Carbene Complexes. Part II.[1] Thermally-induced Isomerisations of *trans*-Platinum(II) and Palladium(II) Complexes and the Chemistry of the *cis*- and *trans*-Isomers

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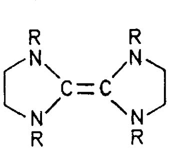
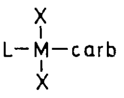
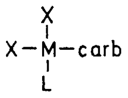
trans-Dihalogenoplatinum(II) or palladium(II) (carbene) complexes are isomerised either thermally or in polar solvents to the thermodynamically more stable *cis*-isomers. Reactivity decreased from Pd^{II} to Pt^{II} and with increasing n-alkyl chain-length of a tertiary phosphine *trans* to the carbene ligand. Properties of *cis*- and *trans*-carbene complexes are compared and certain generalisations emerge. Dichloro-complexes undergo Cl^- displacement (*cis*- more readily than *trans*- and Pd^{II} more than Pt^{II}) by Br^-(LiBr), Me^-(LiMe), H^-(Et_3SiH), and PR_3 ($NaBF_4$/PR_3). *trans*-Hydrido(chloro)platinum(II) and dimethylplatinum(II) carbene complexes are of particular interest.

IN Part I we described reactions of electron-rich olefins, *e.g.* (I), with halide-bridged palladium and platinum dimers to give *trans*/*cis*-carbene complexes (II) and (III) [M = Pd or Pt; X = Cl or Br; carb = $\overline{CNRCH_2CH_2N}R$ (R = Me or Ph), $\overline{CNMe{\cdot}C_6H_4{\cdot}S}$-*o*; L = PR_3 or AsR_3]. Whether the product is the *trans*- or *cis*-isomer, or a mixture of these depends on the reagents, solvent, and reaction conditions. We will show that the formation of the *trans*-complex is kinetically controlled, and the *cis*-isomer is thermodynamically the more favoured. Other topics to be considered relate to (i) *trans*→*cis*-isomerisations, (ii) a comparison of properties of *trans*- with *cis*-isomers, and (iii) a study of the chemistry of some of these complexes. With reference to (iii), no reactions of the co-ordinated carbene ligand were observed, but some interesting halide displacements are described: these are illustrated in Scheme 1, with reference to the Pt^{II} *trans*-complex (IV). It is clear that the carbene ligand is firmly attached to the metal. [Reactions of co-ordinated carbene are best known for alkoxycarbene-chromium(0) derivatives.[2]] The formation and characterisation of stable hydrido- or methyl-metal carbene complexes is noteworthy;[3] they might have been expected to tautomerise by H- or Me-transfer to the (carbene) ligand, as is the case for hydrido-metal ketimides.[4] Attempted preparations of *trans*-dialkylplatinum(II) complexes yield *cis*-isomers.


(I)


(II)

$$L-\underset{X}{\overset{X}{M}}-carb$$


(III)

$$X-\underset{L}{\overset{X}{M}}-carb$$

Isomerisation of trans-*Carbene Complexes*.—*trans*-Carbene complexes (II) are converted, either thermally or in polar solvents, to the corresponding *cis*-isomers. This rearrangement was first noted[5,6] when *trans*-$PtCl_2$($\overline{CNPhCH_2CH_2N}Ph$)($PEt_3$) was heated in order to determine its m.p.; at *ca.* 200° the colour was discharged to produce *cis*-$PtCl_2$($\overline{CNPhCH_2CH_2N}Ph$)($PEt_3$).[5,6] (A single-crystal *X*-ray analysis has established the molecular structure for crystalline forms of both isomers.[5,6]) The work was extended to other ligands and Pd, in order to determine the scope of the isomerisation and to make available a range of *cis*/*trans*-metal–carbene complexes so that generalisations might be possible. In addition, for ^{31}P (ref. 7) and ^{13}C (ref. 8) n.m.r., it was necessary to prepare, by choice of suitable ligands, soluble *cis*-complexes. The complexes, prepared by the isomerisation reaction, with reaction conditions and selected data, are shown in Table 1; some of the compounds are new, whereas others were described in Part I because they are available directly from electron-rich olefins.[1]

As the alkyl chain of the phosphine increases, so too does the difficulty in obtaining the *cis*-isomers (see Table 1). For example, *trans*-$PtCl_2$($\overline{CNPhCH_2CH_2N}Ph$)($PEt_3$) rearranges to the *cis*-isomer in boiling ethanol after 24 h, but under identical conditions *trans*-$PtCl_2$($\overline{CNPhCH_2CH_2N}Ph$)($PBu^n_3$) yields the *cis*- and *trans*-$PtCl_2$($\overline{CNPh_2CH_2CH_2N}Ph$)($PBu^n_3$) mixture in 1 : 10 ratio. A similar trend was also observed in cases where the carbene ligand is $\overline{CNMeCH_2CH_2N}Me$ or $\overline{CNMe{\cdot}C_6H_4\text{-}S}$-*o*. In general, the palladium carbene complexes are more reactive than the corresponding platinum analogues. Thus, although *trans*-$PdCl_2$($\overline{CNPhCH_2CH_2N}Ph$)($PEt_3$) is converted into the *cis*-complex at 65° in methanol within 1 h, *trans*-$PtCl_2$($\overline{CNPhCH_2CH_2N}Ph$)($PEt_3$) was recovered

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[1] Part I, D. J. Cardin, B. Cetinkaya, E. Çetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, 514.

[2] J. A. Connor and E. O. Fischer, *Chem. Comm.*, 1967, 1024; and later papers.

[3] *Cf.* D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.

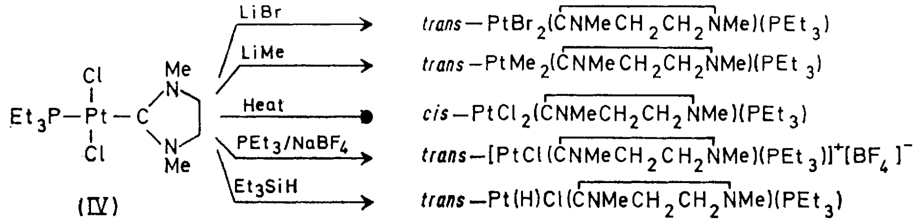
[4] B. Çetinkaya, M. F. Lappert, and J. McMeeking, *Chem. Comm.*, 1971, 215.

[5] D. J. Cardin, B. Çetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 400.

[6] D. J. Cardin, B. Çetinkaya, E. Çetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *J. Organometallic Chem.*, 1972, **44**, C59.

[7] Part IV, D. J. Cardin, B. Çetinkaya, and M. F. Lappert, unpublished work.

[8] Part III, D. J. Cardin, B. Çetinkaya, E. Çetinkaya, M. F. Lappert, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, in the press.



(IV)

unchanged after 3 h in boiling methanol. Furthermore, treatment of $(:\overline{\mathrm{CNMeCH_2CH_2NMe}})_2$ or $(:\overline{\mathrm{CNMe{\cdot}C_6H_4{\cdot}S}}\text{-}o)_2$ with $Pd_2Cl_4L_2$ affords *only* *cis*-complexes, but the corresponding platinum dimers yield mixtures of *cis*- and *trans*-$PtCl_2$(carb)L. The effect of other structural parameters upon propensity for isomerisation is less clear cut: thus, chloro- and bromo-complexes behave similarly; however, the decreasing thermal lability of the *trans*-complexes follows the sequence

$\overline{\mathrm{CNMeCH_2CH_2NMe}} \approx \overline{\mathrm{CNMe{\cdot}C_6H_4{\cdot}S}}\text{-}o >$ $\overline{\mathrm{CNPhCH_2CH_2NPh}}$, which parallels the solubility order. Indeed, the lower solubility of the *cis*- than the *trans*-complex favours the precipitation of the *cis*-isomer and

TABLE 1

cis-Compounds, prepared by isomerisation

Compound [a]	M.p. (t/°C)	Yield (%)	Reaction conditions t/°C	Time (held)	Solvent
$PtCl_2(\overline{CNPhCH_2CH_2NPh})(PEt_3)$	308—315 [b]	80 [c]	78	24 h	Ethanol
$PdCl_2(\overline{CNPhCH_2CH_2NPh})(PEt_3)$	275—290 [b]	81	65	1 h	Methanol
$PtBr_2(\overline{CNPhCH_2CH_2NPh})(PEt_3)$	312—314 [b]	90 [c]	78	24 h	Ethanol
$PdBr_2(\overline{CNPhCH_2CH_2NPh})(PEt_3)$	278—290 [b]	93	65	1 h	Methanol
$PtCl_2(\overline{CNPhCH_2CH_2NPh})(PBu^n_3)$	276—280	59	78	24 h [d]	Ethanol
$PdCl_2(\overline{CNPhCH_2CH_2NPh})(PBu^n_3)$	250—274 [b]	73	65	2 h [d]	Methanol
$PdBr_2(\overline{CNPhCH_2CH_2NPh})(PBu^n_3)$	240—241	70	65	6 h [d]	Methanol
$PtCl_2(\overline{CNPhCH_2CH_2NPh})(PMe_2Ph)$	*ca.* 253 [e]	79	78	24 h	Ethanol
$PtCl_2(\overline{CNPhCH_2CH_2NPh})(AsEt_3)$	265—288 [b]	74	78	24 h	Ethanol
$PtCl_2(\overline{CNMeCH_2CH_2NMe})(PEt_3)$ †	280—290	4	20	3 h	Benzene
$PdCl_2(\overline{CNMeCH_2CH_2NMe})(PEt_3)$ †	245—260 [b]	24	81	15 min	Benzene
$PtBr_2(\overline{CNMeCH_2CH_2NMe})(PEt_3)$ †	268—273	23	81	15 min	Benzene
$PtCl_2(\overline{CNMeCH_2CH_2NMe})(PPr^n_3)$ †	188—195	21	20	2 h	Benzene
$PtCl_2(\overline{CNMeCH_2CH_2NMe})(PBu^n_3)$ †	167—168	15 [c]	20	3 h	Benzene
$PdCl_2(\overline{CNMeCH_2CH_2NMe})(PBu^n_3)$ †	186—188	25	81	15 min	Benzene
$PtCl_2(\overline{CNMeCH_2CH_2NMe})(PMe_2Ph)$ †	240—246 [b]	42	81	20 min	Benzene
$PtCl_2(\overline{CNMeCH_2CH_2NMe})(AsEt_3)$ †	200—240 [b]	16	20	16 h	Benzene
$PtCl_2(\overline{CNMe{\cdot}C_6H_4{\cdot}S}\text{-}o)(PEt_3)$ †	250—275 [b]	46	140	10 min	Xylene
$PdCl_2(\overline{CNMe{\cdot}C_6H_4{\cdot}S}\text{-}o)(PEt_3)$ †	200—255 [b]	57	*ca.* 95	15 min	DMF
$PtCl_2(\overline{CNMe{\cdot}C_6H_4{\cdot}S}\text{-}o)(PBu^n_3)$ †	256—258 [b]	18	140	10 min	Xylene
$PdCl_2(\overline{CNMe{\cdot}C_6H_4{\cdot}S}\text{-}o)(PBu^n_3)$ †	210—270 [b]	67	*ca.* 95	15 min	DMF
$PtCl_2(\overline{CNMe{\cdot}C_6H_4{\cdot}S}\text{-}o)(PMe_2Ph)$ †	259—260	43	140	4 min	Xylene
$PtBr_2(\overline{CNMe{\cdot}C_6H_4{\cdot}S}\text{-}o)(PEt_3)$ †	250—275 [b]	50	140	10 min	Xylene

[a] Compounds indicated by (†) were described in ref. 1, here they are included for the sake of completeness. [b] Decomposes. [c] Also obtained in quantitative yield by heating (*ca.* 200°) the corresponding *trans*-isomer. [d] The *trans*→*cis*-isomerisation was still incomplete. [e] With sublimation.

thus has a major role; but homogeneous isomerisations do also occur, and may be followed by n.m.r. spectroscopy (see above).

TABLE 2

New carbene derivatives, prepared by chloride replacement

	Reactants	Product	Colour	M.p. (t/°C)	(%) Yield
(1) LiBr	*trans*-$\mathrm{PdCl_2(CNPhCH_2CH_2NPh)(PEt_3)}$ →	*trans*-$\mathrm{PdBr_2(CNPhCH_2CH_2NPh)(PEt_3)}$	Pale yellow	190—191	65
	trans-$\mathrm{PtCl_2(CNPhCH_2CH_2NPh)(PEt_3)}$ →	*cis*-$\mathrm{PtBr_2(CNPhCH_2CH_2NPh)(PEt_3)}$ [a]	White	312—314 [b]	74
	trans-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PEt_3)}$ →	*trans*-$\mathrm{PtBr_2(CNMeCH_2CH_2NMe)(PEt_3)}$ [c]	Yellow	173—176	70
	rans-$\mathrm{PdCl_2(CNPhCH_2CH_2NPh)(PBu^n{}_3)}$ →	*trans*-$\mathrm{PdBr_2(CNPhCH_2CH_2NPh)(PBu^n{}_3)}$	Yellow	150—152	83
(2) LiMe	*trans*-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PEt_3)}$ →	*trans*-$\mathrm{PtMe_2(CNMeCH_2CH_2NMe)(PEt_2)}$	White	95—97	73
	cis-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PEt_3)}$ →	*cis*-$\mathrm{PtMe_2(CNMeCH_2CH_2NMe)(PEt_3)}$	White	125—127	62
	trans-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(AsEt_3)}$ →	*trans*-$\mathrm{PtMe_2(CNMeCH_2CH_2NMe)(AsEt_3)}$	Off-white	85—86	72
	cis-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(AsEt_3)}$ →	*cis*-$\mathrm{PtMe_2(CNMeCH_2CH_2NMe)(AsEt_3)}$	Off-white	115—117	60
(3) $\mathrm{NaBF_4}$	$\mathrm{PMe_2Ph}$/*cis*-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PMe_2Ph)}$ →	*trans*-$\mathrm{[PtCl(CNMeCH_2CH_2NMe)(PMe_2Ph)_2]^+BF_4^-}$	White	222—223	67
	$\mathrm{PEt_3}$/*trans*-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PEt_3)}$ →	*trans*-$\mathrm{[PtCl(CNMeCH_2CH_2NMe)(PEt_3)_2]^+BF_4^-}$	White	181—182	65
(4) $\mathrm{Et_3SiH}$	*trans*-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PEt_3)}$ →	*trans*-$\mathrm{Pt(H)Cl(CNMeCH_2CH_2NMe)(PEt_3)}$	White	87—90	83

[a] Also prepared by isomerisation of *trans*-$\mathrm{PtBr_2(CNPhCH_2CH_2NPh)(PEt_3)}$ (see Table 1). [b] Decomposes. [c] Also prepared by bridge splitting reaction.[1]

TABLE 3

Some spectroscopic data for hydrido-platinum complexes

Compound	ν(PtH)/cm^{-1} [a]	τ PtH [b]	J(P–H) (Hz)	J(Pt–H) (Hz)
trans-$\mathrm{Pt(H)Cl(PEt_3)_2}$ [c]	2183	26·9 (t) [d]	14·5	1276
trans-$\mathrm{Pt(H)Cl(CNMeCH_2CH_2NMe)(PEt_3}$	2210	27·4 (d) [d]	18·0	1420
trans-$\mathrm{[Pt(H)(CNMeCH_2CH_2NMe)(PEt_2)_2]^+Cl^-}$	2025 [e]	17·2 (t) [f]	15·0	706
trans-$\mathrm{[Pt(H)(CNMeCH_2CH_2NMe)(PEt_3)_2]^+BF_4^-}$	2040	16·9 (t) [f,g]	17·0	702
trans-$\mathrm{[Pt(H)(PEt_3)_3]^+ClO_4^-}$ [h]	2090 [i]	16·2 [f]	15·0,[j] 15·6 [k]	790

[a] As Nujol mulls. [b] Relative to TMS; d = doublet, t = triplet. [c] See J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075. [d] In $\mathrm{C_6H_6}$. [e] Neat liquid. [f] In $\mathrm{CDCl_3}$. [g] Other signals at τ 5·90 (4, s, $\mathrm{CH_2N}$), 6·45 (6, t, MeN), 7·90 [6, c, $\mathrm{(MeC\mathit{H}_2)_3P}$], 8·5 [9, q, $\mathrm{(\mathit{Me}CH_2)_3P}$]. [h] See ref. 20. [i] In $\mathrm{CHCl_3}$ solution. [j] J(P-*cis*-H). [k] J(P-*trans*-H).

The isomerisation reactions take place under even milder conditions. For instance, in the course of recording the ^{31}P n.m.r. spectrum of *trans*-$\mathrm{PtBr_2(CNMeCH_2CH_2NMe)(PEt_3)}$, it was noted that the intensity of the central peak slowly decreased and a new peak appeared; when the spectrum of the same sample was re-recorded after 2 days, it was found that intensities and positions of the signals were reversed. The second signal was assigned to *cis*-$\mathrm{PtBr_2(CNMeCH_2CH_2NMe)(PEt_3)}$ by comparison with the spectrum of the authentic *cis*-complex.[7]

From an examination of a wide range of complexes, several generalisations may be made. Thus, the main differences between *cis*- and *trans*-carbene complexes are as follows: (i) colour (*cis* are white, *trans* are yellow); (ii) m.p. (*cis* > *trans*); (iii) solubility in non-polar solvents (*trans* > *cis*); (iv) J(Pt–P) (*cis* > *trans*);[7] (v) $\nu(\mathrm{MX_2})$ far-i.r. characteristics [both in number of strong bands (*cis* > *trans*) and position (*trans* > *cis*)];[7] and (vi) thermodynamic stability (*cis* > *trans*). Differences (i)—(v) clearly indicate the similar electronic effects of tertiary phosphines and carbenes; this may be related to their similar *trans*-influence.[6] Although complexes of the type *cis*-$\mathrm{MX_2(PR_3)_2}$ are known to isomerise thermally,[9] photochemically,[10] or in the presence of a catalytic

[9] G. B. Kauffman and L. A. Teter, *Inorg. Synth.*, 1963, **7**, 245.
[10] S. H. Mastin and P. Haake, *Chem. Comm.*, 1970, 202.

amount of a phosphine,[11] the reverse process (*i.e.*, *trans*$\rightarrow$*cis*) is not common.[12] However, the thermal isomerisation of *trans*-PtCl$_2$(NH$_2$R)(CO) [13] and *trans*-PtCl$_2$(NH$_2$R)(Me$_2$SO) [14] have been reported; a tetrahedral transition state has been suggested.[13]

Chloride Displacement Reactions.—Details on the derived new compounds are given in Tables 1—4. The *trans*-chloro-complexes [II; X = Cl, carb = CNRCH$_2$CH$_2$NR (R = Me or Ph) or CNMe·C$_6$H$_4$·S-*o*, L = PR$_3$] in acetone, methanol, or ethanol readily reacts, with the exception of *trans*-PtCl$_2$(CNPhCH$_2$CH$_2$NPh)(PEt$_3$), with an excess of lithium bromide to yield the corresponding bromides. These reactions were carried out for two reasons: (i) to confirm the assignment (far i.r.) for ν(MCl$_2$),[7] and (ii) to look at the reactivity of *trans*-carbene complexes. Analogous reactions of some *cis*-dichloroplatinum(II) carbene complexes have been described.[15] An attempt to convert *trans*-PtCl$_2$(CNPhCH$_2$CH$_2$NPh)(PEt$_3$) into the bromo-analogue at 20° in acetone was unsuccessful. However, under more forcing conditions (heating for 24 h under reflux in ethanol), *cis*-PtBr$_2$(CNPhCH$_2$CH$_2$NPh)(PEt$_3$) was obtained. The formation of *trans*-PdBr$_2$(CNPhCH$_2$CH$_2$NPh)(PEt$_3$), by the former procedure, demonstrates the greater reactivity of Pd^{II} compared with Pt^{II} *trans*-carbene complexes.

The compounds *cis*- and *trans*-PtCl$_2$(CNMeCH$_2$CH$_2$NMe)(AsEt$_3$) and *cis*- and *trans*-PtCl$_2$(CNMeCH$_2$CH$_2$NMe)(PEt$_3$) likewise react with methyllithium to afford the corresponding *cis*- and *trans*-PtMe$_2$(CNMeCH$_2$CH$_2$NMe)(PEt$_3$), *cis*- and *trans*-PtMe$_2$(CNMeCH$_2$CH$_2$NMe)(AsEt$_3$), respectively. The stereochemistry of these compounds was determined by examination of the ^{1}H n.m.r. and i.r. spectra. The ^{1}H n.m.r. spectrum of *trans*-PtMe$_2$(CNMeCH$_2$CH$_2$NMe)(PEt$_3$) (IV) in deuteriobenzene solution shows three 1 : 1 doublets centred at τ 9·68 assigned to the methyl protons of the Me–Pt groups, split by ^{31}P and ^{195}Pt. The assignment was confirmed by examining the n.m.r. spectrum of *trans*-PtMe$_2$(CNMeCH$_2$CH$_2$NMe)(AsEt$_3$) in deuteriobenzene solution; the methyl protons appear as a triplet at τ 9·70. The Me–Pt protons of the *cis*-complexes are so deshielded that they are obscured by the protons of PEt$_3$ or AsEt$_3$ which give rise to two groups of complex multiplets at τ 8·25 and 8·90. However, using deuteriochloroform as solvent, this obscurity was resolved (see Table 4). It is interesting that similar large solvent effects (CDCl$_3$ *vs.* C$_6$D$_6$) are noted in ^{1}H n.m.r. spectra of the carbene complexes derived from the olefin (I; R = Me), which is manifested in changes in chemical shifts associated with the NMe and endocyclic

TABLE 4

^{1}H N.m.r. data [a,b]

trans-PdBr$_2$(CNPhCH$_2$CH$_2$NPh)(PEt$_3$) [c]	2·00—2·76 (10, c, PhN), 5·76 (4, s, CH$_2$N), 8·34—9·03 (15, c, Et$_3$P)
trans-PdBr$_2$(CNPhCH$_2$CH$_2$NPh)(PBu$^n_3$) [c]	1·95—2·65 (10, c, PhN), 5·78 (4, s, CH$_2$N), 8·50—9·30 (27, c, Bu$^n_3$P)
trans-PtMe$_2$(CNMeCH$_2$CH$_2$NMe)(PEt$_3$) [d]	6·75 (6, t, MeN), 7·15 (4, t, CH$_2$N), 8·0—8·80 (15, c, Et$_3$P), 9·68 (6, d, MePt) [J(P–H) = 5·5 Hz, J (Pt–H) = 54·0 Hz]
cis-PtMe$_2$(CNMeCH$_2$CH$_2$NMe)(PEt$_3$) [c]	6·45 (4, s, CH$_2$N), 6·68 (6, t, MeN), 8·32—8·95 (15, c, Et$_3$P), 9·83 (3, d, MePt) [J(P–H) = 8·0 Hz, J(Pt–H) = 63·0 Hz], 9·84 (3, d, MePt [J(P–H) = 7·5 Hz, J(Pt–H) = 72·0 Hz]
trans-PtMe$_2$(CNMeCH$_2$CH$_2$NMe)(AsEt$_3$) [d]	6·80 (6, t, MeN), 7·20 (4, t, CH$_2$N), 8·25—8·70 (15, c, Et$_3$As), 9·70 (6, s, MePt) [J(Pt–H) = 54·0 Hz]
cis-PtMe$_2$(CNMeCH$_2$CH$_2$NMe)(AsEt$_3$) [c]	6·52 (4, c, CH$_2$N), 6·71 (6, t, MeN), 8·44—8·90 (15, c, Et$_3$As), 9·70 (3, s, MePt) [J(Pt–H) = 81·0 Hz], 9·87 (3, s, MePt) [J(Pt–H) = 61·0 Hz]
trans-Pt(H)Cl(CNMeCH$_2$CH$_2$NMe)(PEt$_3$) [d]	6·72 (6, t, MeN), 7·20 (4, t, CH$_2$N), 8·30—8·85 (15, c, Et$_3$P), 27·4 (1, d, HPt) [J(P–H) = 18·0 Hz, J(Pt–H) = 14·20 Hz]
trans-[PtCl(CNMeCH$_2$CH$_2$NMe)(PMe$_2$Ph)$_2$]$^+$BF$_4^-$ [e]	3·30 (10, c, PhP), 7·90 (6, c, MeN), 8·34 (4, c, CH$_2$N), 9·00 (12, t, Me$_2$Ph) [J(P–H) = 8·0 Hz, J(Pt–H) = 28·0 Hz]
trans-[PtCl(CNMeCH$_2$CH$_2$NMe)(PEt$_3$)$_2$]$^+$BF$_4^-$ [c]	6·20 [4, d(br, CH$_2$N] 6·70 (6, t, MeN), 7·90 [6, c, (MeC*H*$_2$)$_3$P], 8·90 [9, q, (*Me*CH$_2$)$_3$P]

[a] τ Values relative to TMS. [b] Information in parentheses refers successively to (i) the number of H atoms; (ii) the nature of the signal (c = complex, d = doublet, q = quintet, s = singlet, t = triplet); (iii) assignment. [c] In CDCl$_3$. [d] In C$_6$D$_6$. [e] In (CD$_3$)$_2$SO.

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[11] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020; J. Chatt and J. M. Davidson, *ibid.*, 1964, 2433.

[12] E. A. Allen, N. P. Johnson, D. T. Rosevear, and W. Wilkinson, *Chem. Comm.*, 1971, 171.

[13] R. Ellis, T. A. Weil, and M. Orchin, *J. Amer. Chem. Soc.*, 1970, **92**, 1078.

[14] Y. N. Kukushkin, Y. E. Vyaz'menski, and E. S. Postnikova, *Zhur. priklad. Khim.*, 1969, **42**, 926 (*Chem. Abs.*, 1969, **71**, 27055z).

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

CH_2 groups of the carbene ligand. A further complication is that *trans*-, unlike *cis*-, $\text{PtMe}_2(\overline{\text{CNMeCH}_2\text{CH}_2\text{N}}\text{Me})(\text{PEt}_3)$ appears to be slowly attacked by chloroform.

In the i.r. spectrum of *trans*-dimethyl compounds, a strong band at 470 cm^{-1} is assigned to $\nu(\text{PtC}_2)$; for tetramethylplatinum(IV) complexes, in which two methyls are *trans* to one another, similar values and assignments have been reported.[16] On the other hand, the stretching modes for the *cis*-dimethyl complexes of platinum(II) have been assigned to bands in the range 500—570 cm^{-1}.[17] Consistent with this, we observe a strong band at 515 cm^{-1}, with a shoulder at 521 cm^{-1} in the spectrum (Nujol mull) of *cis*-$\text{PtMe}_2(\overline{\text{CNMeCH}_2\text{CH}_2\text{N}}\text{Me})(\text{PEt}_3)$.

The use of methyl-lithium to prepare platinum(II)–methyl complexes is well established.[18] But the derived compounds, like other Pt^{II} dialkyls, invariably have had the *cis*-configuration. [Traces of *trans*-$\text{PtMe}_2(\text{PEt}_3)_2$ have been obtained by repeated distillation of the corresponding *cis*-dimethyl compound.[19]] It is not clear why carbene and phosphine ligands have differing roles in control of this reaction, especially as there is evidence of a similarity in their *trans*-influence;[6] this does not, however, preclude that their *trans*-effect may be different.

One of our objectives in preparing these methyl complexes was to see whether methyl migration from metal to the highly electrophilic carbene carbon[8] might be induced. Accordingly, a benzene solution of the *trans*-complex (IV) was heated with triethylphosphine in benzene under reflux. After $1\frac{1}{2}$ h, the starting platinum compound was recovered (90%). It may be that, as for the hydride (see below), tautomerisation from alkyl(carbene)- or hydrido(carbene)- into alkyl-metal complex is thermodynamically unfavourable.

In the presence of the appropriate neutral ligand (L), addition of sodium perchlorate to an acetone solution of $\text{PtXCl(PEt}_3)_2$ [X = H, Cl, Br, *o*- or *p*-$\text{F}\cdot\text{C}_6\text{H}_4$; L = Py, PR_3, P(OR)_3, CNR, or CO] removes the chloride as sodium chloride to give the cationic complex *trans*-$[\text{PtX(L)}(\text{PEt}_3)_2]^+[\text{ClO}_4]^-$.[20] Cationic carbene complexes have previously been synthesised by reaction of a cationic isonitrile precursor with an alcohol or primary amine.[21] We now find that *cis*- or *trans*-carbene complexes (II) or (III) behave similarly and afford cationic carbene complexes of the type *trans*-$[\text{PtCl(carb)L}_2]^+[\text{BF}_4]^-$ (carb = $\overline{\text{CNMeCH}_2\text{CH}_2\text{N}}\text{Me}$; L = PMe_2Ph or PEt_3). As expected, in the ^{1}H n.m.r. spectrum of the triethylphosphine complex, the methyl resonance from PEt_3 appears as a 1 : 4 : 6 : 4 : 1 quintet. The dimethylphenylphosphine complex is just adequately soluble in deuteriochloroform to show three triplets, and it is soluble in DMSO.

Free carbenes insert into Si–H bonds, and silanes are good traps for nucleophilic carbenes derived from Group VIA metal complexes.[22] In an attempt similarly to trap the carbene from (IV), the complex was heated in benzene under reflux with an excess of triethylsilane (1 : 3): *trans*-$\text{Pt(H)Cl}(\overline{\text{CNMeCH}_2\text{CH}_2\text{N}}\text{Me})(\text{PEt}_3)$ was obtained. (Some *cis*-platinum dihalides are converted into hydrides by silanes; an initial oxidative addition of silane followed by reductive elimination of chlorosilane has been suggested as the reaction sequence.[23])

In the i.r. spectrum of *trans*-$\text{Pt(H)Cl}(\overline{\text{CNMeCH}_2\text{CH}_2\text{N}}\text{Me})(\text{PEt}_3)$, a strong band at 2210 cm^{-1} is assigned to ν(PtH). The configuration of this complex is readily determined from the n.m.r. coupling constants (for comparison with other platinum hydrides, see Table 3). The Pt–H ^{1}H n.m.r. resonance appears as a doublet (at τ 27·4) due to coupling with the ^{31}P nucleus, J(P–H) = 18·0 Hz, and platinum satellites of *ca.* $\frac{1}{4}$ intensity, J(Pt–H) = 1420 Hz. Whereas *cis*-$\text{PtCl}_2(\text{PR}_3)_2$ reacts with triethylsilane to yield *trans*-$\text{Pt(H)Cl}(\text{PR}_3)_2$,[23] *cis*-$\text{PtCl}_2(\overline{\text{CNMeCH}_2\text{CH}_2\text{N}}\text{Me})(\text{PEt}_3)$ did not produce the expected hydride but a very air-sensitive, unidentified oil.

Attempts to transfer hydride from platinum to carbene carbon by treatment of *trans*-$\text{Pt(H)Cl}(\overline{\text{CNMeCH}_2\text{CH}_2\text{N}}\text{Me})(\text{PEt}_3)$ with triethylphosphine in benzene at 20° resulted in the formation of an extremely hygroscopic material *trans*-$[\text{Pt(H)}(\overline{\text{CNMeCH}_2\text{CH}_2\text{N}}\text{Me})(\text{PEt}_3)_2]^+\text{Cl}^-$. The ^{1}H n.m.r. spectrum is entirely consistent with the proposed structure (see Table 3). The absence of ν(Pt–Cl) in the far-i.r. spectrum and the appearance of a 1 : 4 : 6 : 4 : 1 quintet (methyls of triethylphosphine) also support the cationic structure. [The phosphine was used because it was considered (see ref. 4) that tautomerisation required initial conversion to the *cis*-hydridocarbene complex, thus its role was to have been both that of a catalyst and as a displacing ligand.] The complex was converted into the stable tetrafluoroborate (see Table 3) by treatment with sodium tetrafluoroborate in acetone.

EXPERIMENTAL

General Procedure.—These were as described in Part I.[1] Starting materials were mentioned there and triethylsilane was a generous gift from Dr. S. Takahashi.

Preparation of cis-*Carbene Complexes.*—These compounds were prepared by the isomerisation of the appropriate *trans*-complexes in appropriate solvents (see Table 1). The general procedure was as follows. The *trans*-complex was heated and the yellow colour of the solution was discharged. Upon cooling, white crystals of the *cis*-isomer

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were deposited. The crystals were filtered off, washed with ether, and dried *in vacuo*.

Attempts to isomerise the complexes *trans*-MX_2(carb)L, where carb = $\overline{\mathrm{CNMeCH_2CH_2N}}\mathrm{Me}$ or $\overline{\mathrm{CNMe{\cdot}C_6H_4{\cdot}S}}$-*o* [heating (24 h) in ethanol under reflux] were unsuccessful. Therefore, in these cases the isomerisations were carried out without a solvent (usually at 150—200° for 1 h). The *cis*-complexes were finally crystallised from chloroform–ether.

Analytical data on new compounds are shown below. Others were described in Part I.[1] Further data are in the Tables.

cis-*Dichloro*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*platinum*(II) (Found: C, 41·7; H, 4·8; N, 4·6. $C_{21}H_{29}Cl_2N_2PPt$ requires C, 41·6; H, 4·8; N, 4·6%), cis-*dichloro*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*palladium*(II) (Found: C, 48·9; H, 5·8; N, 5·5. $C_{21}H_{29}Cl_2N_2PPd$ requires C, 48·7; H, 5·6; N, 5·6%), cis-*dibromo*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*platinum*(II) (Found: C, 37·6; H, 4·2; N, 4·2. $C_{21}H_{29}Br_2N_2PPt$ requires C, 36·3; H, 4·2; N, 4·0%, cis-*dibromo*-(1,3-*diphenylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*palladium*(II) (Found: C, 42·7; H, 5·0; N, 4·9. $C_{21}H_{29}Br_2N_2PPd$ requires C, 41·6; H, 4·8; N, 4·6%), cis-*dichloro*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*tri*-n-*butylphosphine*)*platinum*(II) (Found: C, 46·4; H, 5·85; N, 4·1. $C_{27}H_{41}Cl_2PPt$ requires C, 46·95; H, 5·9; N, 4·05%), cis-*dichloro*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*tri*-n-*butylphosphine*)*palladium*(II) (Found: C, 54·0; H, 7·1; N, 4·8. $C_{27}H_{41}Cl_2N_2PPd$ requires C, 53·9; H, 6·8; N, 4·7%), cis-*dibromo*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*tri*-n-*butylphosphine*)*palladium*(II) (Found: C, 46·75; H, 6·0; N, 4·0. $C_{27}H_{41}Br_2N_2PPd$ requires C, 46·9; H, 5·9; N, 4·05%), cis-*dichloro*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*dimethylphenylphosphine*)*platinum*(II) (Found: C, 44·6; H, 4·2; N, 4·4. $C_{23}H_{25}Cl_2N_2PPt$ requires C, 44·1; H, 3·7; N, 4·5%), cis-*dichloro*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*triethylarsine*)-*platinum*(II) (Found: C, 39·5; H, 4·5; N, 4·4. $C_{21}H_{29}AsCl_2N_2Pt$ requires C, 38·8; H, 4·5; N, 4·3%).

Chloride Replacement. (*a*) *Reactions with lithium bromide*. The *trans*-dichloride was treated with an excess of lithium bromide (*ca*. 10-fold) in acetone at 20° for 24 h. The solvent was removed *in vacuo* and the residue was washed with water (3 × 15 ml) and then recrystallised (Me_2CO–Et_2O). The following derivatives were prepared in this way: trans-*dibromo*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*palladium*(II) (Found: C, 41·6; H, 5·0; N, 4·7. $C_{21}H_{29}Br_2N_2PPd$ requires C, 41·6; H, 4·8; N, 4·6%), trans-*dibromo*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*tri*-n-*butylphosphine*)*palladium*(II) (Found: C, 47·2; H, 6·3; N, 4·1%; *M*, 662. $C_{27}H_{41}Br_2N_2PPd$ requires C, 46·9; H, 5·9; N, 4·05%; *M*, 690), trans-*dibromo*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*platinum*(II) (Found: C, 23·8; H, 4·6; N, 4·9. Calc. for $C_{11}H_{21}Br_2N_2PPt$: C, 23·1; H, 4·4; N, 4·9%).

Under identical conditions, *trans*-dichloro(1,3-diphenylimidazolidin-2-ylidene)(triethylphosphine)platinum(II) did not react with lithium bromide. However, when the reactants were heated (24 h) in ethanol under reflux, a white solid was precipitated which was washed successively with water, ethanol, and ether; it was identified as *cis*-dibromo(1,3-diphenylimidazolidin-2-ylidene)(triethylphosphine)platinum(II) (Found: C, 37·8; H, 4·50; N, 4·3. Calc. for $C_{21}H_{29}Br_2N_2PPt$: C, 36·3; H, 4·2; N, 4·0%).

(*b*) *Reactions with methyl-lithium*. The same general procedure was used for all the reactions. The appropriate dichloride (0·5 mmol) dissolved or suspended in benzene (20 ml) was treated with methyl-lithium (0·6 mmol) in ether (2 ml), and the reaction mixture was stirred at 20° for 1 h. The solution was evaporated to a small volume (*ca*. 10 ml) *in vacuo*, and was filtered. The filtrate was evaporated to dryness and ether (5—10 ml) was added to the residue. Upon cooling (−20°), white crystals of the dialkyl complex separated out. The complexes prepared in this way were: trans-*dimethyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*platinum*(II) (Found: C, 35·95; H, 7·5; N, 6·4. $C_{13}H_{31}N_2PPt$ requires C, 35·4; H, 7·05; N, 6·35%), ν(PtC) 471s, cis-*dimethyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*platinum*(II) (Found: C, 35·9; H, 7·3; N, 6·3. $C_{13}H_{31}N_2PPt$ requires C, 35·4; H, 7·05; N, 6·35%), ν(PtC) 515s, 521sh, trans-*dimethyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylarsine*)*platinum*(II) (Found: C, 32·35; H, 6·6; N, 5·9. $C_{13}H_{31}AsN_2Pt$ requires C, 32·2; H, 6·4: N, 5·8%), ν(PtC) 470s, cis-*dimethyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylarsine*)*platinum*(II) (Found: C, 32·4; H, 6·6; N, 5·85. $C_{13}H_{31}AsN_2Pt$ requires C, 32·2; H, 6·4; N, 5·8%), ν(PtC) 520s or 533m cm^{-1}.

(*c*) *Reactions with sodium tetrafluoroborate*. Dimethylphenylphosphine (0·1 ml) was added to a suspension of *cis*-dichloro(1,3-dimethylimidazolidin-2-ylidene)(dimethylphenylphosphine)platinum(II) (0·1700 g, 0·34 mmol) and sodium tetrafluoroborate (0·0370 g, 0·34 mmol) in acetone (20 ml). The mixture was stirred at 20° for 2 h. The acetone was replaced by methanol (10 ml). Upon cooling (−20°), white crystals separated out, which were washed with ether, and identified as trans-*chloro*(1,3-*dimethylimidazolidin*-2-*ylidene*)*bis*(*dimethylphenylphosphine*)*platinum*(II) *tetrafluoroborate* (0·1560 g) (Found: C, 36·2; H, 4·8; N, 4·0. $C_{21}H_{32}BClF_4N_2P_2Pt$ requires C, 36·4; H, 4·6; N, 4·0%), ν(CN) 1540s or 1520sh; ν(PtCl) 311m cm^{-1}.

trans-*Chloro*(1,3-*dimethylimidazolidin*-2-*ylidene*)*bis*(*triethylphosphine*)*platinum*(II) *tetrafluoroborate* (0·4230 g) (Found: C, 31·6; H, 6·3; N, 4·3. $C_{17}H_{40}BClF_4N_2P_2$ requires C, 30·8; H, 6·1; N, 4·3%), ν(CN) 1540s or 1520sh; ν(PtCl) 298m cm^{-1}, was similarly prepared from *trans*-dichloro(1,3-dimethylimidazolidin-2-ylidene)(triethylphosphine)platinum(II) (0·4820 g, 1·00 mmol), sodium tetrafluoroborate (0·120 g, 1·10 mmol), and triethylphosphine (0·2 ml, 0·170 g, 1·4 mmol).

(*d*) *Reactions with triethylsilane*. Triethylsilane (0·71 ml, 2·5 mmol) was added to a solution of *trans*-dichloro(1,3-dimethylimidazolidin-2-ylidene)(triethylphosphine)platinum(II) (0·8000 g, 1·67 mmol) in benzene (30 ml). This solution was heated under reflux for *ca*. 20 min, whereafter it was concentrated to *ca*. 7 ml. To this, n-hexane (20 ml) was added to yield trans-*hydridochloro*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*platinum*(II) (0·6160 g) (Found: C, 29·4; H, 6·1; N, 6·4. $C_{11}H_{26}ClN_2PPt$ requires C, 29·45; H, 4·8; N, 6·25%).

Under identical conditions, the *cis*-isomer with triethylsilane did not give the expected compound; instead an oily material was obtained which was not characterised.

Reaction of trans-*Hydridochloro*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*platinum*(II) *with Triethylphosphine*.—Addition of triethylphosphine (0·1 ml, 0·85 g, 0·72 mmol) to a solution of the *trans*-hydride (0·2450 g, 0·55 mmol) in benzene (10 ml) at 20° did not cause any significant colour change, but the ^1H n.m.r. spectrum of the mixture (see Table 3) indicated that a reaction had taken place. Volatiles were removed under reduced pressure and the residue was washed with ether to obtain a hygroscopic solid (0·2488 g, 80%) believed to be *trans*-[PtH-$(\overline{\mathrm{CNMeCH_2CH_2N}}\mathrm{Me})(\mathrm{PEt_3})_2]^+\mathrm{Cl}^-$ (on the basis of spectroscopic data, see Table 3). A solution of this solid (0·2410 g, 0·43 mmol) in acetone (10 ml) was stirred at 20° with sodium tetrafluoroborate (0·0500 g, 0·45 mmol) for 2 h. The solvent was evaporated and the residue was taken up in chloroform (5 ml). Addition of ether (10 ml) to the solution gave a solid which was recrystallised (MeOH–$\mathrm{Et_2O}$) and identified as trans-*hydrido*(1,3-*dimethylimidazolidin*-2-*ylidene*)*bis*(*triethylphosphine*)*platinum*(II) *tetrafluoroborate* (0·1596 g, 60%) (Found: C, 33·3; H, 6·7; N, 4·8. $\mathrm{C_{17}H_{41}BF_4N_2P_2Pt}$ requires C, 33·1; H, 6·65; N, 4·55%), m.p. 105—108°.

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