^{1}H Nuclear Magnetic Resonance Spectra of Carbene Complexes of Platinum(II) and Palladium(II)

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The ^{1}H n.m.r. spectra of the complexes *cis*-$[MCl_2\{C(NHR^1)(NR^2R^3)\}(PR_3)]$, *trans*-$[PtCl\{C(NHR^1)(NR^2R^3)\}(PR_3)_2]ClO_4$, *cis*-$[MCl_2\{C(OR^4)(NHR^1)\}(PR_3)]$, and *trans*-$[MCl\{C(OR^4)(NHR^1)\}(PR_3)_2]ClO_4$ (M = Pt or Pd; R^1 = Me, Ph, or *p*-MeC_6H_4; R^2 = H or Me; R^3 = Me, Ph, or *p*-MeC_6H_4; R^4 = Me or Et and PR_3 = PMe_2Ph, PEt_3, or PPr^n_3 as appropriate) are described in detail and used to assign configurations to the carbene ligands in solution.

We have recently described a series of uncharged and cationic carbene complexes of platinum(II) and palladium(II).[1,2] Since the *X*-ray determined structure[3] of one member of the series, *cis*-$[PtCl_2\{C(OEt)NHPh\}PEt_3]$, shows bond orders of greater than one between the carbene carbon and attached heteroatoms, restricted rotation about these bonds is expected for this compound and its analogues. Restricted rotation has been demonstrated elsewhere, for example, the cation *trans*-$[PtCl\{C(NHMe)_2\}(PEt_3)_2]^+$ was shown to be a mixture of isomers in solution,[2] but precise assignment of the configurations of the isomers was not attempted.

Clark and his co-workers[4] have observed restricted rotation about the platinum–carbene bond of *trans*-$[Pt\{C(NHC_6H_4CH_3)(NHEt)\}(CNEt)(PMe_2Ph)_2](PF_6)_2$ in solution. Its origin was not discussed, but since the Pt–C bond order in such complexes is close to unity,[3,5] the cause is probably steric.

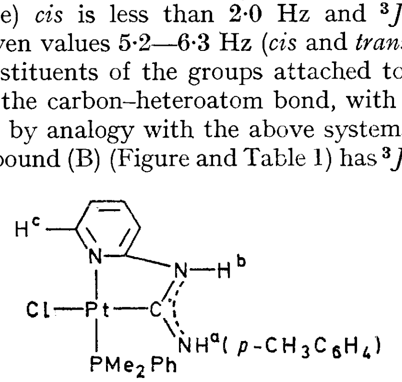
To gain more precise information on the above observations, we have examined in detail the ^{1}H n.m.r. spectra of a number of uncharged and cationic carbene complexes. Some complexes of the series are new and their analytical details, *etc.*, are shown in Table 1. Major details of their spectra, which are often solvent dependent, are shown in Tables 1 and 2 and are discussed below; the full details of these spectra have been deposited in Supplementary Publication No. 20929 (20 pp.).†

Assignment of Configurations.—The overall geometry of the ligands about the metal has been assigned using the typical patterns shown by phosphine ligands (particularly PMe_2Ph)[2,4] when *cis* or *trans* to each other and by analogy with *X*-ray structural data in the solid state, *e.g.* of *cis*-$[PtCl_2\{C(NHPh)OEt\}(PEt_3)]$. ^1J(PtP) Values have also been used (see later).

The configuration of the carbene ligands themselves has, in previous work, mainly been assigned by consideration of steric effects, although Fischer has used homo-allylic coupling within the carbene moiety to assign the positions of carbene substituents relative to each other.[6]

The feature of the series studied here is the ^{195}Pt nuclear spin which allows observation of the coupling constants between the metal and the carbene heteroatom substituents. In particular ^3J(PtCNH) is greater when the proton is *trans* to platinum than when it is *cis*; our evidence is as follows.

First, larger coupling constants for *trans*- *vs.* *cis*-substituents in an unsaturated system are expected by analogy with such couplings in organic amides[7] [*e.g.* $H^1C(O)NH^2H^3$ has $^3J(H^1H^2)$ 2·1 Hz (*cis*) and $^3J(H^1H^3)$ 13 Hz (*trans*)] and olefins[8] [*e.g.* $H^1(R)C{=}C(H^2)H^3$ has $^3J(H^1H^2)$ 8·6—11·4 Hz (*cis*) and $^3J(H^1H^3)$ 17·2—18·3 Hz (*trans*)]. For the compounds *trans*-$[PtX(L)_2\{C(O)NMe_2\}]$ (X = Cl, I, NCO; L = PPh_3, PMe_2Ph, or $AsPh_3$), ^3J(PtCNMe) *cis* is less than 2·0 Hz and ^3J(PtCNMe) *trans* is given values 5·2—6·3 Hz (*cis* and *trans* positions of the substituents of the groups attached to platinum are about the carbon–heteroatom bond, with respect to the metal) by analogy with the above systems.[9] Moreover, compound (B) (Figure and Table 1) has $^3J(PtCHN^b)$ 65 Hz (H^b must be *trans* to Pt) and $^3J(PtNCH^c)$ 24 Hz (H^c must be *cis* to Pt). Thus we have assigned the *trans*-configuration to (PtCNH) groups with a large coupling constant and the *cis*-configuration to those with a small one. In this series, the N*H*R^1 resonance is clearly at lower field where R^1 is an aromatic group than when R^1 is an aliphatic group.



Structure of compound (B)

Using the above criteria we have assigned completely

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, index issue.

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TABLE 1

Coupling constants and isomer distribution for Classes I, II, and III [a]

Compound	^3J(PtCNH)	^4J(PtCNCH)	Solvent	Isomer [b]
Class I				
cis-[$PtCl_2\{C(NH$*p*-$C_6H_4Me)NMe_2\}(PMe_2Ph)$]	84·0	n.r.	$(CD_3)_2SO$	(Ia) [c] (100)
		7·0 5·4	CD_3OD	(Ia) [c] (100)
trans-[$PtCl\{C(NH$*p*-$C_6H_4Me)NMe_2\}(PMe_2Ph)_2][ClO_4]$	90·0	6·8 5·5	$CDCl_3$	(Ia) [c] (*ca.* 90)
	m	4 m		* (*ca.* 10)
		6·8 5·5	CD_3OD	(Ia) [c] (*ca.* 90)
		6·8 5·5		* (*ca.* 10)
trans-[$PtCl\{C(NHMe)NMe_2\}(PMe_2Ph)_2][ClO_4]$	89·0	6·0 4·7 6·0 [d]	$CDCl_3$	(Ia) (*ca.* 84)
	m	4·5 3·5 5·0 [d]		* (*ca.* 16)
	90·0	6·0 4·5 6·5 [d]	$(CD_3)_2CO$	(Ia) (*ca.* 80)
	m	4·6 m		* (*ca.* 20)
		6·4 5·2	CD_3OD	(Ia) (*ca.* 50)
		4·3 4·2		* (*ca.* 50)
cis-[$PdCl_2\{C(NH$*p*-$C_6H_4Me)NMe_2\}(PMe_2Ph)$]			$CDCl_3$	(Ia) [c] (100)
[$PtCl\{C(NHC_5H_4N)(NH$*p*-$C_6H_4Me)\}(PMe_2Ph)][ClO_4]$ [Compound (B)]	65·0 (H^b) [e] ^3J($PtNCH^c$) 24·0		$CDCl_3$	
Class II				
cis-[$PtCl_2\{C(NHPh)_2\}(PPr^n{}_3)$]	80·0		$(CD_3)_2SO$	(IIb) (*ca.* 60)
	28·0 85·0			(IIa) (*ca.* 40)
trans-[$PtCl\{C(NHMe)_2\}(PMe_2Ph)_2][ClO_4]$	31·0 92·0		$(CD_3)_2SO$	(IIa) (100)
	m 90·0	8·4 6·5	$(CD_3)_2CO$	(IIa) (100)
		8·4 6·4	CD_3OD	(IIa) (100) [f]
trans-[$PtCl\{C(NHMe)_2\}(PEt_3)_2][ClO_4]$	33·0 89·0	8·0 6·4	CD_2Cl_2	(IIa)(*ca.* 80)
	84·0	6·4		(IIb) (*ca.* 20)
trans-[$PtBr\{C(NHMe)_2\}(PEt_3)_2][ClO_4]$	33·0 90·0	8·3 6·5	CD_2Cl_2	(IIa) (*ca.* 80)
	87·0	6·5		(IIb) (*ca.* 20)
Class III				
cis-[$PtCl_2\{C(NH$*p*-$C_6H_4Me)NMePh\}(PMe_2Ph)$]	90·0	7·2	$CDCl_3$	(IIIa) [c] (*ca.* 90)
	m	5·4		(IIIb) [c] (*ca.* 10)
	87·0	7·2	$(CD_3)_2CO$	(IIIa) [c] (*ca.* 83)
	82·0	5·6		(IIIb) [c] (*ca.* 17)
	84·0	n.r.	$(CD_3)_2SO$	(IIIa) [c] (*ca.* 60)
	85·0	n.r.		(IIIb) [c] (*ea.* 40)

[a] Coupling constants ±0·1 Hz. [b] Approximate amount (%) in parentheses. [c] P–*Me* pattern shows restricted rotation. [d] Value for NHMe group. [e] ^{195}Pt Satellites of H^a obscured by phenyl pattern. [f] Hindered rotation pattern, see text. m = masked by other resonances. n.r. = ^{195}Pt satellites not resolved.

* See text.

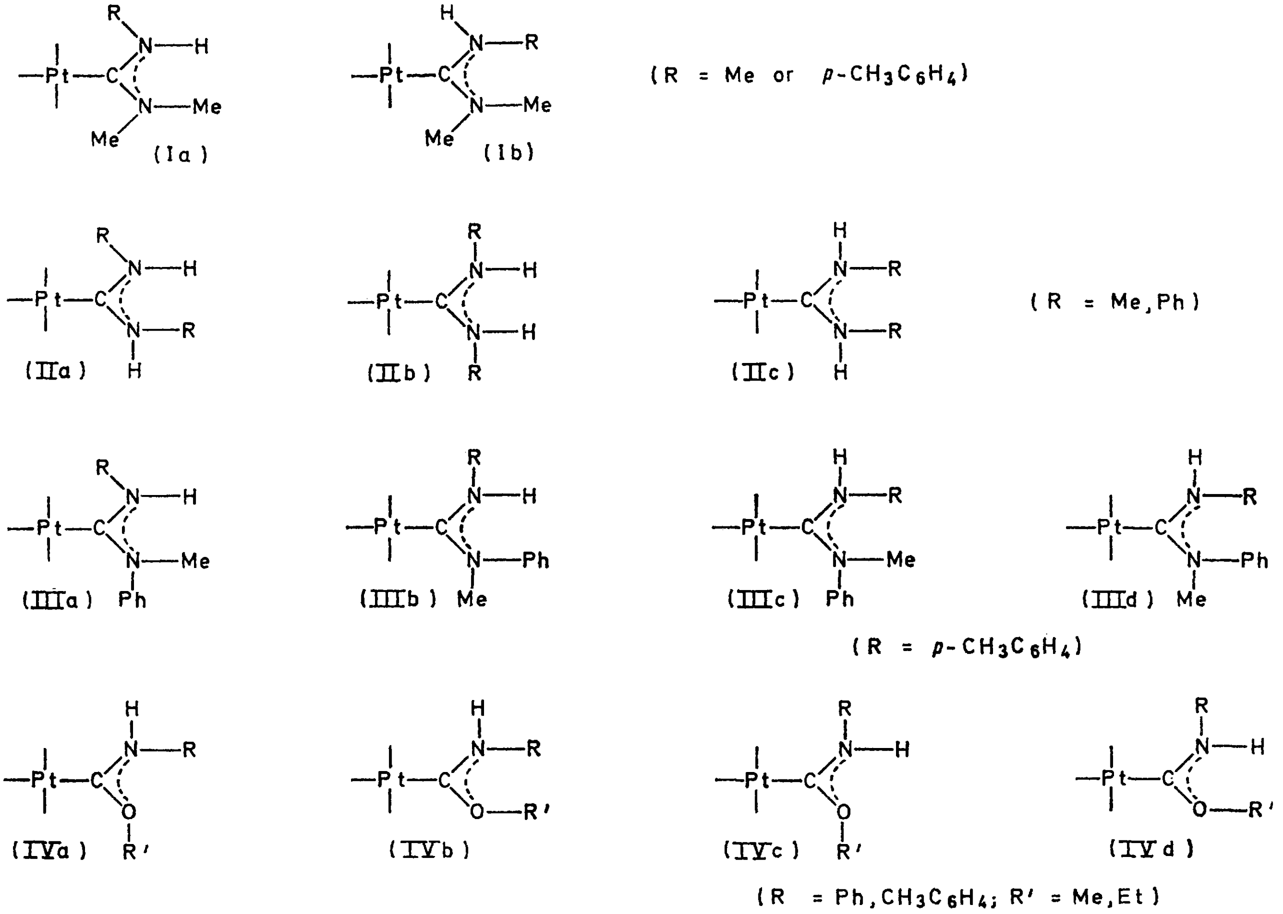
TABLE 2

Coupling constants and isomer distribution for Class IV and palladium compounds

Compound	^3J(PtCNH)	^4J(PtCOCH)	Solvent	Isomer
cis-[PtCl$_2${C(NH*p*-C$_6$H$_4$Me)OMe}(PMe$_2$Ph)]	19·0	5·5	CDCl$_3$ }	(IVa) (*ca.* 50)
	77·0	5·5		(IVc) [a] (*ca.* 50)
		6·4	CD$_3$OD }	(IVa) (*ca.* 30)
		6·4		(IVc) [a] (*ca.* 70)
	20·0	n.r.	(CD$_3$)$_2$SO }	(IVa) (*ca.* 50)
	74·0	n.r.		(IVc) [a] (*ca.* 50)
trans-[PtCl{C(NH*p*-C$_6$H$_4$Me)OMe}(PMe$_2$Ph)][ClO$_4$]	20·0	5·4	CDCl$_3$	(IVa) (100)
cis-[PtCl$_2${C(NHPh)OEt}(PPr$^n_3$)]	75·0	10 [b]	CDCl$_3$	(IVc) or (IVd) (100)
	67·0	10 [b]	(CD$_3$)$_2$CO	(IVc) or (IVd) (100)
cis-[PtCl$_2${C(NHPh)OEt}(PEt$_3$)]	65·0	n.r.	(CD$_3$)$_2$SO) }	(IVc) or (IVd) (*ca.* 60)
	17·5	n.r.		(IVa) (*ca.* 40)
trans-[PtCl{C(NHPh)OEt}(PEt$_3$)$_2$][ClO$_4$]	20·0	6·0	CDCl$_3$	(IVa) (100)
cis-[PtCl$_2${C(NH*p*-C$_6$H$_4$Me)OEt}(PMe$_2$Ph)]	19·0	9·0	CDCl$_3$	(IVb) (100)
	17·0	*	(CD$_3$)$_2$SO }	(IVb) (*ca.* 60)
	70·0	*		(IVc) or (IVd) (*ca.* 40) [a]
trans-[PtCl{C(NH*p*-C$_6$H$_4$Me)OEt}(PMe$_2$Ph)$_2$][ClO$_4$]	22·0	6·0	CDCl$_3$	(IVa) (100) [a]
cis-[PdCl$_2${C(NHPh)OMe}(PMe$_2$Ph)]			(CD$_3$)$_2$SO }	(IVc) or (IVd) (*ca.* 50) [a]
				(IVa) or (IVb) (*ca.* 50)
trans-[PdCl{C(NHPh)OMe}(PMe$_2$Ph)$_2$][ClO$_4$]			(CD$_3$)$_2$SO }	(IVc) or (IVd) (*ca.* 90) [a]
				(IVc) or (IVd) (*ca.* 10) [a]
cis-[PdCl$_2${C(NH*p*-C$_6$H$_4$Me)OMe}(PMe$_2$Ph)]			(CD$_3$)$_2$SO }	(IVc) or (IVd) (*ca.* 60) [a]
				(IVc) or (IVd) (*ca.* 40) [a]
trans-[PdCl{C(NH*p*-C$_6$H$_4$Me)OMe}(PMe$_2$Ph)$_2$][ClO$_4$]			(CD$_3$)$_2$SO }	(IVc) or (IVd) (*ca.* 86) [a]
				(IVc) or (IVd) (*ca.* 14) [a]

[a] P–*Me* Pattern shows hindered rotation, see text. [b] AB Pattern, see text. n.r. = not resolved.

* See text.



SCHEME

Possible configurations of carbene ligands the configurations of most of the above platinum–carbene complexes, in solution. Configurations of palladium compounds are assigned by analogy. The compounds studied fall into the four classes shown in the Scheme according to the substituents carried by the carbene carbon atom. Each class contains a number of possible isomers and their assignments and distributions for the various compounds are shown in the Tables. The isomer distribution is generally dependent on the solvent.

Compounds of Class I (*Table* 1).—All these complexes contain the $-NMe_2$ group and where resolution is achieved, two distinct values of ^4J(PtCNMe) are seen. By the above reasoning, the higher value (4·5—7 Hz) corresponds to the *trans*-methyl group and the lower range (3·3—5·4 Hz) corresponds to the *cis*-methyl group. The predominant isomer is (Ia) [^3J(PtCNH) 84—90 Hz] for the compounds *cis*-$[PtCl_2\{C(NH\textit{p}\text{-}CH_3C_6H_4)(NMe_2)\}PMe_2Ph]$ and *trans*-$[PtCl\{C(NH\textit{p}\text{-}CH_3C_6H_4)(NMe_2)\}(PMe_2Ph)_2]ClO_4$ and both compounds have two P–Me resonance patterns indicating that there is no plane of symmetry through the P–Pt–P system. Therefore there must be restricted rotation about the Pt–C bond,[4] which models show, is apparently caused by the bulky *p*-$CH_3C_6H_5$ group which is *cis* to platinum. The palladium compound is analogous.

In accord with the above suggestion, replacing the *p*-$CH_3C_6H_4$ group by the small methyl group removes the above restricted rotation, as evidenced by the spectrum of *trans*-$[PtCl\{C(NHMe)(NMe_2)\}(PMe_2Ph)_2]ClO_4$ in $CDCl_3$ or $(CD_3)_2CO$ solutions. In CD_3OD solution, this latter compound also gives about 50% of an isomer with *cis*-phosphine ligands, which still has free rotation about the Pt–C bond. The value of ^4J(PtCNMe) is lower for the *cis*-compound, where the carbene ligand is *trans* to phosphorus, than for the *trans*-isomer where the carbene ligand is *trans* to the lower *trans*-influence chloride. Similarly, a smaller coupling has been observed when hydride rather than chloride is *trans* to carbene.[2]

Assignment of configuration to the minor isomers of this series has been prevented because of overlap of their characteristic resonance pattern with that of the major isomer.

Table 1 also includes data for compound (B). The assignment of coupling constants shown is consistent with the postulated structure which must be planar since the P–Me groups are equivalent. Moreover, the low value of ν(PtCl) (310 cm^{-1}) is expected for Cl *trans* to carbene and in its ^{31}P spectrum in $CDCl_3$ solution ^1J(PtP) 3468 Hz [$\delta = +154{\cdot}3$ to high field of trimethyl phosphite (tmp)], a value expected for phosphorus *trans* to the low *trans*-influence nitrogen atom.

Compounds of Class II (*Table* 1).—For compounds with $-C(NHMe)_2$ ligands the *amphi*-configuration (IIa) is predominant, as would be expected by analogy with the $[CH_3C(NHMe)_2]^+$ ion.[2] The isomer distribution is solvent dependent and the isomer (IIb) is only observed in CD_2Cl_2 or $CDCl_3$ solution.

The P–*Me* triplet of triplets observed for $(CD_3)_2SO$ or $(CD_3)_2CO$ solutions of the compound *trans*-$[PtCl\{C(NHMe)_2\}(PMe_2Ph)_2]ClO_4$ shows that there is free rotation about the Pt–C bond.[4] However, in CD_3OD solution, two triplets of triplets are observed, indicative of hindered rotation.[4] Since the steric barrier of this carbene ligand is the least of those studied, the hindrance is probably caused by solvation of the carbene by CD_3OD *via* a deuterium (hydrogen) bonding interaction. All the spectra of this compound are consistent with only the (IIa) isomer existing in solution. The alternative, an exactly equal mixture of the (IIb) and (IIc) isomers seems highly unlikely, especially since the (IIc) isomer has not been observed in any spectrum.

The compound *cis*-$[PtCl_2\{C(NHPh)_2\}(PPr^n_3)]$ is unusual since the (IIb) isomer predominates in $(CD_3)_2SO$ solution probably because steric strain due to mutual interaction of the bulky phenyl groups is least for this configuration. The N–*Me* chemical shifts and ^4J(PtCNCH) values differ depending upon whether the N–Me groups are *cis* or *trans* to the metal, ranges found for latter are ^4J(PtCNCH) *trans*, 8—8·4; ^4J(PtCNCH) *cis*, 6·4—6·5 Hz.

Compounds of Class III (*Table* 1).—Only one example of this Class has been investigated. As is expected on steric grounds, it shows only the (IIIa) and (IIIb) isomers in solution, the isomer ratio depending upon the solvent. Restricted rotation about the Pt–C bond occurs for both isomers since in both the bulky phenyl group is *cis* to the metal. In $(CD_3)_2CO$ and $CDCl_3$ solutions, the chemical shift of the –CNMe group is greater when it is *trans* to the metal than when it is *cis*.

The ^{31}P n.m.r. spectrum of this compound in $(CD_3)_2SO$ solution confirms the presence of two isomers, both with ^1J(PtP) values in the region expected for phosphorus *trans* to chlorine, rather than carbene [isomer (IIIa) (60%) $\delta = +159{\cdot}5$ p.p.m., ^1J(PtP) 3934 Hz; isomer (IIIb) (40%) $\delta = +158{\cdot}5$ p.p.m., ^1J(PtP) 4012 Hz; both resonances to high field relative to tmp].

Compounds of Class IV (*Table* 2).—For this Class, isomerisation about C–N bonds is shown by a clear difference in ^3J(PtCNH) values. These values are less than corresponding ones for similar compounds of other classes. Assignment of isomers involving the COR grouping is more tentative because mixtures of isomers of one compound in a particular solvent are not clearly observed. However, models of *trans*-$[PtCl\{C(NH\textit{p}\text{-}C_6H_4Me)OEt\}(PMe_2Ph)_2]ClO_4$ show that a *cis*-OCH_2 group could, by steric interaction, cause restricted rotation about the Pt–C bond. Moreover, isomers of several compounds of this class have been observed whose ^4J(PtCOCH) values fall in two ranges, 5·4—6·4 or *ca.* 9 Hz. Thus *trans*-$[PtCl\{C(NH\textit{p}\text{-}CH_3C_6H_4)OEt\}(PMe_2Ph)_2]ClO_4$ is assigned the (IVa) configuration (Scheme) because ^3J(PtCNH) and ^4J(PtCOCH) have low values (22 and 6 Hz) and therefore the N*H* and OCH_2 groups are *cis* to the metal. Moreover, although the *p*-tolyl group is *trans* to the metal, the P*Me* resonance pattern shows restricted rotation about the Pt–C bond, confirming that the OCH_2 group is *cis*. Configuration (IVa) is also assigned to the one isomer of *trans*-[PtCl{C(NHPh)OEt}$(PEt_3)_2$]ClO_4 by similar arguments.

In $CDCl_3$ solution, *cis*-[$PtCl_2${C(NH*p*-$CH_3C_6H_4$)OEt}-(PMe_2Ph)] has the (IVb) configuration since ^3J(PtCNH) is small, but ^4J(PtCOCH) is large (9 Hz) and there is free rotation about the Pt–C bond. Thus the OCH_2 group is *trans* to platinum. In $(CD_3)_2SO$ solution, however, a mixture of isomers occurs. The predominant one is assigned configuration (IVb) since ^3J(PtCNH) is small and there is free rotation about the Pt–C bond. The other isomer has the tolyl group *cis* to platinum and the resulting restricted rotation about the Pt–C bond leads to an AB pattern for the OCH_2 group which overlaps with the OCH_2 pattern of the isomer (IVb) so that ^4J(PtCOCH) cannot be determined.

Similarly in $(CD_3)_2SO$ solution, *cis*-[$PtCl_2${C(NHPh)-OEt}(PEt_3)] is a mixture of isomers with *cis*- and *trans*-CNH groups, but both isomers show AB patterns for the OCH_2 resonance. The overlap of these patterns prevents determination of ^4J(PtCOCH), but the (IVa) configuration may be assigned to the minor isomer because an AB pattern can only arise from restricted rotation about the Pt–C bond which, since the phenyl group is *trans* to platinum, must mean that the OCH_2 group is *cis* to the metal. The other assignments in this Table follow from similar arguments.

In $(CD_3)_2SO$ solution, *cis*-[$PtCl_2${C(NH*p*-$CH_3C_6H_4$)-OMe}(PMe_2Ph)] shows two ^{31}P signals ($\delta = +158{\cdot}9$ and $+159{\cdot}1$ relative to trimethyl phosphite) corresponding to the equal mixture of isomers observed in the ^1H spectrum. The values of ^1J(PtP) (3730 and 3746 Hz respectively) are in the range expected for phosphorus *trans* to chloride and confirm the *cis*-configuration about the metal for both isomers.

The palladium analogues of these compounds (Table 2) also show isomerisation but may only be classified into two general groupings on the assumption that restricted rotation about the Pd–C bond indicates that the bulky phenyl or tolyl groups are *cis* to palladium and free rotation means that these groups are *trans*. Isomerisation about the C–O bond clearly occurs but it is not possible to assign the configurations.

CONCLUSION

The carbene ligands of this study show restricted rotation about their C–N or C–O bonds and the ratio of isomers observed in solution is strongly dependent on solvent. Although it is not possible to decide whether the predominant isomer observed is favoured by kinetic or thermodynamic factors, nevertheless it is generally the one with least steric interaction within the carbene grouping, *i.e.* configurations (Ia), (IIa), (IIIa), (IVa), and (IVc) predominate. However, in cases where the metal carries bulky groups there is probably little energy difference between the various configurations.

Restricted rotation about the metal–carbon bond appears to be caused by steric interaction of large carbene substituents with metal substituents.

EXPERIMENTAL

^1H and ^{31}P N.m.r. spectra were measured on a Jeol PS 100 instrument relative to tetramethylsilane and trimethyl phosphite respectively. I.r. spectra were recorded on a Perkin-Elmer 557 spectrometer and conductivities were measured using a Portland Electronics bridge. A Kofler hot stage was used for m.p. measurement and microanalyses were by Mr. A. G. Olney of these laboratories.

Isonitriles were prepared by standard techniques and metal complexes by published methods.[1,2,10] Analytical data, *etc.*, for new compounds have been deposited in the Supplementary Publication (see above).

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[3/1639 *Received, 3rd August*, 1973]

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