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Bis-Carbene Complexes of Palladium(II)*

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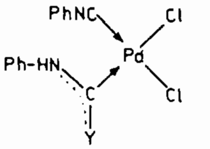
Isocyanide complexes of the type, cis-[$Pd(RNC)_2Cl_2$]-(R=p-$MeOC_6H_4$,p-MeC_6H_4 *Ph or* p-$NO_2C_6H_4$) *react under appropriate conditions with methanol or primary and secondary amines to give the bis-carbene complexes* cis-[$Pd\{C(NHR)Y\}_2Cl_2$] (Y = *MeO,* p-$MeOC_6H_4NH$, p-MeC_6H_4NH, *PhNH,* Me_2N *or* $Ph(Me)N$).

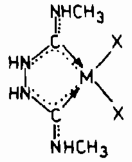
The chloride ligands appear to be loosely bound to the central metal as to give partial dissociation in methanolic solution and to be easily replaced by other anionic or neutral ligands. This is also confirmed by the low values of Pd-Cl stretching frequencies (263-305 cm^{-1}). cis-[$Pd\{C(NHPh)NH$p-$MeC_6H_4\}_2Cl_2$] *reacts with sodium perchlorate to give a cationic binuclear complex with bridging chloride,* [$Pd\{C(NHPh)NH$p-$MeC_6H_4\}_2Cl]_2[ClO_4]_2$. *Conductivity and molecular weight measurements are reported. The ir and p.m.r. spectra are discussed in relation to the nature of the carbene ligands and the configuration of the complexes.*

Introduction

In the last few years the reaction of Fe^{II}, Pd^{II}, Pt^{II} isocyanide complexes with various nucleophiles such as alchohols or amines have extensively studied.[1-11] In all of these cases either neutral or cationic carbene compounds have been obtained. In a previous paper[2] we have reported that the complex *cis*-[Pd(PhNC)$_2$Cl$_2$] reacts with methanol or *p*-toluidine to give products of the type:



where Y = MeO or *p*-MeC$_6$H$_4$NH. We have now found that both the coordinated isocyanides of the starting compound undergo a similar reaction under appropriate conditions, yielding neutral bis-carbene derivatives. On the other hand, some recent re-investigations on the "Chugaev's salt" and related compounds[12-15] have led to the characterisation of neutral and cationic complexes in which a cyclic bidentate carbene ligand is present:



(M = Pd^{II} or Pt^{II}; X = neutral or anionic ligand)

Experimental Section

The isocyanides and the starting complexes, *cis*-[Pd(RNC)$_2$Cl$_2$], were prepared by literature methods[2,16]. Aniline and N-metlylaniline were distilled before use. All other chemicals were reagent grade and were used without further purification. Conductivity measurements were takn using an LKB 8300 B conductivity bridge. Molecular weights were determined in 1,2-dichloroethane solution with a Mechrolab osmometer, at 37°C temperature. I.r. spectra were recorded with a Perkin - Elmer 621 spectrophotometer in the region 4000 - 250 cm^{-1} and with a Beckman I.R. 11 in the region 350-180 cm^{-1}. Both exachlorobutadiene mulls (4000-1300 cm^{-1}) and nujol mulls (1700-180 cm^{-1}) were used. The spectra were calibrated against carbon monoxide, polystyrene film or water vapour. P.m.r. spectra were taken with a Hitachi - Perkin - Elmer R 20 A instrument, at 34°C temperature, with T.M.S. as internal standard.

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Preparation of cis-$[Pd\{C(NHR)NHR'\}_2X_2]$ *(R = p-$MeOC_6H_4$, p-MeC_6H_4, Ph, p-$NO_2C_6H_4$; R' = p-$MeOC_6H_4$, p-MeC_6H_4, Ph; X = Cl, Br, or N_3).* The starting complex, *cis*-$[Pd(RNC)_2Cl_2]$, (2 mmoles) dissolved or suspended in chloroform was treated with an excess of the amine, $R'NH_2$, (complex/amine molar ratio = 1/4). The reaction mixture was stirred for three days at room temperature, then treated with charcoal and filtered. The resulting clear solution was taken to small volume under reduced pressure. Addition of ether precipitated the bis-diamino-carbene complexes, which were purified by two or three reprecipitations from the same solvents. (Yields = 80-90%). When R = *p*-$NO_2C_6H_4$, after 3 days stirring the reaction mixture consisted of a yellow solid, which was filtered off, and a red-orange solution, from which the product was recovered in a 50% yield. Molecular weight measurements of *cis*-$[Pd\{C(NHPh)NH$*p*-$MeC_6H_4\}_2Cl_2]$ gave a value of 600 (Calcd mol. wt. = 597.8).

The deuterio-complex, *cis*-$[Pd\{C(NDPh)ND$*p*-$MeC_6H_4\}_2Cl_2]$, was obtained by dissolving the corresponding nondeuteriated compound in MeOD. After one day the exchange reaction was complete, and the product was recovered by removal of solvent under reduced pressure.

The complexes, *cis*-$[Pd\{C(NHPh)NH$*p*-$MeC_6H_4\}_2Br_2]$ and *cis*-$[Pd\{C(NHPh)_2\}_2(N_3)_2]$, were prepared from the corresponding chloro-derivatives by metathetical reactions with NaBr and NaN_3 respectively, in methanol/chloroform (1/1) mixture. (Yields = 70-80%).

Reaction of cis-$[Pd(PhNC)_2Cl_2]$ *with dimethylamine.* Gaseous dimethylamine was bubbled into a chloroform suspension of the starting complex (2 mmoles) until a clear solution was obtained (*ca.* 15 min). The reaction mixture was allowed to stand at room temperature for 2 hours, then the excess of amine was removed by a stream of nitrogen. The solution was taken to dryness under vacuum, leaving a crude product, which was purified by reiterated precipitations from methanol with ether (Yield = 83%).

Reaction of cis-$[Pd($p-$MeC_6H_4NC)_2Cl_2]$ *with N-methylaniline.* The starting complex (4 mmoles) dissolved in chloroform was treated with an excess of N-methylaniline (16 mmoles). After three days the reaction mixture still showed a strong band at about 2200 cm^{-1} of the unreacted coordinated isocyanide. A further excess of the amine was then added and the solution was allowed to stand at room temperature for another three days. Since after this treatment the reaction was not yet complete, the solution was refluxed for *ca.* 12 hours then treated with charcoal and taken to dryness under reduced pressure. The resulting crude product contained only traces of incompletely reacted materials, which were separated from the bis-carbene complex by chromatography through a silica gel column, using dichloromethane as eluent. The unreacted materials passed first, whereas the bis-carbene derivative was tenaciously retained by the silica gel as to require a large volume of dichloromethane in order to recover the pure product in about 30% yield.

Preparation of cis-$[Pd\{C(NHR)OMe\}_2Cl_2]$ *(R = p-MeC_6H_4, p-MeC_6H_4 or Ph).* A suspension of the starting complex, *cis*-$[Pd(RNC)_2Cl_2]$ (4 mmoles), in a methanol/chloroform (5/1) mixture was refluxed for about 4 hours (R = Ph), 6 hours (R = *p*-Me-C_6H_4), 10 hours (R = *p*-$MeOC_6H_4$), in order to drive the reaction to completion (disappearance of $\nu(N{\equiv}C)$ bands). In all cases some decomposition occured. The reaction mixture was taken to dryness under reduced pressure, leaving a brown solid, which was dissolved in dichloromethane and treated with charcoal. After filtration, the clear solution was concentrated to small volume and the product precipitated on adding an ether/light petroleum ether (1/1) mixture. It was purified by reprecipitation from the same solvents (Yields = 30-50%).

The complex *cis*-$[Pd\{C(NHPh)OMe\}_2Cl_2]$ was also prepared by keeping a suspension of the starting compound (2 mmoles) in methanol at 40°C for one weak. The reaction mixture was then worked up as above (Yield 60%). For this bis-carbene complex molecular weight measurements gave a value of 456 (Calcd. mol. wt. = 447.6).

Preparation of $[Pd\{C(NHPh)NH$p-$MeC_6H_4\}_2Cl]_2[ClO_4]_2$. The complex *cis*-$[Pd\{C(NHPh)NH$*p*-$MeC_6H_4\}_2Cl_2]$ (1 mmole) dissolved in methanol (40 ml) was treated with a slight excess of $NaClO_4 \cdot H_2O$ and stirred for 2 hours. After removal of the solvent under vauum the solid residue was treated with dichloromethane in order to separate the soluble product from the insoluble salts (NaCl and $NaClO_4$ in excess). The CH_2Cl_2 solution was dried with sodium sulphate, treated with charcoal and eventually taken to small volume under reduced pressure. Slow addition of ether gave greenish crystals of the chloro-bridged complex (Yield = 60%).

Preparation of $[Pd\{C(NHPh)NH$p-$MeC_6H_4\}_2(PPh_3)Cl][ClO_4]$. This compound can be prepared in two ways:

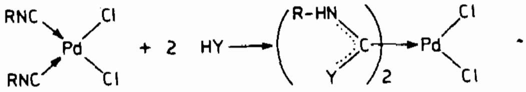
(i) The neutral complex, *cis*-$[Pd\{C(NHPh)NH$*p*-$MeC_6H_4\}_2Cl_2]$ (1 mmole), dissolved in acetone was treated with a slight excess of $NaClO_4{\cdot}H_2O$ and the stocheiometric amount of PPh_3. After two hours stirring, the reaction mixture is taken to dryness and the solid residue treated with chloroform. After filtration the solution was concentrated to small volume under reduced pressure. Addition of ether gave a white precipitate, which was purified by recrystallization from the same solvents (Yield = 90%).

(ii) The chloro-bridged compound, $[Pd\{C(NHPh)NH$*p*-$MeC_6H_4\}Cl]_2[ClO_4]_2$ (0.5 mmoles) dissolved in chloroform was trated with PPh_3 (1 mmole). The resulting solution was worked up as above.

Preparation of $[Pd\{C(NHPh)NH$p-$MeC_6H_4\}_2(bipy)][ClO_4]_2$. The neutral complex, *cis*-$[Pd\{C(NHPh)NH$*p*-$MeC_6H_4\}_2Cl_2]$ (1 mmole), dissolved in a chloroform-methanol (1/1) mixture was treated with $NaClO_4.H_2O$ (3mmoles) and α, α'bipyridyl (1.3 mmoles). The reaction mixture was stirred for one hour and then worked up as in the previous preparation (method *i*). Yield is close to quantitative (*ca.* 95%).

Results and Discussion

The bis-carbene complexes have been obtained according to the following reaction:



(1)

(R = p-MeOC$_6$H$_4$, p-MeC$_5$H$_4$, Ph or p-NO$_2$C$_5$H$_4$; Y MeO, p-MeOC$_6$H$_4$NH, p-MeC$_6$H$_4$NH, PhNH, Me$_2$N or Ph(Me)N).

An excess of the nucleophile, HY, is usually required in order to drive the reaction to completion. The ease of this reaction depends on the nature of HY in the sense that amines react much faster than methanol. Moreover, aliphatic amines are more reactive than aromatic ones: dimethylamine, for instance, reacts completely in *ca.* two hour, whereas aromatic amines require about 2-3 days at room temperature. The reaction with N-methylaniline is unexpectedly very slow: even after one week at room temperature and several hours at boiling chloroform temperature the reaction mixture still showed traces of the coordinated unreacted isocyanide (ν(N$\equiv$C) at $\sim$2200 cm^{-1}). In this case the bis-carbene complex could be separated from the other products by chromatographic methods. The nature of group R affects mainly the reaction with methanol. The observed reactivity order is PhNC > p-MeC$_6$H$_4$NC > p-MeOC$_6$H$_4$NC. The same order was also found in a kinetic study on the reaction of *cis*-[Pd(PPh$_3$)(RNC)Cl$_2$] with p-toluidine,[9] which showed that electron-releasing groups reduce the reactivity of coordinated isocyanides towards nucleophiles.

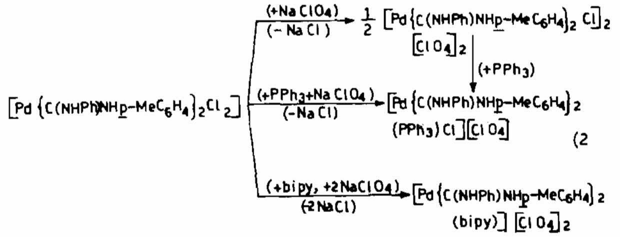
Analytical and phisical data are reported in Table I. Molecular weight measurements in 1,2-dichloroethane show that the neutral bis-carbene complexes are monomeric in this solvent.

These compounds behave as non-electrolytes in halogenated solvents such as dichloromethane or 1,2-dichloroethane. However, in methanolic solution they show molar conductivity values varying in the range 30-51 ohm^{-1} cm^2 mole^{-1}. This fact is attributed to dissociation equilibria of the type:

$$[\mathrm{Pd}\{\mathrm{C(NHR)Y}\}_2\mathrm{X}_2] + \mathrm{Solv} \rightleftharpoons [\mathrm{Pd}\{\mathrm{C(NHR)Y}\}_2(\mathrm{Solv})\mathrm{Cl}]^+ + \mathrm{Cl}^-$$

which become appreciable in methanol because of its higher coordinating properties.

The chloride ligands in the neutral derivatives are easily replaced by other anionic or neutral ligands. Metathetical reactions with sodium bromide or azide give the corresponding bromo- or azido-derivatives. The reactions with neutral ligands are shown in the following scheme:



These reactions provide further evidence of the property of the carbene ligands to give cationic complexes.[6-8] The analytical and physical data of these products are also reported in Table I. The conductivity values correspond to those of uni-univalent or bi-univalent electrolytes. The reaction with sodium perchlorate yields a chlorobridged binuclear compound, the structure of which is confirmed by the bridge-splitting reaction with the stocheiometric amount of triphenylphosphine.

Infrared Spectra. The characteristic i.r. bands of the compounds studied are reported in Table II.

The N–H, C—N and C—O—Me stretching frequencies of the bis-carbene derivatives are close to those found for other neutral or cationic palladium and platinum carbene complexes.[2,3,5,8,14,17,18] The ν (N-H) bands fall in the range 3110-3390 cm^{-1}. They are shifted to 2262-2526 cm^{-1} in the deuteriated product [Pd{C(NDP)NDp-MeC$_6$H$_4$}$_2$Cl$_2$].

The presence of many ν(N-H) absorptions in the same complex may be accounted for by hydrogen bonding in the solid state. It can be also noted that ν(N-H) values of methoxy-amino-carbene are generally lower than those of the corresponding diaminocarbenes. The strong broad band at 1536-1557 cm^{-1} arises from a carbon-nitrogen stretch with a considerable double bond character between the two atoms.

Table I. Analytical and Physical Data of Neutral and Cationic Palladium(II)-bis-Carbene Derivatives.

Compounds	Colour	C Calcd.	C Found.	H Calcd.	H Found.	N Calcd.	N Found.	X Calcd.	X Found.	M.p.[a] (°C)	Λ[b] (ohm^{-1}. cm^2 . mole^{-1})
[Pd{C(NHPh)NHp-MeC$_6$H$_4$}$_2$Cl$_2$]	ivory	56.25	56.1	4.72	4.7	9.37	9.3	11.86	11.5	140-150 dec.	51
[Pd{C(NHPh)NHp-MeC$_5$H$_4$}$_2$Br$_2$]	ivory	48.97	49.2	4.11	4.2	8.16	8.1	23.27	22.9	150 dec.	46
[Pd{C(NHPh)$_2$}$_2$Cl$_2$]	ivory	54.80	55.1	4.25	4.3	9.83	9.9	12.44	12.2	127	50.5
[Pd{C(NHPh)$_2$}$_2$(N$_3$)$_2$]	pale-yellow	53.57	54.0	4.15	4.15	24.03	23.7	—	—	148 dec.	30
[Pd{C(NHPh)NMe$_2$}$_2$Cl$_2$]	white	45.63	45.8	5.11	5.1	11.83	11.7	14.97	14.8	214 dec.	54
[Pd{C(NHPh)OMe}$_2$Cl$_2$]	white	42.93	43.0	4.05	4.1	6.26	6.3	15.84	15.5	130 dec.	30.5
[Pd{C(NHp-NO$_2$C$_5$H$_4$)NHp-MeC$_6$H$_4$}$_2$Cl$_2$]	yellow	48.89	49.0	3.81	3.9	12.22	12.1	10.31	10.2	141 dec.	48.5
[Pd{C(NHp-MeC$_6$H$_4$)$_2$}$_2$Cl$_2$]	off-white	57.57	57.7	5.15	5.2	8.95	8.9	11.33	11.2	196 dec.	47
[Pd{C(NHp-MeC$_5$H$_4$)N(Me)Ph}$_2$Cl$_2$]	white	57.57	57.8	5.15	5.1	8.95	9.0	11.33	11.1	198 dec.	34
[Pd{C(NHp-MeC$_6$H$_4$)OMe}$_2$Cl$_2$]	white	45.45	45.7	4.66	4.7	5.89	5.8	14.91	15.0	130-135 dec.	33
[Pd{C(NHp-MeOC$_6$H$_4$)$_2$}$_2$Cl$_2$]	off-white	52.23	52.4	4.68	4.7	8.12	8.0	10.28	10.1	135-145 dec.	47.5
[Pd{C(NHp-MeOC$_5$H$_4$)NHp-MeC$_6$H$_4$}$_2$Cl$_2$]	off-white	54.77	54.9	4.90	5.0	8.52	8.4	10.78	10.6	145-155 dec.	48.5
[Pd{C(NHp-MeOC$_6$H$_4$)OMe}$_2$Cl$_2$]	white	42.58	42.7	4.39	4.5	5.52	5.4	13.97	14.0	110-115 dec.	35
[Pd{C(NHPh)NHp-MeC$_6$H$_4$}(PPh$_3$)Cl]ClO$_4$	white	59.78	59.5	4.69	4.7	6.06	5.9	7.67	7.4	140-150 dec.	84
[Pd{C(NHPh)NHp-MeC$_5$H$_4$}$_2$(bipy)][ClO$_4$]$_2$	white	51.74	51.4	4.11	4.0	9.53	9.4	8.04	8.0	252	161
[Pd{C(NHPh)NHp-MeC$_6$H$_4$}$_2$Cl]$_2$[ClO$_4$]$_2$	greenish	50.81	50.4	4.26	4.4	8.46	8.3	10.71	10.5	135-145 dec.	147

[a] All melting points are uncorrected. [b] Methanol solutions. C = 10^{-3} *M*, at 25°C

Table II. Characteristic i.r. absorptions (cm^{-1}).

Compounds	ν(N-H)	$\nu(C\stackrel{...}{=}N)$	ν(Pd-X)	Other bands
$[Pd\{C(NHPh)NH\textit{p}\text{-}MeC_6H_4\}_2Cl_2]$	3383 m, 3316 w 3208 ms,br, 3175 sh, 3115 w	1555 s 1536 s	288 s,br 270 sh	
$[Pd\{C(NDPh)ND\textit{p}\text{-}MeC_6H_4\}_2Cl_2]$	2526 m, 2459 w, 2347 ms, 2262 w ν(N-D)	1545 ms	289 s 263 ms	
$[Pd\{C(NHPh)NH\textit{p}\text{-}MeC_6H_4\}_2Br_2]$	3390 m, 3312 w 3210 ms,br, 3170 sh, 3110 w	1540 s	232 ms, 225 sh, 217 s	
$[Pd\{C(NHPh)_2\}_2Cl_2$	3380 m, 3310 w, 3210 m,br 3170 sh, 3110 w,	1543 s,br	294 s 270 s	
$[Pd\{C(NHPh)_2\}_2(N_3)_2]$	3385 m, 3310 w, 3270 m 3210 m, 3170 sh, 3115 w	1545 s,br	373 ms 345 ms	2057 s $\nu(N{\equiv}N)$ 2038 s
$[Pd\{C(NHPh)NMe_2\}_2Cl_2]$	3193 ms, 3180 sh, 3140 mw	1557 s,br	290 sh 274 s,br	
$[Pd\{C(NHPh)OMe\}_2Cl_2]$	3230 sh, 3190 ms.br, 3140 mw	1545 s,br	305 s 283 s, 265 sh	1245 s $\nu(C\stackrel{...}{=}O\text{-}Me)$
$[Pd\{C(NH\textit{p}\text{-}NO_2C_6H_4)NH\textit{p}\text{-}MeC_6H_4\}_2Cl_2]$	3284 mw, 3210 m 3175 sh, 3120 w	1548 s,br	299 ms 280 ms	1511 $\nu(N\text{-}O)_{asym}$ 1340 $\nu(N\text{-}O)_{sym}$
$[Pd\{C(NH\textit{p}\text{-}MeC_6H_4)\}_2Cl_2]$	3386 m, 3332 mw, 3250 m, 3210 m, 3160 sh, 3115 w	1540 vs,br	295 s 280 sh, 267 ms	
$[Pd\{C(NH\textit{p}\text{-}MeC_6H_4)N(Me)C_6H_5\}_2Cl_2]$	3335 mw, 3160 m, 3110 w	1545 s	290 ms 276 m	
$[Pd\{C(NH\textit{p}\text{-}MeC_6H_4)OMe\}_2Cl_2]$	3230 sh, 3185 s,br, 3120 sh	1540 vs,br	302 s 283 s	1250 s $\nu(C\stackrel{...}{=}O\text{-}Me)$
$[Pd\{C(NH\textit{p}\text{-}MeOC_6H_4)_2\}_2Cl_2]$	3382 m, 3310 sh, 3260 sh, 3210 m,br, 3120 w	1543 vs,br	298 sh, 281 s, 267 sh	
$[Pd\{C(NH\textit{p}\text{-}MeOC_6H_4)NH\textit{p}\text{-}MeC_6H_4\}_2Cl_2]$	3380 m, 3310 sh, 3260 sh, 3210 m, 3170 sh, 3110 w	1542 vs	298 sh 281 s, 268 sh	
$[Pd\{C(NH\textit{p}\text{-}MeOC_6H_4)OMe\}_2Cl_2]$	3230 sh, 3195 ms,br, 3130 sh	1540 vs,br	301 s 280 s	1250 s $\nu(C\stackrel{...}{=}O\text{-}Me)$
$[Pd\{C(NHPh)NH\textit{p}\text{-}MeC_5H_4\}_2(PPh_3)Cl]ClO_4$	3375 m,w, 3300 m,br, 3240 sh	1542 s,br	302 ms	1095 s,br ν(Cl-O) 620 s δ(Cl-O)
$[Pd\{C(NHP)NH\textit{p}\text{-}MeC_5H_4\}_2(bipy)][ClO_4]_2$	3308 ms, 3240 ms,br	1542 s,br		1085 s,br ν(Cl-O) 620 s δ(Cl-O)
$[Pd\{C(NH\textit{p}\text{-}MeC_6H_4\}_2Cl]_2[ClO_4]_2$	3370 mw, 3300 m, 3260 m, 3150 sh	1543 s,br	296 s,br 280 sh	1090 s,br ν(Cl-O) 621 s δ(Cl-O)

vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

It is only slightly affected by deuteration. In the methoxy-amino-carbene groups another strong band at *ca.* 1250 cm^{-1} is assigned to a $C\stackrel{...}{=}O\text{-}Me$ stretching mode.[17,18] All neutral bis-carbene derivatives show at least two ν(Pd-X) bands, supporting a *cis* configuration for these compounds.[19] In the case of the complex $[Pd\{C(NHPh)_2\}_2(N_3)_2]$, the *cis* structure is also supported by the presence of two $\nu(N{\equiv}N)$ absorptions at 2038 and 2057 cm^{-1} respectively. It is to be noted, therefore, that the *cis* structure of the starting bis-isocyanide complexes is retained in reaction 1. The low values of ν(Pd-Cl) (263-305 cm^{-1}) indicate rather weak palladium--chloride bonds owing to the high *trans*-influence of the carbene ligands.[1,2,3,8,18] This is reflected by the extensive dissociation of Pd-Cl bond in methanol and by the tendency to give cationic complexes according to the scheme 2. The two carbene ligands in the complex $[Pd\{C(NHPh)NH\textit{p}\text{-}MeC_6H_4\}_2(PPh_3)Cl][ClO_4]$, are probably in *cis* position to each other, as they are in the parent compound, *cis*-$[Pd\{C(NHPh)NH\textit{p}\text{-}MeC_6H_4\}_2Cl_2]$. The position of the ν(Pd-Cl) band (302 cm^{-1}) in the phosphine derivative is not decisive for assigning its structure on the basis of *trans*-influence arguments.

P.m.r. Spectra. The p.m.r. data of the bis-carbene complexes soluble in $CDCl_3$ are shown in Table III. The assignment of N-H resonances is based on their disappearance after treatment of the $CDCl_3$ solution with D_2O. The methoxy-amino-carbene ligands are characterized by N-H signals occurring at very low values (−1.5 to −1.0 τ).

In the diammino-carbene groups the N-H bands are not clearly observable, since they fall in the same range as those of the phenyl protons (1.4-4.0 τ), their presence being deduced from the integration values before and after D_2O treatment. This is also confirmed by the occurrence at 3.19 τ of a N-H signal, which is not masked by the phenyl absorptions, in the complex $[Pd\{C(NH\textit{p}\text{-}MeC_6H_4)N(Me)Ph\}_2Cl_2]$. The diammino-carbene derivatives show a further deuterio-sensitive band at *ca.* −0.5 τ, which has relative intensity less than one and probably arises from N-H protons in hydrogen-bonded molecules or, alternatively, in different isomeric species in solution.

The lower values of τ (N-H) in the methoxy-amino-carbenes compared with those of diamino-carbenes indicate a more acidic character of N-H protons in the former compounds (this is also reflected by the lower values of N-H shetching frequencies, as seen before).

Resonances due to O-CH_3 and N-CH_3 groups of the carbene ligands occur at 5.23-5.28 τ (for the methyl attached to oxygen) and at 6.92 τ (for the methyl attached to nitrogen), in good agreement with the corresponding values reported in the literature for

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(18) H.C. Clark and M.H. Chisholm, *Inorg. Chem.*, *10*, 1711 (1971).
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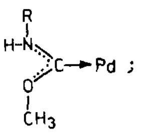
Table III. P.m.r. data for some bis-carbene complexes[a] (τ).

Compounds	Phenyl protons	N-CH$_3$ O-CH$_3$	$-C_6H_4-CH_3$ $-C_6H_4-OCH_3$	N—H
$[Pd\{C(NHPh)NHp\text{-}MeC_6H_4\}_2Cl_2]$	1.4-4.0[b] [~10.5]	—	7.76 s, 7.82 s,br, 7.95 sh [3]	−0.45 [~0.5]
$[Pd\{C(NDPh)NDp\text{-}MeC_6H_4\}_2Cl_2]$	1.4-4.0[b] [9]	—	7.80 s,br, 7.95 sh[3]	—
$[Pd\{C(NHPh)OMe\}_2Cl_2]$	2.2-3.2 m [5]	5.23 s[3]	—	−1.9 [1]
$[Pd\{C(NDPh)OMe\}_2Cl_2]$[c]	2.2-3.2 m [5]	5.23 s[3]	—	—
$[Pd\{C(NHp\text{-}MeC_6H_4)N(Me)Ph\}_2Cl_2]$	2.0-3.1 m [~9][d]	6.92 s[3]	7.73 s [3]	3.19 [~1][d]
$[Pd\{C(NDp\text{-}MeC_6H_4)N(Me)Ph\}_2Cl_2]$[c]	2.0-3.1 m [9]	6.92 s[3]	7.73 s [3]	—
$[Pd\{C(NHp\text{-}MeC_6H_4)OMe\}_2Cl_2]$	2.82 q [4]	5.28 s[3]	7.74 s [3]	−1.6 [1]
$[Pd\{C(NDp\text{-}MeC_6H_4)OMe\}_2Cl_2]$[c]	2.82 q [4]	5.28 s[3]	7.74 s [3]	—
$[Pd\{C(NHp\text{-}MeOC_6H_4)_2\}_2Cl_2]$	1.6-3.9[b] [~4.8]		6.27 s,br, 6.32 sh[3]	−0.56 [~0.3]
$[Pd\{C(NDp\text{-}MeOC_6H_4)_2\}_2Cl_2]$[c]	1.6-3.9[b] [4]		6.27 s,br, 6.32 sh[3]	—
$[Pd\{C(NHp\text{-}MeOC_6H_4)NHp\text{-}MeC_6H_4\}_2Cl_2]$	1.5-4.0[b] [~9.7]		6.26 s,br, 6.30 sh([3] 7.73 s,br [3]	−0.48 [~0.4]
$[Pd\{C(NDp\text{-}MeOC_6H_4)NDp\text{-}MeC_6H_4\}_2Cl_2]$[c]	1.5-4.0[b] [8]		6.25 s,br, 6.29 sh[3] 7.73 s,br [3]	—
$[Pd\{C(NHp\text{-}MeOC_6H_4)OMe\}_2Cl_2]$	2.97 q [4]	5.27 s[3]	6.28 s [3]	−1.5 [1]

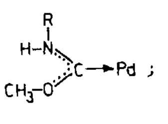
[a] in CDCl$_3$ solution, $\tau \pm 0.02$; integration values in parentheses; [b] set of broad multiplets; [c] not isolated, obtained after D$_2$O treatment; [d] the phenyl protons and N-H signals slightly overlap; s = singlet, m = multiplet, q = quartet, sh = shoulder, br = broad.

other palladium(II)- and platinum(II)-carbene derivatives.[3,8,13,14,17,18]

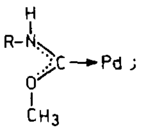
It is known that amidinium salts[20] and carbene complexes of chromium[21] or platinum[6,8] show hindered rotation about the C-N or C-O bonds. In the case of a methoxy-amino-carbene group four possible isomers may be present in solution:[6,8]



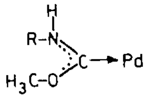
(A)



(B)

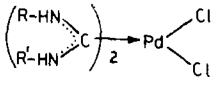


(C)



(D)

Assuming that free rotation occurs in the C→Pd bond, the number of possible isomers in a bis-carbene complex is given by the combinations of (A), (B), (C) and (D) structures. In this way four symmetric isomers of the type $[Pd(A)_2Cl_2]$ (or $[Pd(B)_2Cl_2]$ etc.) and six of the type $[Pd(A)(B)Cl_2]$ (or $[Pd(A)(B)Cl_2]$ etc.) can be obtained, the former showing only one O-CH$_3$ resonance and the latter two equivalent ones. The same considerations can be extended to the bis-di-amino-carbene



when R≠R'. In the case of R=R' the total number of possible isomers is reduced to six. If there were hindered rotation also about the C→Pd bond, the number of possible isomers should be considerably higher in any case. The p.m.r. spectra of the bis-methoxy-amino-carbene derivatives show only one isomer to be present in solution. Moreover, the occurrence of one sharp O-CH$_3$ resonance indicates that this isomer is of the type $[Pd(A)_2Cl_2]$. One isomeric species is also observed for $[Pd\{C(NHp\text{-}MeC_6H_4)N(Me)Ph\}_2Cl_2]$. In the case of the other bis-diamino-carbene complexes the spectra are characterized by broad unresolved multiplets for the phenyl protons and by broad resonances (half band widths = 6-9 c.p.s.), often followed by shoulders, for the methyl protons of $-C_6H_4-CH_3$ or $-C_6H_4-OCH_3$ groups. This is probably due to the presence of more than one isomer in solution.

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