·85q(18) *J*(ar)8·0
trans-$[PtCl\{C(NHMe)NHEt\}(PEt_3)_2]^+$			(6·0—7·1)m(5) [d] 8·72(3) ^3J(HNCH)5·0	n.o.	8·15m(12) 8·9q(18) *J*(ar)8·0
trans-$[PtCl\{C(NHPh)OEt\}(PEt_3)_2]^+$ [e]	2·3—2·9m	4·95—5·4m	8·55t [f] ^3J(HCCH)7·0	n.o.	8·1m 8·9q
trans-$[PtH\{C(NHPh)NMe_2\}(PEt_3)_2]^+$	(2·0—2·4)m(2)(*o*) (2·6—3·0)m(3)(*mp*)		6·35t(3) 6·60t(3) ^4J(PtH)4·5	1·30(∼1)	8·3m(12) 9·01q(18) *J*(ar)8·2
trans-$[PtH\{C(NH\text{-}p\text{-}NO_2C_6H_4)NMe_2\}(PEt_3)_2]^+$ [g]	1·84m(4)		6·30t(3) 6·54t(3) ^4J(PtH)4·5	0·92(∼1)	8·3m(12) 9·02q(18) *J*(ar)8·2
trans-$[PtH\{C(NHPh)NHMe\}(PEt_3)_2]^+$ [g]	(2·1—2·4)m(2)(*o*) (2·5—3·1)m(3) (*mp*)		6·72(3) [b] ^3J(HNCH)5·0 ^4J(PtH)5·2	0·55(∼1) 2·0(∼1) [h]	8·25m(12) 8·98q(18) *J*(ar)8·2
trans-$[PdCl\{C(NHPh)NHMe\}(PPh_3)_2]^+$	(2·1—3·2)m(35)		7·12d(3) ^3J(HNCH)4·5	1·33(∼1) 2·05(∼1) [h]	
trans-$[PdCl\{C(NDPh)NDMe\}(PPh_3)_2]^+$ [e]	(2·1—3·2)m(35)		7·12s(3)		
trans-$[PdCl\{C(NHPh)NH\text{-}p\text{-}CH_3C_6H_4\}(PPh_3)_2]^+$	(2·0—3·4)m(39)		7·66s(3)	0·51(2)	
trans-$[PdCl\{C(NDPh)ND\text{-}p\text{-}CH_3C_6H_4\}(PPh_3)_2{}^+$	(2·0—3·4)m(39)		7·65s(3)		
cis-$[PtCl_2\{C(NHPh)OEt\}(PPr^n_3)]$	(1·95—2·3)m(2)(*o*) (2·7—2·85)m(3)(*mp*)	4·8—5·3m 4·6—5·3(m) [i]	8·72t [f] ^3J(HCCH)7·0 ^4J(PtH)∼7 [c]	0·30(1)	

[a] In CDCl$_3$ solution unless otherwise stated, $\tau \pm 0{\cdot}02$, *J* values Hz ± 0·04; integration values in parentheses. [b] Obtained after D$_2$O treatment. [c] Obtained after treatment with D$_2$O and decoupling. [d] Complex pattern of multiplets, see text. [e] Not isolated. [f] O–CH$_2$–*CH*$_3$. [g] Values of τ(Pt–*H*) fall at 18·5 and 18·3 for the phenyl- and *p*-nitrophenyl-derivatives respectively. Only the central triplet has been observed owing to solubility limits. *J*(PH) ≃ 15—17 Hz, confirming the *trans*-configuration. [h] N–H Signal partially overlaps phenyl resonances but was clearly identified by deuteriation. [i] In (CD$_3$)$_2$CO solution. m = Multiplet, q = quintet, s = singlet, t = triplet, n.o. = not observed, *o* = *ortho*, *mp* = *meta* and *para*, *J*(ar) = separation of adjacent resonances.

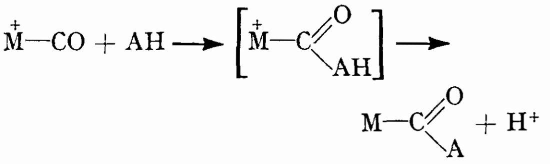
TABLE 3

N.m.r. data for isonitrile and amidino-complexes [a]

Compound	Phenyl	N-CH$_2$	N-CH$_3$	PEt$_3$
trans-$[PtCl(MeNC)(PEt_3)_2]ClO_4$			6·31t(3) ^4J(PtH)20·8	7·84m(12) 8·85q(18) *J*(ar)8·0
trans-$[PtCl(PhNC)(PEt_3)_2]ClO_4$	2·39m(5)			7·78m(12) 8·78q(18) *J*(ar)8·0
trans-$[PtCl\{C(NH\text{-}p\text{-}NO_2C_6H_4)NMe\}(PEt_3)_2]$ [b]	1·75—2; 2·15—2·5(4)		7·0t(3)	8·14m(12) 8·90q(18) *J*(ar)8·2
trans-$[PtCl\{C(NHPh)NMe\}(PEt_3)_2]$ [b]	2·44—3·44m(5)		7·12m(3)	8·2m(12) 8·96q(18) *J*(ar)8·0
trans-$[PtCl\{C(NHPh)NEt\}(PEt_3)_2]$ [b]	2·3—3·2m(5)	6·50m(2)	8·83t(3) ^3J(HCCH)7·0	8·1m(12) 8·96q(18) *J*(ar)8·0
trans-$[PtBr\{C(NHPh)NEt\}(PEt_3)_2]$ [b]	2·37—3·25m(5)	6·58m(2)	8·88t(3) ^3J(HCCH)7·0	8·1m(12) 8·96q(18) *J*(ar)8·0
trans-$[PtBr\{C(NHPh)NPh\}(PEt_3)_2]$ [b]	2·1—3·3m(10)			8·1m(12) 8·96q(18) *J*(ar)8·0

[a] In CDCl$_3$ solution; $\tau \pm 0{\cdot}02$, *J* values Hz ± 0·04. [b] The location of the NH proton is uncertain, see text. m = Multiplet, q = quintet, t = triplet; *J*(ar) = separation of adjacent resonances.

where deprotonation is easy. This behaviour is probably a consequence of the greater basicity of nitrogen



(4)

over oxygen, as has been suggested by Treichel.[11] Following this route, some hydrido-derivatives of platinum(II) with the hydride *trans* to a Pt–C σ-bond have been prepared. They are viscous orange-red oils, which do not crystallise even at −80°. Their i.r. spectra (Table 1) show rather low values of ν(Pt–H) at 1953—1972 cm^{-1}. Further work is in progress to completely characterise these compounds.

I.r. Spectra.—The characteristic i.r. absorptions of the compounds studied are shown in Table 1. All those containing the perchlorate anion show bands in the ranges 1035—1140 cm^{-1} [ν(Cl–O)] and 618—625 cm^{-1} [δ(Cl–O)] typical of this anion.[12]

Co-ordinated isocyanide has ν(N≡C) at a higher position relative to the free ligand, as is usually observed. Moreover, the complexes [PdCl(RNC)$_2${C(RNH)NH*p*-CH$_3$C$_6$H$_4$}]ClO$_4$ show only one ν(N≡C) band, consistent with a *trans*-configuration for the isonitrile ligands. By analogy with these and the platinum complexes the phosphine ligands in the other palladium derivatives are assigned the *trans*-configuration. The platinum complexes also show a band at *ca.* 420 cm^{-1} attributable to ν(Pt–P) for a *trans*-phosphine complex.[13]

The carbene and amidino-complexes have bands in the range 3060—3371 cm^{-1} assigned to ν(N–H), which shift to 2265—2550 cm^{-1} in deuteriated compounds. The assignment of ν(C⩦N) in the 1500—1600 cm^{-1} region in which δ(N–H) also occurs, follows since ν(C⩦N) changes only slightly on passing to the deuterio-compounds; coupling between the C⩦N stretching and N–H deformation vibrations is therefore not extensive.

Both sets of frequencies are close to those found for the neutral platinum and palladium carbene complexes,[1,2] suggesting that the electronic configuration of the carbene ligand is not greatly affected on passing from neutral to cationic complexes.

The stretching frequencies ν(Pt–Cl) and ν(Pd–Cl) fall in the range 295—310 cm^{-1} which is a little higher than the range of ν(M–Cl) found for neutral, non-ionic carbene complexes of *cis*-configuration,[1,2] perhaps because of the charge carried by the cationic compounds. The relatively low values of ν(M–Cl) suggest a high *trans*-influence of carbene ligands, of the order of that exerted by tertiary phosphines.[14] The rather low ν(Pt–H) values (*ca.* 2050 cm^{-1}) are also compatible with a high *trans*-influence of carbene ligands and close to the value of ν(Pt–H) *trans* to tertiary phosphine or phosphite in the compounds *trans*-[PtH(L′)(L)$_2$] [L′ = PEt$_3$ or P(OMe)$_3$].[5]

When the carbene ligand is converted to the amidino-ligand, the *trans*-(Pt–Cl) stretching frequency is lowered by a further 30—40 cm^{-1} (Table 2), to the region normally found for Pt–Cl *trans* to an anionic σ-bonded carbon ligand such as a methyl group.[13]

N.M.R. Spectra.—In Table 2 are shown data for the cationic carbene complexes, which are conveniently soluble. Also included are a few data for a neutral *cis*-complex, extensive measurements being prevented by the low solubility of these compounds.[1,2,7]

The *trans*-configuration of the cationic complexes follows from the 1 : 4 : 6 : 4 : 1 pattern for the methyl resonance of the PEt$_3$ ligands.

Assignment of N–H resonances, when observed, follows from their disappearance on addition of D$_2$O to the system. These resonances are broad, difficult to integrate accurately, and occur in the range τ −0·4—2·05.

Resonances due to methyl or methylene groups directly attached to nitrogen or oxygen substituent atoms of the carbene ligands occur in the region τ 6—7·5 (attached to N) and τ 4·5—5·5 (attached to O). These resonances are complex due to coupling with N–H protons, CH$_3$ protons, and ^{195}Pt as appropriate. Coupling constants have been assigned, however, after simplifying the resonance pattern by addition of D$_2$O (to remove N–H coupling) and for an ethyl group, by decoupling the CH$_3$ resonance from the CH$_2$. These assignments are shown in Table 2. Resonances due to CH$_3$ of an ethyl group attached to oxygen or nitrogen occur in the region τ 8·55—8·72.

Resonances due to phenyl groups appear in the regions 1·7—2·4 (*ortho*-protons) and 2·5—3·1 (*meta*- and *para*-protons). The assignments follow from the integration values, but are masked when PPh$_3$ is a co-ligand, by the phenyl groups of the phosphine. The methyl resonance of an *N*-tolyl group occurs at *ca.* τ 7·6.

Amidinium salts [15] and carbene complexes of chromium [16] are known to exhibit hindered rotation about the C–N or C–O bonds. In general a carbene ligand (RHN⩦C⩦NHR′) could have four possible isomeric forms in solution (*b*), (*c*), (*d*), or (*e*), or three forms if R = R′. More than one isomer has been observed in solution when R or R′ or both is a methyl group, since more than one methyl resonance per NCH$_3$ group has been observed (see Table 3). When R = Ph and R′ = Me *ca.* 90% of the complex is in one isomeric form. Where R = Me and R′ = Me or Et a more equal mixture of isomers

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[11] P. M. Treichel, J. J. Benedict, R. W. Hess, and J. P. Stenson, *Chem. Comm.*, 1970, 1627.

[12] H. Colm, *J. Chem. Soc.*, 1952, 4282.

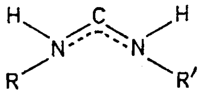
[13] D. M. Adams, 'Metal-Ligand and Related Vibrations,' E. Arnold, London, 1967, p. 328, and references therein.

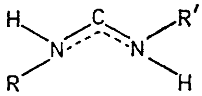
[14] R. L. Richards, *13th International Conference on Co-ordination Chemistry*, Poland, 1970.

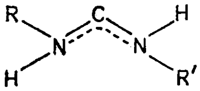
[15] G. S. Hammond and R. C. Newman, jun., *J. Phys. Chem.*, 1963, **67**, 1655.

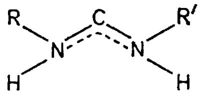
[16] J. A. Connor and E. O. Fischer, *J. Chem. Soc.* (*A*), 1969, 578 and references therein.

appears to be present. In a preliminary communication[17] it was suggested that the complex *cis*-[$PtCl_2${C(OEt)NHPh}PPr^n_3] gave a mixture of isomers in solution, however our later and more accurate measurements show that only one isomer is present in $CDCl_3$ solution. The other compounds of Table 2 also show only one isomeric form. As has been suggested previously,[6,17] mainly on steric grounds, probably the most favourable configurations are (*c*) and (*d*). When the groups R and R′ are small, such as methyl, it appears that other isomers may exist.


(*b*)


(*c*)


(*d*)


(*e*)

It is notable (Table 2), that ^4J(PtCNCH) is less when the carbene ligand is *trans* to the high *trans*-influence hydride ligand (*ca.* 5 Hz) than when it is *trans* to the chloride or bromide ligands of low *trans*-influence (*ca.* 7 Hz). A similar effect on ^2J(PtCH) has been noted for compounds where the CH_3 group replaces the carbene ligand.[18]

In Table 3 are shown the n.m.r. spectra of the neutral amidino-complexes, together with those of some previously unreported isonitrile complexes. The amidino-complexes show N–CH_2 and N–CH_3 resonance values at somewhat higher field than their carbene analogues and the phenyl absorptions appear as a broad complex multiplet. The spectra show only one isomer to be present in solution. In these compounds, although the N–H absorption was clearly shown in their i.r. spectra, it could not be detected in the n.m.r. possibly because it was too broad to distinguish from the background or masked by phenyl absorptions. It is thus uncertain whether the proton resides on only one nitrogen atom and there may be a dynamic equilibrium between the two possible positions. The formulae of these compounds as written are not intended to imply a known position of the proton.

Although by reaction (1), using EtOH as nucleophile, we were unable to isolate *trans*-[PtCl{C(OEt)NHPh}$(PEt_3)_2$]ClO_4 free from the parent isonitrile complex,[16] its pertinent n.m.r. features could be observed in solution and are shown in Table 2. Clark, however, by a modification of reaction (1) has isolated cationic carbene complexes containing an oxygen or sulphur hetero-atom.[6] It is not clear at the present time in what way modifications of reaction conditions and co-ligands influence the course of the carbene-forming reaction, but variations of this type and of the metal atom should provide information on the factors involved in the activation of co-ordinated isonitrile and related ligands towards nucleophilic attack.

EXPERIMENTAL

The isonitrile starting complexes were prepared by published methods.[1,2,5] All other chemicals were reagent grade and were used without further purification. Conductivity measurements were taken using an LKB 8300B or Portland Electronics conductivity bridge. Molecular weights were determined with a Hitachi–Perkin-Elmer 116 osmometer and m.p.s with a Kofler hot stage. I.r. spectra were recorded using Perkin-Elmer 621, Unicam SP 1200, and Grubb–Parsons DM4 instruments, calibrated against carbon monoxide, polystyrene film, or water vapour as appropriate. Varian HA 100, Jeol C60HL, and Jeol PS100 instruments were used for n.m.r. spectral measurements, with TMS as internal standard. Microanalyses were by Mr. A. G. Olney of Sussex University and Dr. Strauss, Microanalytical Laboratory, Oxford University.

General preparative methods are given below, analytical data *etc.* for compounds prepared are in Table 1.

Preparation of trans-[PtX{C(NHR)NR′R″}$(PEt_3)_2$]ClO_4 (X = H, Cl, *or* Br; R = Ph *or* Me; R′ = H *or* Me; R″ = Ph, Me, *or* Et).—Liquid amines were added in excess to the *trans*-[PtX(RNC)$(PEt_3)_2$]ClO_4 starting complexes to give a clear solution which was stirred for *ca.* 15 min then evaporated to dryness under reduced pressure, leaving a white solid which was recrystallised from ethanol. Gaseous methylamine and dimethylamine were bubbled into an ether suspension of the isonitrile compound until a clear solution was obtained (*ca.* 30 min) then removal of amine and some solvent by a stream of dinitrogen caused the white product to precipitate. Yields were close to quantitative.

Preparation of trans-[PtCl{C(NHR)NH*p*-$CH_3C_6H_4$}$(PEt_3)_2$]ClO_4 (R = Ph *or* *p*-$NO_2C_6H_4$).—The complexes *trans*-[PtCl(RNC)$(PEt_3)_2$]ClO_4 (*ca.* 1 mmol) were dissolved in chloroform (50 ml) and treated with an excess of *p*-toluidine. The solution was refluxed for three days, then treated with charcoal, filtered, and concentrated under reduced pressure to *ca.* 10 ml. Addition of ether–light petroleum (1 : 1) precipitated the white complexes which were purified by reprecipitation from the same solvents (80% yield).

Preparation of trans-[PdCl{C(NHR)NH*p*-$CH_3C_6H_4$}$(L)_2$]ClO_4 (R = Ph, *p*-$NO_2C_6H_4$; L = PBu^n_3, PPh_3, PhNC, *p*-$NO_2C_6H_4$NC).—The complex *cis*-[PdCl{C(NHR)NH*p*-$CH_3C_6H_4$}L][2] (1 mmol), dissolved or suspended in acetone (50 ml) was treated with stirring with the ligand L (1 mmol) and an excess of sodium perchlorate and after 1 h the resulting solution was evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane, treated with charcoal, filtered, and the solution concentrated under reduced pressure. Addition of ether–light petroleum (1 : 1) precipitated the product which was purified by reprecipitation from the same solvents.

Preparation of Deuterio-compounds.—In general the non-deuteriated compound was dissolved in either CH_3OD or $CDCl_3$–D_2O and the solution shaken until exchange was complete (up to 3 days). Removal of solvent under reduced pressure then gave the deuterio-compound which was identified by the i.r. spectrum (Table 1)

Reactions with Alcoholic KOH —To a solution of the [PtX{C(NHR)NR′R″}$(PEt_3)_2$]ClO_4 compound in ethanol

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[17] E. M. Badley, B. J. L. Kilby, and R. L. Richards, *J. Organometallic Chem.*, 1971, **27**, C37.

[18] H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, 1970, **9**, 1226.

was added the stoicheiometric quantity of alcoholic KOH and the mixture refluxed for 4 h then the solvent removed under reduced pressure. The residue was recrystallised from ethanol or benzene–hexane except where X = H, when only viscous oils were obtained on evaporation of solvent.

Protonation of Amidino-complexes.—To a solution of the amidino-complex in ethanol was added the stoicheiometric quantity of perchloric acid in water. After stirring for 1 h, removal of solvent under reduced pressure gave a white solid which was washed with water and dried. The compound was identified as the parent cationic carbene complex by its i.r. spectrum (80—85% yield).

We thank the S.R.C. for studentships (to E. M. B. and B. J. L. K.) and the Italian C.N.R. for partial support of this work.

[2/493 *Received, 3rd March,* 1972]