Decarbonylation of 1. The reaction was started by injecting 9.0 mL of a 0.065 M solution of 1 in ether into vigorously stirred (magnetic stirring bar) known amounts of CO-saturated ether under CO. The change of gas volume as a function of time was plotted, and the initial rates were determined below 5% conversion. The total volume of gas evolved during the reaction corresponded to 0.98 ± 0.02 mol of CO/mol of 1.

Decarbonylation of 1 in the presence of $HCo(CO)_4$ was performed in the gasometric apparatus described above by first adding 1.0 mL of a 0.590 M solution of $HCo(CO)_4$ in *n*-octane to 10.0 mL of CO-saturated ether and then starting the reaction by injecting 9.0 mL of a 0.0612 M solution of 1 in ether. Immediately CO evolution set in and ceased after 6 h at 1.93 mol of CO/mol of 1. The IR spectrum of the product showed the formation of 0.90 mol of $Co_2(CO)_8$/mol of 1 and 0.07 mol of 2/mol of 1 but practically no ethyl formate, and 0.80 mol of ethanol/mol of 1 was found by GLC.

Reduction of 1 with H_2. A 5-mL sample of a 0.065 M solution of 1 in ether was placed at 0 °C in a 20-mL stainless-steel rocking autoclave and pressurized to 83 bar with H_2. After 5 h of agitation at 20 °C the IR spectrum of the reaction mixture showed quantitative conversion to $Co_2(CO)_8$ and ethyl formate in a 1:2 molar ratio.

Reaction of Ph_3P with 1 or 2. These reactions were performed in the gasometric apparatus described above and started by injecting neat 2 or ether solutions of 1 into solutions containing known amounts of Ph_3P. In both cases crystalline 3 could be prepared in at least 80% yield from the reaction mixtures by evaporating the solvent and recrystallizing the residue from a 20-fold benzene–heptane (1:8) mixture.

Reduction of 2 with $HCo(CO)_4$. The reaction was started by injecting neat 2 into the vigorously stirred and thermostated solution of $HCo(CO)_4$ in *n*-octane under CO. The change of IR spectra was followed from samples taken with a cold (−10 °C) syringe and measured in a cold (0 °C) CaF_2 IR cell. (Absorbancies: 1857 ($\epsilon_M(Co_2(CO)_8)$ 1735),[26] 1737 (ϵ_M(EtOCHO) 1050), and 1692 cm^{-1} ($\epsilon_M(2)$ 1266 $cm^2\ mmol^{-1}$).) Initial rates were calculated from graphical plots below 10% conversions.

Registry No. 1, 86970-71-0; 2, 86970-72-1; EtOCOCOCl, 4755-77-5; $NaCo(CO)_4$, 14878-28-5; oxalyl chloride, 79-37-8; $HCo(CO)_4$, 16842-03-8; Ph_3P, 603-35-0.

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Synthesis, Characterization, and Solution Behavior of (η^3-Allyl)(carbene)palladium(II) Complexes

A. Scrivanti*

Centro Chimica Metallorganica C.N.R., 35100 Padova, Italy

G. Carturan

Facoltà Chimica Industriale, S. Marta, Venezia, Italy

B. Crociani

Istituto Chimica Generale, 90123 Palermo, Italy

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The complexes $[PdCl(\eta^3\text{-allyl})(CNC_6H_4X)]$ (η^3-allyl = η^3-2-MeC_3H_4, C_6H_4X = *p*-C_6H_4Cl, *p*-C_6H_4OMe, *p*-C_6H_4Me) undergo selective nucleophilic attack by HNR'_2 (R′ = Me, Et) on the isocyanide carbon atom. Under mild conditions the reaction gives allyl carbene complexes of the type $[PdCl(\eta^3\text{-allyl})\{C(NHC_6H_4X)(NR'_2)\}]$. These products have been characterized and identified by usual spectroscopic techniques. Variable-temperature NMR experiments allow the detection of solution conformers of the allyl carbene complexes and the study of interconversion equilibria among different isomers. Results are interpreted and discussed in terms of restricted rotation around the $Pd-C_{carbene}$ bond, which results in preferential conformations.

Introduction

In transition-metal allyl complexes, the nature of ancillary ligands affects and sometimes promotes the reactivity of the allylic moiety in both catalytic and stoichiometric processes.[1-4] Following our interest in the synthesis and reactivity of allylic platinum(II) and palladium(II) complexes,[5,6] we have investigated the preparation of new derivatives having allyl and carbene ligands coordinated on the same metal center. The simultaneous presence of these groups on the same complex molecule might result in cooperative bonding effects leading to new reactions involving either the allyl or the carbene moieties or both. Although carbene complexes with a variety of ancillary ligands have been extensively studied,[7,8] to the

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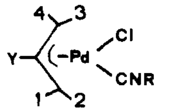
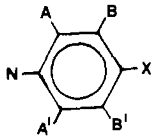
Table I. Analytical Data and Characteristic IR Bands for Complexes [PdCl(η^3-2-YC$_3$H$_4$)(CNR)]

compd			anal. data^b			IR absorptns, cm^{-1}		
Y	R	mp,^{a} °C	% C	% H	% N	ν(C≡N)^c	$\Delta\nu$^{c,d}	ν(Pd–Cl)^e
H	p-C$_6$H$_4$OMe	101	41.3 (41.80)	3.6 (3.83)	4.2 (4.43)	2175	50	278
H	p-C$_6$H$_4$C	112	37.8 (37.48)	3.0 (2.83)	4.5 (4.37)	2180	55	285
Me	CH$_3$	103	30.6 (30.28)	4.4 (4.49)	4.6 (4.46)	2215	70	280
Me	p-C$_6$H$_4$Me	108	45.8 (45.88)	4.3 (4.49)	4.5 (4.46)	2180	54	275
Me	p-C$_6$H$_4$OMe	100	43.4 (43.66)	4.2 (4.27)	4.3 (4.24)	2189	63	280
Me	p-C$_6$H$_4$Cl	113	39.4 (39.49)	3.2 (3.31)	4.4 (4.19)	2182	56	272

[a] All compounds decompose on melting. [b] Calculated values in parentheses. [c] Dichloromethane solution. [d] $\Delta\nu = \nu_{\text{coord}} - \nu_{\text{free ligand}}$. [e] Nujol mulls.

Table II. ^{1}H NMR Data for Complexes [PdCl(η^3-2-YC$_3$H$_4$)(CNR)]^a

compound		 allylic resonances					 isocyanides resonances		
Y	R	1	2	3	4	Y	AA′	BB′	others
H	p-C$_6$H$_4$OMe	4.50 (J_5 = 7.0)	3.47 (J_5 = 13.0)	2.96 (J_5 = 12.0)	4.25 (J_5 = 7.0)	5.52	7.36 (J_{AB} = 9.0)	6.88	3.81 (OMe)
H	p-C$_6$H$_4$Cl	4.59 (J_5 = 7.0)	3.55 (J_5 = 13.0)	3.05 (J_5 = 12.0)	4.31 (J_5 = 7.0)	5.59	7.40 (s)		
CH$_3$	CH$_3$	4.18 (J_4 = 2.5)	3.19	2.69	3.89 (J_1 = 2.5)	1.93			3.37 (CH$_3$)
CH$_3$	p-C$_6$H$_4$Me	4.30 (J_4 = 3.0)	3.31	2.82	4.01 (J_1 = 3.0)	2.02	7.32 (J_{AB} = 9.0)	7.20	2.36 (Me)
CH$_3$	p-C$_6$H$_4$OMe	4.29 (J_4 = 1.5)	3.31	2.84	4.02 (J_1 = 1.5)	2.02	7.36 (J_{AB} = 9.5)	6.88	3.81 (OMe)
CH$_3$	p-C$_6$H$_4$Cl	4.34 (J_4 = 1.0)	3.32	2.86	4.06 (J_1 = 1.0)	2.02	7.40 (s)		

[a] δ values, ±0.01 ppm; J values, ±0.5 Hz; spectra recorded in CDCl$_3$ solutions at 243 K; at instrument temperature (303 K) a relatively slow syn–anti dynamic process takes place.

best of our knowledge, no transition-metal–allyl–carbene system has been isolated and characterized so far.

Experimental Section

Materials, Instrumentation, and General Procedures. Solvents were dried and distilled under nitrogen and degassed by freeze–pump–thaw cycles. Standard techniques were employed for manipulation of air-sensitive compounds.[9] Dimers [PdCl(η^3-allyl)]$_2$ and isocyanides were prepared by literature methods.[10,11]

Isocyanides were stored in Schlenk tubes in the dark under nitrogen at −10 °C and were distilled or sublimed before each reaction. Amines, NHMe$_2$, and NHEt$_2$ were dried over KOH pellets.

IR spectra were recorded on a Perkin-Elmer Model 597 spectrophotometer as Nujol mulls using CsI windows. NMR spectra were recorded on a Varian FT 80 A spectrometer in CDCl$_3$ solution; in some cases samples were prepared at −80 °C under vacuum.

Other chemicals were of analytical grade and were used without further purification.

Preparation of [PdCl(η^3-allyl)(CNR)] Complexes (Allyl = C$_3$H$_5$, 2-MeC$_3$H$_4$; R = Me, p-C$_6$H$_4$OMe, p-C$_6$H$_4$Me, p-C$_6$H$_4$Cl). The general procedure for the synthesis of these complexes has been reported previously.[5] A typical preparation for [PdCl(η^3-2-MeC$_3$H$_4$)(CNMe)] is described. Methyl isocyanide (0.10 g, 2.4 mmol) was diluted in a Schlenk tube with 45 mL of diethyl ether and transferred under N$_2$ into a dropping funnel maintained under N$_2$ and connected to the reaction flask. This solution was added dropwise to a stirred suspension of [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$ (0.47 g, 1.2 mmol) in Et$_2$O at 0 °C under N$_2$ over 1 h. After being left standing for an additional hour at room temperature, the suspension was evaporated at reduced pressure to 25 mL and then diluted with 40 mL of n-hexane. The product appeared as an ivory crystalline solid that was filtered and dried at reduced pressure (yield 0.50 g, 88%).

Analytical and spectroscopic data for the new complexes are reported in Tables I and II.

Reaction of Allyl Isocyanide Complexes with NHMe$_2$ and NHEt$_2$. a. Preparation of Allyl Carbene Derivatives. The synthesis of carbene complexes [PdCl(η^3-2-MeC$_3$H$_4$){C(NHR)(NR′$_2$)}] (R = p-C$_6$H$_4$Cl, p-C$_6$H$_4$Me, p-C$_6$H$_4$OMe; R′ = Me, Et) was performed by using the general procedure reported in detail for R = p-C$_6$H$_4$OMe and R′ = Me. A tetrahydrofuran solution of NHMe$_2$ was obtained by bubbling dry NHMe$_2$ into the solvent. The solution was titrated, and upon solvent addition, the amine concentration was adjusted to 0.22 M. This solution (50 mL) was treated with [PdCl(η^3-2-MeC$_3$H$_4$)(CN-p-C$_6$H$_4$OMe)] (0.83 g, 2.5 mmol) at room temperature. The addition was made by injection through a septum cup of an almost saturated solution of the complex in tetrahydrofuran. The reaction mixture was put aside for 2 h and then evaporated to dryness under reduced pressure. The solid residue was dissolved in CH$_2$Cl$_2$; the resulting solution was treated with activated charcoal, filtered, concentrated, diluted with n-hexane, and left at −20 °C. The off-white product was recovered by filtration and dried (yield 0.76 g, 81%). Analytical

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Table III. Analytical Data and Characteristic IR Bands for Carbene Complexes $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\{C(NHR)(NR'_2)\}]$

compound			anal. data[b]			IR absorptns,[c] cm^{-1}		
R	R'	mp,[a] °C	% C	% C	% N	ν(N-H)	ν(C-N)	ν(Pd-Cl)
$p\text{-}C_6H_4Me$	Me	73	47.0 (46.81)	6.0 (5.89)	7.7 (7.80)	3200 m, br 3130 sh	1545 s	270 m
$p\text{-}C_6H_4Me$	Et	80	49.6 (49.62)	6.4 (6.51)	7.1 (7.24)	3190 m, br, 3120 sh	1530	267 m
$p\text{-}C_6H_4OMe$	Me	62	44.5 (44.82)	5.4 (5.64)	7.6 (7.47)	3210 m, br, 3140 sh	1545 s	265 m
$p\text{-}C_6H_4OMe$	Et	141	47.2 (47.66)	5.9 (6.25)	7.1 (6.95)	3180 m, br, 3120 sh	1545 s	265 m
$p\text{-}C_6H_4Cl$	Et	71	44.1 (44.19)	5.2 (5.44)	6.6 (6.87)	3185 ms, 3125 sh	1545 s	267 m

[a] All compounds decompose on melting. [b] Calculated values in parentheses. [c] Nujol mulls.

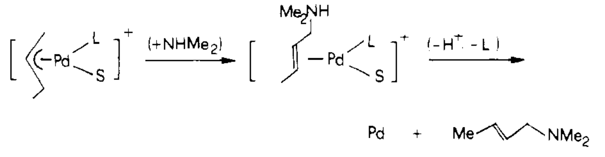
and infrared data for the carbene products are reported in Table III.

b. Reactions Occurring with Formation of Pd Metal. When the complexes $[PdCl(\eta^3\text{-}C_6H_5)(CNR)]$ are reacted with secondary amines under the same experimental conditions as in a, extensive decomposition to Pd metal and other unidentified products was observed. Analogous decomposition occurred in the reactions of $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(CNMe)]$ with $NHMe_2$ and/or $NHEt_2$.

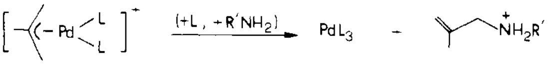
Results and Discussion

Nucleophilic Attack on $[PdCl(\eta^3\text{-allyl})(isocyanide)]$ Complexes by NHR'_2. The reaction of the complexes listed in Table I with secondary amines may follow different pathways depending on the site of nucleophilic attack.

It is well-known that NHR'_2 nucleophiles attack the coordinated allyl moiety yielding allylamines and palladium metal or palladium(0) derivatives[2,12,13] according to eq 1a and 1b. These complexes may also undergo migratory insertion of isocyanide into the palladium–allyl bond, as in the case of the reactions in the presence of other entering ligands such as PPh_3 or a second isocyanide molecule[5] (eq 2). Complexes $[PdCl(\eta^3\text{-}2\text{-}YC_3H_4)(CNR)]$

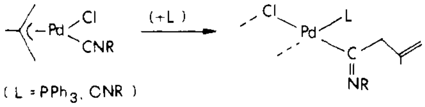


(1a)



(1b)

(L = phosphine, S = solvent)



(2)

(L = PPh₃, CNR)

(Y = H, Me; R = Me, $p\text{-}C_6H_4Me$, $p\text{-}C_6H_4OMe$, $p\text{-}C_6H_4Cl$) display $\nu(C\equiv N)$ vibrations of coordinated isocyanide in the range 2190–2180 cm^{-1}, with a high-frequency shift of 50–60 cm^{-1} relative to the free ligand (see Table I). As for other isocyanide complexes,[14] this fact suggests that the terminal carbon of the isocyanide is susceptible to nucleophilic attack to give diaminocarbene of the type II (eq 3). Under our experimental conditions, reaction 2 is never

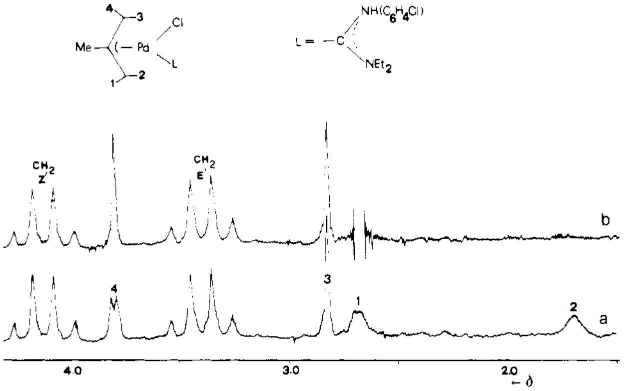
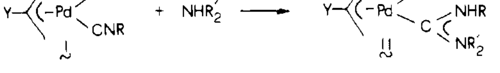


Figure 1. ^1H NMR spectrum of $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\{C(NHC_6H_4Cl)(NEt_2)\}]$ at 325 K in $CDCl_3$ solution, in 1.5–4.5 ppm region: a, assignment of allyl protons; b, decoupling of allyl proton 2 and assignment of methylenic E' and Z' protons of NEt_2 group (see insert of Table III).



(3)

observed, whereas the occurrence of reactions 1a,b and 3 depends essentially on the nature of the Y and R substituents.

For Y = H, precipitation of palladium metal occurs regardless of the nature of the coordinated isocyanide, indicating a preferential nucleophilic attack on the allyl moiety (reaction 1a). In contrast, for Y = Me the reaction course is controlled by the nature of the isocyanide; nucleophilic attack involves selectively the terminal carbon of aromatic isocyanides with almost quantitative formation of allyl carbene complexes II, whereas, in the case of methyl isocyanide, formation of palladium metal is again observed.

The influence of the nature of the allyl group may be properly related to the inductive effect of the 2-methyl substituent rather than to steric requirements; this agrees with the reduced reactivity of $\eta^3\text{-}2\text{-}MeC_3H_4$ complexes compared to the $\eta^3\text{-}C_3H_5$ analogues.[4,15,16] The influence of the isocyanide is clearly due to the higher electrophilic character of the terminal carbon atom in coordinated aryl isocyanides[17] compared to alkyl analogues.

Characterization of η^3-Allyl Carbene Complexes. For compounds II, satisfactory analytical data (Table III)

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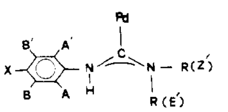
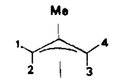
Table IV. ^{1}H NMR Data for [PdCl(η^3-2-MeC$_3$H$_4$)(carbene)] Complexes[a]





		allyl resonances					carbene resonances				
X	R'	1[b]	2	3	4[b]	Me	NH	R'(Z')	R'(E')	AA, BB', J_{AB}	X
Me	Me	2.70	1.77	2.87	3.80	1.42	7.29	3.68	3.07	7.06, 7.53, 8.0	2.27
Me	Et	2.69	1.72	2.84	3.79	1.40	7.25	4.16[c]	3.42[c]	7.08, 7.52, 8.5	2.27
								1.29[d]			
OMe	Me	2.70	1.78	2.84	3.80	1.43	7.63	3.69	3.07	7.54, 6.80, 9.0	3.75
OMe	Et	2.73	1.74	2.83	3.80	1.51	7.33	4.17[c]	3.42[c]	7.54, 6.81, 9.0	3.78
								1.32[d]			
Cl	Et	2.68	1.74	2.84	3.80	1.45	7.44	4.10[c]	3.42[c]	7.64, 7.24, 9.0	

[a] δ values, 0.01 ppm; *J* values, ±0.5 Hz; spectra recorded in CDCl$_3$ at 325 K. [b] J_{1-4} = 2.5 Hz. [c] CH$_2$ (q, *J* = 7.5 Hz). [d] CH$_3$ (t, *J* = 7.5 Hz).

were obtained according to the proposed formulation. The diaminocarbene group is characterized by the typical N–H and C$\overset{\cdots}{-}$N stretching vibrations in the ranges 3200–3120 and 1545–1530 cm^{-1}, respectively.

Type II structure is definitely assigned on the basis of ^{1}H NMR results, reported in Table IV (CDCl$_3$ solutions at 325 K).

In all cases, the typical AMYZ–Me pattern of 2-MeC$_3$H$_4$ allyl protons was recognized, confirming that the allyl group is not involved in the NHR'$_2$ nucleophilic attack on starting complexes I. Figure 1 shows the spectrum of [PdCl(η^3-2-MeC$_3$H$_4$){C(NHC$_6$H$_4$Cl)(NEt$_2$)}] in the 4.5–1.5 ppm region. The signals at 1.75, 2.68, 2.84, and 3.80 ppm have an integration ratio of 1:1:1:1 and were attributed to the allyl protons (as indicated in Table IV and Figure 1 (inserts) on the basis of the following considerations. Signal 4 at 3.8 ppm appears as a doublet with $J \simeq 2.5$ Hz, which is the typical long-range syn–syn coupling generally observed for palladium(II) η^3-allyl complexes.[18] Signal 1 at 2.68 ppm, although broad, has also a doublet shape. Upon irradiation of 1, doublet 4 collapses to a sharp singlet (Figure 1b), thereby confirming that both signals 1 and 4 correspond to syn protons; moreover, the concomitant disappearance of signal 2 is observed, due to spin saturation transfer, suggesting an exchange process between the corresponding protons.[19] This fact, paralleled by their broad appearance, may be rationalized in terms of a relatively slow syn–anti exchange between protons 1 and 2. As demonstrated in a number of cases,[20] syn–anti proton exchange occurs for protons bonded to allyl carbons in a cis position to the ligand having the larger trans influence; therefore, since the carbene group definitely has a larger trans influence than the chloride ligand, our decoupling and spin saturation transfer results support the assignments made. The same features were observed for all compounds listed in Table IV.

In regard to the carbene moiety, again taking the complex [PdCl(η^3-2-MeC$_3$H$_4$){C(NHC$_6$H$_4$Cl)(NEt$_2$)}] as an example, the singlet resonance at 7.30 ppm was attributed to the NH group, since the signal disappears upon D$_2$O addition to the CDCl$_3$ solution owing to the immediate H–D exchange. NEt$_2$ proton resonances appear at 4.10 and 3.42 ppm (CH$_2$ quartets) and at 1.29 ppm (CH$_3$ triplet) in a 2:2:6 integration ratio; the presence of two sets of signals for CH$_2$ protons is due to the different geometrical positions of Et groups, namely, *Z'* and *E'* (see Table IV (insert), while methyl resonances appear accidentally degenerate. Our assignments are based on previous attributions for analogous cases.[21,22]

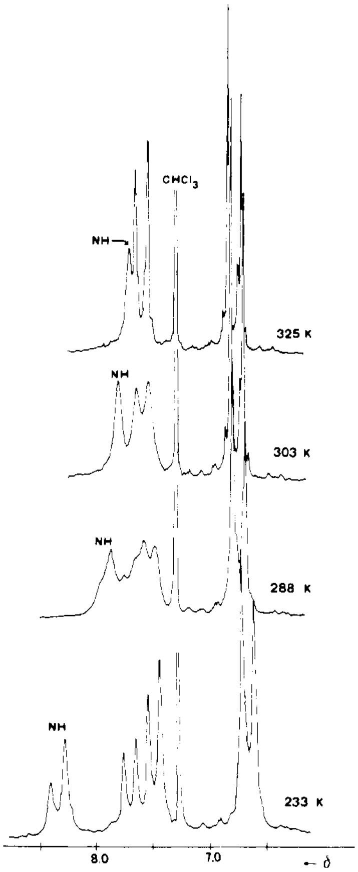


Figure 2. Variable-temperature ^{1}H NMR experiments for [PdCl(η^3-2-MeC$_3$H$_4$){C(NHC$_6$H$_4$OMe)(NMe$_2$)}] in CDCl$_3$ solution. Spectra show evolution of –NHC$_6$H$_4$– signals with temperature.

Similar results were obtained for the other allyl carbene complexes prepared here. In particular, the diaminocarbene ligands with NMe$_2$ substituents exhibit two well-separated methyl signals (see Table IV).

Conformational Equilibria. Solution Behavior of Allyl Carbene Complexes. X-ray structures of diaminocarbene complexes indicate that the carbene carbon

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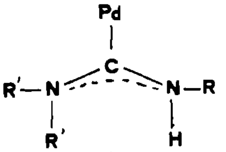
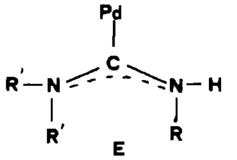
is essentially sp^2 hybridized with C–N bond distances shorter than those expected for single bonds,[8] in accordance with the high-frequency values of the corresponding ν(C$\overset{..}{-}$N) bands. Due to this partial double-bond character, restricted rotation around these bonds may give rise to different configurations in solution. In our particular case only *Z* and *E* rotational isomers are possible.



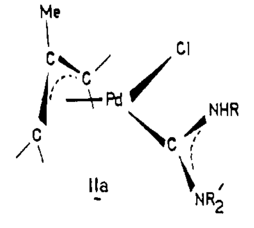
Z



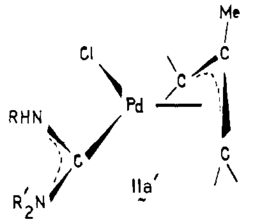
E

In trisubstituted diaminocarbene derivatives of this type, the *Z* configuration predominates in solution,[23,24] whereas the *E* conformer rarely has been observed,[23] due to steric repulsion between the R and R′ substituents. In our system, there was no spectral evidence of any contribution of the unfavorable *E* configuration so that it will not be considered in the following discussion.

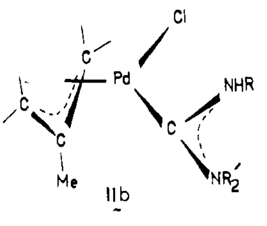
With the assumption of a rigid molecular structure for II (*Z* configuration), with restricted rotation around the Pd–C$_{carbene}$ bond and with the planar carbene moiety perpendicular to the average metal coodination plane, two diastereoisomers IIa and IIb may be present. Because of the asymmetric nature of the carbene ligand and the typical coordination mode of the allyl group, each diastereoisomer displays the corresponding enantiomer, IIa′ and IIb′, respectively.



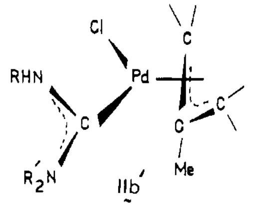
IIa



IIa′



IIb



IIb′

In the ^{1}H NMR spectra at 325 K, a single set of signals was observed (see Table IV), suggesting either preferential formation of a single diastereoisomer from reaction 3 or the occurrence of fast dynamic processes which interconvert conformers IIa and IIb. The real presence of two distinct species in CDCl$_3$ solution was demonstrated by variable-temperature experiments performed in the range 233–325 K. For semplicity, we refer to the case of [PdCl(η^3-2-MeC$_3$H$_4$){C(NHC$_6$H$_4$OMe)(NMe$_2$)}]. Figure 2 shows the observed spectral evolution in the 6.0–9.0 ppm range where only the signals of the –NHC$_6$H$_4$– group are extant, apart from the peak of the nondeuterated solvent.

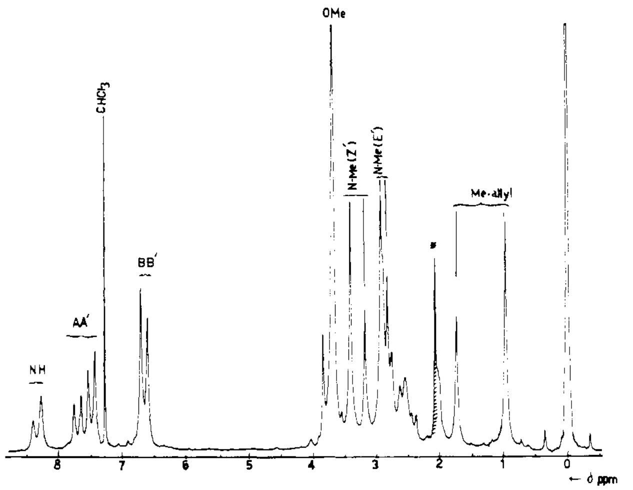


Figure 3. ^{1}H NMR spectrum of [PdCl(η^3-2-MeC$_3$H$_4$){C(NHC$_6$H$_4$OMe)(NMe$_2$)}] in CDCl$_3$ solution at 233 K (asterisk (*) = impurity).

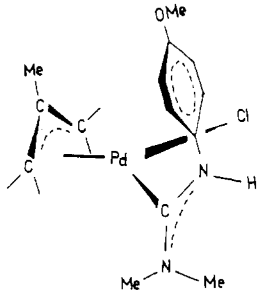


Figure 4. Perspective drawing proposed for IIa conformer.

The 7.63 ppm single resonance of NH and AA′BB′ phenyl ring proton patterns split into two distinct sets of signals as the temperature is lowered; the δ(NH) peak in markedly shifted downfield to 8.23 and 8.36 ppm at 233 K, where the low-temperature limiting spectrum is reached. The complete spectrum at 233 K is shown in Figure 3 where the assignment of relevant signals is reported. It may be noted that the resonances at 325 K of NH (7.63 ppm), 2-Me-allyl (1.43 ppm), NMe$_2$ (3.69 and 3.07 ppm), and the AA′BB′ pattern (7.06, 7.53 ppm) are now split into 1:1.5 integration ratio signals, thus demonstrating the occurrence of two species IIa and IIb at low temperature.

From the coalescence temperature (308 K) and the $\Delta\nu$ separation (61 Hz) of the Me-allyl signals in the low-temperature limiting spectrum (233 K) a ΔG^* rotational barrier of 15.4 ± 1 kcal mol^{-1} can be estimated.[25]

The other carbene derivatives exhibit the same fluxional behavior with comparable coalescence temperatures of the Me–allyl resonances and relative populations of conformers IIa and IIb (e.g., 310 K with a 1:1.8 integration ratio for [PdCl(η^3-2-C$_3$H$_4$){C(NHC$_6$H$_4$Me)(NMe$_2$)}]), even though in some cases the overlap with other signals hampered an accurate evaluation of these parameters.

Scheme I shows the possible mechanisms of interconversion between these species: both rotation around Pd–C$_{carbene}$ (equilibrium i) and the usual $\eta^3 \rightleftarrows \eta^1 \rightleftarrows \eta^3$ allyl dinamic process (equilibrium ii) are taken into consideration. The IIa $\rightleftarrows$ IIb interconversion mechanism involving rotation of the η^3-allyl moiety around its bond axis to the Pd center has not been considered in Scheme I; as a matter of fact this dynamic process has never been observed for [PdCl(η^3-allyl)(L)] complexes. It is noteworthy that mechanism ii implies the simultaneous observation of

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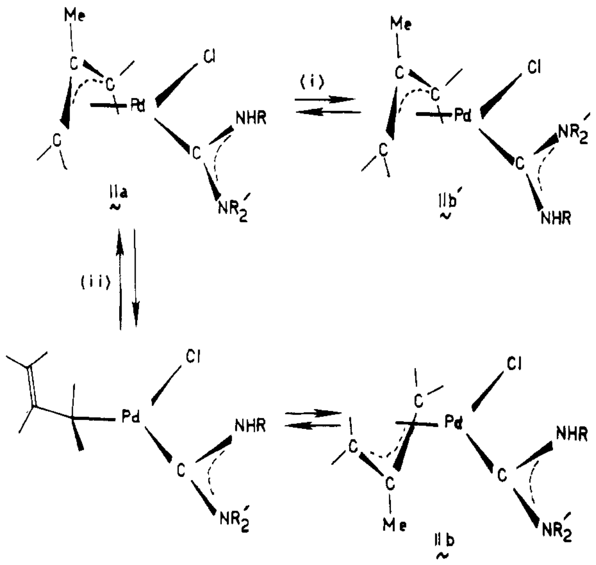
Scheme I



syn–anti interconversion of allyl protons. This was demonstrated at 325 K on the basis of spin saturation transfer between protons 1 and 2; indeed, the spectrum shows distinct signals for each of the four allyl protons, suggesting that the dynamic process is rather slow even at 325 K on the NMR time scale. Therefore, in the range of explored temperatures the observed interconversion between IIa and IIb proceeds essentially by mechanism i which evidently has less demanding energetics.

Incipient decomposition of the complexes at higher temperatures (>325 K) prevented any further study of other dynamic processes such as those involving rotation around the C–N bonds of the carbene group.

In the IIa and IIb spectra (see Figure 3) the BB′ and –OMe resonances practically coincide, whereas the corresponding AA′ signals, as well as NMe_2 and allyl methyl resonances, appear well separated. This fact may reasonably be related to the geometrical position of these groups. In particular, it may be observed that the allyl methyl protons have quite different shieldings (1.75 and 0.96 ppm). The 1.75 ppm chemical shift is in line with those of 2-Me protons in complexes $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(CNR)]$ (see Table II); at variance, the 0.96 ppm signal appears shifted remarkably upfield, probably due to the shielding effect of the phenyl ring current of the $-NHC_6H_4OMe$ moiety in enantiomeric species, IIa and IIa′, which display appropriate orientation of the $\eta^3\text{-}2\text{-}MeC_3H_4$ and $-C_6H_4OMe$ groups (Figure 4). Similar shielding effects of aromatic rings on η^3-allyl group protons of Mo, W, and Fe complexes have been recognized as valuable probes in perfecting the assignments of relevant conformers in solution.[26,27]

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Registry No. I (R = $p\text{-}C_6H_4OMe$, Y = H), 87069-99-6; I (R = $p\text{-}C_6H_4Cl$, Y = H), 87070-00-6; I (R = CH_3, Y = Me), 87070-01-7; I (R = $p\text{-}C_6H_4Me$, Y = Me), 87070-02-8; I (R = $p\text{-}C_6H_4OMe$, Y = Me), 87070-03-9; I (R = $p\text{-}C_6H_4Cl$, Y = Me), 87070-04-0; II (R = $p\text{-}C_6H_4Me$, R′ = Me), 87088-23-1; II (R = $p\text{-}C_6H_4Me$, R′ = Et), 87070-05-1; II (R = $p\text{-}C_6H_4OMe$, R′ = Me), 87070-06-2; II (R = $p\text{-}C_6H_4OMe$, R′ = Et), 87070-07-3; II (R = $p\text{-}C_6H_4Cl$, R′ = Et), 87070-08-4.

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