

Reactions of 1,4-Diazabutadienes with Chloro-bridged Palladium(II) and Platinum(II) Allyl Derivatives

BRUNO CROCIANI*, TRISTANO BOSCHI and PAOLO UGUAGLIATI

Centro Chimica Tecnologia Composti Metallorganici Elementi Transizione C.N.R., Istituto Chimica Industriale, Via Marzolo 9, Padua, Italy

Received August 14, 1980

The 1,4-diazabutadienes (or α -diimines) $R-N=C(R')-C(R'')=N-R$, DAB, ($R = p-C_6H_4OMe$, $R' = R'' = H$, DAB^I; $R = p-C_6H_4OMe$, $R' = H$, $R'' = Me$, DAB^{II}; $R = p-C_6H_4OMe$, $R' = R'' = Me$, DAB^{III}; $R = t-Bu$, $R' = R'' = H$, DAB^{IV}) react with the allylic compounds $[PdCl(\eta^3-2-Y-C_3H_4)]_2$ ($Y = H$: all; $Y = Me$: Meall) and $[PtCl(C_3H_5)]_4$ in the presence of $NaClO_4$ yielding the cationic complexes $[M(\eta^3-2-Y-C_3H_4)(DAB)]ClO_4$ ($M = Pd$, I; $M = Pt$, II). The ¹H and ¹³C NMR spectra indicate a σ, σ' -N,N' chelation of DAB. In the complexes with the asymmetric ligand DAB^{II} a fast syn-syn, anti-anti, exchange of the allylic protons occurs at room temperature in $CDCl_3$. In acetonitrile a partial dissociation of DAB is observed, with the following order of stability constants: DAB^{III} > DAB^I and Pt \gg Pd. In the absence of $NaClO_4$, equilibria are established involving the starting reactant $[PdCl(\eta^3-Meall)]_2$, binuclear species $\{[PdCl(\eta^3-Meall)]_2(DAB)\}$, III (in which DAB acts as a bidentate bridging ligand) and ionic complexes $[Pd(\eta^3-Meall)(DAB)]^+[PdCl_2(\eta^3-Meall)]^-$, IV. These equilibria were studied in various solvents by variable temperature ¹H NMR spectra, electronic spectra, molecular weight and conductivity measurements. The complexes III can be isolated as solids and are the predominant species in concentrated solution only with DAB^I and DAB^{IV}, both having $R' = R'' = H$. With DAB^{III}, the predominant species in $CDCl_3$ at $-40^\circ C$ is a complex of type IV. A similar compound, $[Pd(\eta^3-Meall)(bipy)]-[PdCl_2(\eta^3-Meall)]$, is also obtained in the reaction with 2,2'-bipyridine.

Introduction

The chemistry of palladium and platinum allyl derivatives has been extensively studied with a special focus on the fluxional behaviour of the allylic moiety [1]. The dimer $[PdCl(\eta^3-all)]_2$ and tetramer

$[PtCl(all)]_4$ easily undergo bridge-splitting reactions with a large variety of mono- and bidentate ligands to yield in general mononuclear complexes containing a trihapto η^3 -allyl group. Some monohapto η^1 -allyl derivatives of platinum(II) have been also isolated [2]. As a preliminary step towards the study of the reactions with organometallic 1,4-diazabutadiene ligands, derived from the complex *trans*- $[PdCl\{\dot{C}(=Np-C_6H_4OMe)C(Me)=Np-C_6H_4OMe\}(PPh_3)_2]$ (which contains a σ -bonded 1,4-bis(*p*-methoxyphenyl)1,4-diaza-3-methylbutadiene-2-yl group [3]), we have investigated the reactivity of some simpler α -diimines towards $[PdCl(\eta^3-2-Y-C_3H_4)]_2$ ($Y = H$, Me) and $[PtCl(C_3H_5)]_4$, in order to ascertain the type of bonding of these ligands (σ -monodentate, σ, σ -bridging bidentate, σ, σ - or σ, π -chelating bidentate [4, 5]) and the possible fluxional behaviour in the systems.

Experimental

The 1,4-diazabutadiene ligands (DAB^I, DAB^{III}, DAB^{IV}) and the starting complexes $[PdCl(\eta^3-2-Y-C_3H_4)]_2$ ($Y = H$, Me) and $[PtCl(C_3H_5)]_4$ were prepared by standard methods [6–8]. All other chemicals and solvents were reagent grade, and were used without further purification.

$R-N=C(Me)-CH=N-R$ ($R = p-C_6H_4OMe$: DAB^{II})

A 40% aqueous solution of methylglyoxal (2.25 g, 12.5 mmol) was slowly added dropwise to a stirred solution of *p*-anisidine (98% purity, 3.14 g, 25 mmol) in ca. 7 ml of methanol, at $-20^\circ C$. After the addition, the reaction mixture was kept at $-10^\circ C$ for one day. The yellow product was filtered off, washed with water and dried *in vacuo* (1.24 g, 35% yield). This compound is rather unstable at room temperature and must be stored at $-10^\circ C$ under N_2 atmosphere.

$[M(\eta^3-Meall)(DAB)]ClO_4$ ($M = Pd, Pt; Y = H, Me$)

a) The dimer $[PdCl(\eta^3-Meall)]_2$ (0.5 mmol) dissolved in ca. 50 ml of dichloromethane was treated

* Author to whom correspondence should be addressed.

with DAB (1 mmol) and then with a solution of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (0.281 g, 2 mmol) in 5 ml of methanol. A white precipitate of NaCl was immediately formed. After stirring for 30 min the reaction mixture was evaporated to dryness and the residue treated with dichloromethane and charcoal. After filtration the clear solution was concentrated to a small volume at reduced pressure and the product was precipitated by addition of diethyl ether. All the cationic complexes were purified by recrystallization from dichloromethane/diethyl ether (Yields 80–95%). With the unstable DAB^{II} ligand, the reactants were initially mixed together at 0 °C. After stirring for 15 min, the reaction mixture was worked up at room temperature as quickly as possible.

b) The compound $[\text{PtCl}(\text{all})]_4$ (0.272 g, 0.25 mmol) suspended in *ca.* 50 ml of dichloromethane was treated with DAB (1 mmol) and then with a solution of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (0.281 g, 2 mmol) in 5 ml of methanol. The resulting reaction mixture was worked up as described above to give pure, well-defined products only with DAB^{I} and DAB^{III} (Yields 80–90%).

$[\text{Pd}(\eta^3\text{-Meall})(\text{bipy})] \text{BF}_4$

The dimer $[\text{PdCl}(\eta^3\text{-Meall})]_2$ (0.197 g, 0.5 mmol) dissolved in *ca.* 50 ml of dichloromethane was treated with 2,2-bipyridine (0.156 g, 1 mmol) and then with a solution of NaBF_4 (0.22 g, 2 mmol) in 5 ml of methanol. The reaction mixture was worked up as described above to yield the white cationic complex (0.324 g, 80%).

Reactions of $[\text{PdCl}(\eta^3\text{-Meall})]_2$ with DAB in the Absence of NaClO_4

DAB^{I}

Addition of DAB^{I} (0.134 g, 0.5 mmol) to $[\text{PdCl}(\eta^3\text{-Meall})]_2$ (0.197 g, 0.5 mmol; molar ratio $\text{DAB}^{\text{I}}/\text{Pd}$ 1/2) dissolved in *ca.* 30 ml of benzene gave an orange solution, from which a yellow precipitate began to separate after a few minutes. After stirring for 2 h, the product $\{[\text{PdCl}(\eta^3\text{-Meall})]_2(\text{DAB}^{\text{I}})\}$ (0.310 g) was filtered off, washed with benzene and dried *in vacuo*.

The same reaction in methanol gave a red solution from which a yellow precipitate began to separate after a few minutes. The mixture was concentrated to a small volume at reduced pressure and the precipitation was completed with diethyl ether. This product (0.300 g) was found to be identical to that prepared in benzene on the basis of elemental analysis and IR spectra. Similar results are obtained in chlorinated solvents such as dichloromethane, chloroform and 1,2-dichloroethane.

DAB^{II}

In the reaction with DAB^{II} , carried out under the same experimental conditions, extensive decomposition occurred as to prevent the isolation of any pure product.

DAB^{III}

The ligand DAB^{III} (0.5 mmol) was added to $[\text{PdCl}(\eta^3\text{-Meall})]_2$ (0.5 mmol) dissolved in *ca.* 30 ml of benzene. After 30 min the yellow solution was concentrated to a small volume, whereupon yellow crystals of DAB^{III} were obtained. The precipitation was completed by addition of diethyl ether. From the mother liquor, upon concentration and dilution with a diethyl ether/*n*-hexane (1/1 v/v mixture, a second yellow precipitate is formed, which consists of $[\text{PdCl}(\eta^3\text{-Meall})]_2$ and a small amount of DAB^{III} . The same results are obtained in chloroform and methanol: in both cases the colour of the initial reaction solution is red-orange.

DAB^{IV}

Addition of DAB^{IV} (0.084 g, 0.5 mmol) to $[\text{PdCl}(\eta^3\text{-Meall})]_2$ in *ca.* 30 ml of benzene (or dichloromethane) gave a yellow solution, from which the product $\{[\text{Pd}(\eta^3\text{-Meall})]_2(\text{DAB}^{\text{IV}})\}$ (0.24 g) was precipitated after concentration to a small volume and addition of *n*-pentane. Attempts to recrystallize this compound from a dilute benzene/*n*-pentane solution yielded crystals of $[\text{PdCl}(\eta^3\text{-Meall})]_2$.

Bipy

The dimer $[\text{PdCl}(\eta^3\text{-Meall})]_2$ (0.197 g, 0.5 mmol) was treated with bipy (0.078 g, 0.5 mmol) in *ca.* 30 ml of dichloromethane (or methanol). The resulting yellow solution was concentrated at reduced pressure and the pale-yellow product $[\text{Pd}(\eta^3\text{-Meall})(\text{bipy})][\text{PdCl}_2(\eta^3\text{-Meall})]$ (0.26 g) was precipitated upon addition of *n*-hexane (diethyl ether for methanol).

In all cases, the same final products are obtained if the starting compounds are reacted with a DAB/Pd molar ratio of 1/1.

Physical Measurements

Microanalyses were performed by A. Berton and G. Biasioli of the Microanalytical Laboratory, Laboratorio Radioelementi C.N.R., Padua. Molecular weights were determined using a Knauer osmometer in 1,2-dichloroethane and benzene at 37 °C. The conductivity measurements were carried out with a Philips PR9500 bridge at 20 °C. ^1H NMR spectra were recorded on a Varian EM-390 90 MHz spectrometer with tetramethylsilane (TMS) as internal standard; ^{13}C NMR spectra were obtained on a Bruker WP 60FT at room temperature with dichloromethane- d_2 or TMS as internal standard. Electronic spectra in solution were recorded with a Bausch-

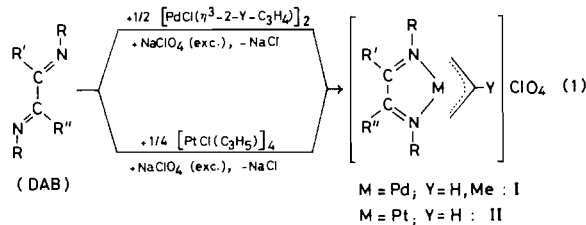
Lomb Spectronic 210 UV spectrophotometer in the range 650–250 nm at 25 °C, using quartz cells of 1 cm path length. Infrared spectra were recorded with a Perkin-Elmer 597 instrument, using hexachlorobutadiene mulls and NaCl plates in the range 4000–1300 cm^{-1} , Nujol mulls and CsI in the range 1700–250 cm^{-1} .

Results and Discussion

The reactions of organic 1,4-diaza-1,3-butadienes (DAB), $\text{R}-\text{N}=\text{C}(\text{R}')-\text{C}(\text{R}'')=\text{N}-\text{R}$ ($\text{R} = p\text{-C}_6\text{H}_4\text{OMe}$, $\text{R}' = \text{R}'' = \text{H}$, DAB^{I} ; $\text{R} = p\text{-C}_6\text{H}_4\text{OMe}$, $\text{R}' = \text{H}$, $\text{R}'' = \text{Me}$, DAB^{II} ; $\text{R} = p\text{-C}_6\text{H}_4\text{OMe}$, $\text{R}' = \text{R}'' = \text{Me}$, DAB^{III} ; $\text{R} = t\text{-Bu}$, $\text{R}' = \text{R}'' = \text{H}$, DAB^{IV}) with $[\text{PdCl}(\eta^3\text{-}2\text{-Y-C}_3\text{H}_4)]_2$ ($\text{Y} = \text{H}$: all; $\text{Y} = \text{Me}$: Meall) or $[\text{PtCl}(\text{all})]_4$ yield different products depending on whether NaClO_4 is present or not.

Reactions in the Presence of NaClO_4

In the presence of an excess of NaClO_4 , the reactions lead to the formation of intensely coloured ($\text{R} = p\text{-C}_6\text{H}_4\text{OMe}$) cationic complexes according to eqn. 1:



The reactions with $[\text{PtCl}(\text{all})]_4$ yield well-defined products only with the ligands DAB^{I} and DAB^{III} . The cationic compound $[\text{Pd}(\eta^3\text{-Meall})(\text{bipy})]\text{BF}_4$ can be prepared in a similar way starting from $[\text{PdCl}(\eta^3\text{-Meall})]_2$, 2,2'-bipyridine (bipy) and NaBF_4 .

The analytical and physical data are reported in Table I.

The complexes *I* and *II* are uni-univalent electrolytes in methanolic solutions. The presence of the ClO_4^- anion is confirmed by the typical IR absorptions at *ca.* 1090 cm^{-1} [$\nu(\text{Cl}-\text{O})$] and *ca.* 624 cm^{-1} [$\delta(\text{Cl}-\text{O})$]. The 1,4-diazabutadienes are σ, σ' - $\text{N}_2\text{N}'$ chelated to the central metals, as indicated by the downfield shifts of the signals $\delta(\text{N}=\text{C}-\text{H})$ and $\delta(\text{N}=\text{C})$ in the ^1H and ^{13}C NMR spectra, compared to those of the free ligands [4, 5] (Tables II and III). The relatively high value (74.4 Hz) of $^3\text{J}_{\text{Pt}-\text{H}}$ for the $\delta(\text{N}=\text{C}-\text{H})$ signal of $[\text{Pt}(\eta^3\text{-all})(\text{DAB}^{\text{I}})]\text{ClO}_4$ is also in agreement with a *trans* $\text{Pt}-\text{N}=\text{C}-\text{H}$ arrangement [9].

In general, all the C- and N-substituent protons of DAB are deshielded upon coordination. The ^1H NMR spectra show also the characteristic features

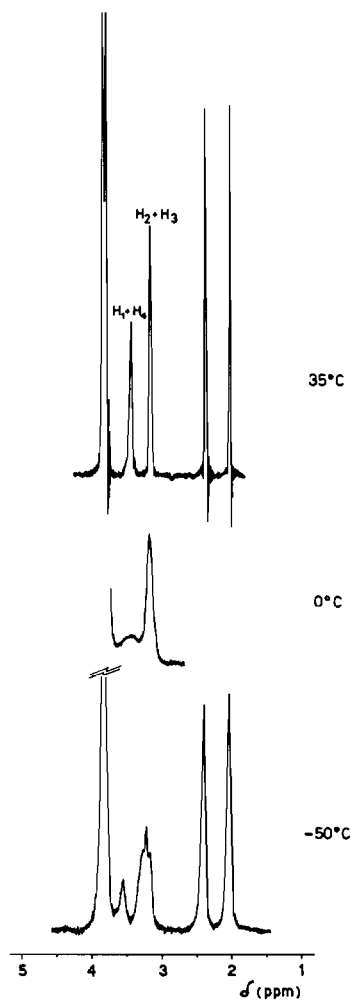


Fig. 1. Variable temperature ^1H NMR spectrum of $[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{I}})]\text{ClO}_4$ in CDCl_3 .

of η^3 -allyl groups, with separate resonances for the *syn* (H_1 , H_4) and *anti* (H_2 , H_3) protons (the numbering of the allylic protons is reported in Table II). These spectra are rather simple for palladium(II) derivatives, since no coupling between *syn* and *anti* protons was observed within the resolution limit of the spectrometer. In the case of platinum(II) complexes, however, the η^3 -all resonances are much more complicated due to coupling with the ^{195}Pt isotope and to a small *syn-anti* coupling of *ca.* 2 Hz [10].

The presence of a plane of symmetry in the cationic derivatives of DAB^{I} , DAB^{III} and DAB^{IV} does not allow one to investigate any fluxional behaviour other than *syn-anti* exchange. This is not the case for $[\text{Pd}(\eta^3\text{-}2\text{-Y-C}_3\text{H}_4)(\text{DAB}^{\text{II}})]\text{ClO}_4$ containing an asymmetrically C-substituted α -diimine. The spectra of these compounds at various temperatures indicate that a fast *syn-syn*, *anti-anti* exchange (on the NMR time scale) occurs at 35 °C, when only one

TABLE I. Analytical, Physical Data and Selected IR Bands (cm^{-1}).

Compound	Colour	Melting Point ($^{\circ}\text{C}$) ^a	C ^b (%)	H (%)	N (%)	Cl (%)
$[\text{PdCl}(\eta^3\text{-all})(\text{DAB}^{\text{I}})]\text{ClO}_4$	red-purple	147	44.6 (44.29)	4.1 (4.11)	5.3 (5.44)	7.0 (6.88)
$[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{I}})]\text{ClO}_4$	red	183	45.0 (45.38)	4.4 (4.38)	5.2 (5.29)	6.8 (6.70)
$[\text{Pt}(\eta^3\text{-all})(\text{DAB}^{\text{I}})]\text{ClO}_4$	red-brown	189	37.9 (37.78)	3.4 (3.50)	4.7 (4.64)	5.9 (5.87)
$[\text{Pd}(\eta^3\text{-all})(\text{DAB}^{\text{II}})]\text{ClO}_4$	red-brick	97	45.2 (45.38)	4.3 (4.38)	5.3 (5.29)	6.8 (6.70)
$[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{II}})]\text{ClO}_4$	red-brick	126	46.6 (46.42)	4.7 (4.64)	5.1 (5.15)	6.4 (6.52)
$[\text{Pd}(\eta^3\text{-all})(\text{DAB}^{\text{III}})]\text{ClO}_4$	yellow	199	46.7 (46.42)	4.6 (4.63)	5.1 (5.16)	6.5 (6.52)
$[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{III}})]\text{ClO}_4$	orange	164	47.1 (47.41)	5.0 (4.88)	4.9 (5.03)	6.5 (6.36)
$[\text{Pt}(\eta^3\text{-all})(\text{DAB}^{\text{III}})]\text{ClO}_4$	red-orange	234	39.8 (39.91)	3.9 (3.99)	4.4 (4.43)	5.7 (5.61)
$[\text{Pd}(\eta^3\text{-all})(\text{DAB}^{\text{IV}})]\text{ClO}_4$	white	189	37.4 (37.60)	6.1 (6.07)	6.7 (6.75)	8.6 (8.54)
$[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{IV}})]\text{ClO}_4$	white	212	39.4 (39.17)	6.5 (6.34)	6.5 (6.53)	8.4 (8.26)
$[\text{Pd}(\eta^3\text{-Meall})(\text{bipy})]\text{BF}_4$	white	277	41.3 (41.57)	3.8 (3.74)	7.0 (6.93)	
$\{[\text{PdCl}(\eta^3\text{-Meall})]_2(\text{DAB}^{\text{I}})\}$	yellow	153	43.3 (43.53)	4.6 (4.57)	4.2 (4.23)	10.8 (10.71)
$\{[\text{PdCl}(\eta^3\text{-Meall})]_2(\text{DAB}^{\text{IV}})\}$	pale-yellow	157	38.2 (38.45)	6.2 (6.10)	5.0 (4.98)	12.5 (12.61)
$[\text{Pd}(\eta^3\text{-Meall})(\text{bipy})]^+$ $[\text{PdCl}_2(\eta^3\text{-Meall})]^-$	lemon-yellow	195	39.5 (39.30)	3.9 (4.03)	5.1 (5.09)	13.0 (12.89)

^aUncorrected values: all compounds decompose on melting. ^bCalcd. values in parenthesis. ^c 10^{-3} M MeOH solutions at 20 $^{\circ}\text{C}$. of the *para*-substituted phenyl groups around 1600 and 1500 cm^{-1} .

sharp signal was observed for the *anti* protons and a separate one for the *syn* protons. At lower temperatures these signals progressively broaden and eventually at -50 $^{\circ}\text{C}$ (the lowest temperature examined) four resonances are detected (Fig. 1). Because some decomposition occurs in solution with time, the mechanism of the dynamic process was no further investigated. It is likely that the interchange of the coordination sites of the two nitrogen atoms, generating a time averaged plane of symmetry through the molecule, takes place *via* a monodentate DAB^{II} intermediate, as was proposed for cationic $\text{Pd}(\eta^3\text{-allyl})$ complexes with chelating N-ligands [11], but a rotation of the $\eta^3\text{-allyl}$ group around its bond axis to the central metal may also be operative [10].

The ^{13}C NMR spectra are reported in Table III together with the labelling of diazabutadiene and allylic carbons. The assignment of the ^{13}C signals is mainly based on the coupling with ^1H and for the complex $[\text{Pt}(\eta^3\text{-all})(\text{DAB}^{\text{I}})]\text{ClO}_4$ also with the ^{195}Pt isotope. In the latter case, the assignment of the phenyl ring carbons $\text{C}_{2,6}$ is clearly indicated by the

higher value of $^3J_{\text{Pt-C}} = 18.5$ Hz as compared to $\text{C}_{3,5}$ ($^4J_{\text{Pt-C}} = 0$). The $\text{C}_{3,5}$ chemical shifts fall in the narrow range 114.86–115.64 ppm, as expected for *meta* carbons of *para*-substituted phenyl groups [12].

Upon coordination, a down-field shift is observed not only for $\delta(\text{C}=\text{N})$, but also for the signals of C- and N-substituents of DAB such as $\delta(\text{C-Me})$ and $\delta(\text{N-CMe}_3)$. When the N substituent is the *p*- $\text{C}_6\text{H}_4\text{-OMe}$ group, the $\text{C}_{2,6}$ and C_4 carbon atoms appear to be the more deshielded by mesomeric effect, being *ortho* and *para* respectively to the coordinated nitrogen atom. In general, these effects parallel those observed in the corresponding ^1H NMR spectra, and indicate a marked decrease of electron density on the coordinated ligand. In other words, σ -donation seems to be predominant in the metal–DAB bond of these cationic derivatives. The metal \rightarrow ligand π back-donation becomes more relevant in complexes of low-valent metals, such as $[\text{Fe}(\text{CO})_3\text{-}(\text{Pr}^i\text{N}=\text{CH}-\text{CH}=\text{NPr}^i)]$ [5a], $[\text{M}(\text{CO})_4(\text{DAB}^{\text{IV}})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $[\text{Mo}(\text{CO})_{4-n}(\text{DAB}^{\text{IV}})(\text{PR}_3)_n]$

Λ_M (ohm ⁻¹ cm ² mol ⁻¹) ^c	$\nu(\text{Cl-O})$	$\delta(\text{Cl-O})$	$\nu(\text{C=N})^d$	Other Bands
88	1085s,br	622s	1568sh,br	
99	1095s,br	623s	1588s,br	
84	1085s,br	623s	1562s,br	
82	1090s,br	624s	1543m,br	
77	1090s,br	623s	1540m,br	
86	1095s,br	624s	n.o.	
97	1095s,br	624s	n.o.	
76	1095s,br	625s	n.o.	
98	1090s,br	623s	1606mw	
92	1095s,br	624s	1611mw	
104				1100s,br; 1060s,br; 1040sh: $\nu(\text{B-F})$; 524ms: $\delta(\text{B-F})$
74			1567ms; 1560sh	278ms: $\nu(\text{Pd-Cl})$
37			1616ms	276s: $\nu(\text{Pd-Cl})$
84				270s; 256s; $\nu(\text{Pd-Cl})$

^dThe assignment of $\nu(\text{C=N})$ bands for the ligands with $\text{R} = p\text{-C}_6\text{H}_4\text{OMe}$ is complicated by the occurrence of intense absorptions

($n = 1, 2$) [13], all containing a $\sigma, \sigma', \text{N}, \text{N}'$ chelating diazabutadiene. In these compounds π back-donation results in an increased electron density on the $\text{N}=\text{C}-\text{C}=\text{N}$ unit and correspondingly in a higher shielding of the imino carbons in the ¹³C NMR spectra.

The small π contribution in the Pd-DAB^{IV} bond is also indicated by the small shift to lower frequency (*ca.* 20 cm⁻¹) of the C=N stretching vibrations of $[\text{Pd}(\eta^3\text{-2-Y-C}_3\text{H}_4)(\text{DAB}^{\text{IV}})]\text{ClO}_4$ relative to that of free DAB^{IV} (1630 cm⁻¹). Much higher shifts to lower frequency have been reported for DAB^{IV} complexes with considerable extent of π back-donation [13, 14].

The electronic spectra of the cationic derivatives of DAB^I, DAB^{II} and DAB^{III} ($\text{R} = p\text{-C}_6\text{H}_4\text{OMe}$) are characterized by a series of bands in the frequency range 18,000–28,000 cm⁻¹, which give rise to a rather broad absorption with a main maximum surrounded by one or more shoulders and with molar extinction coefficients varying from 5000 to 19,000 cm⁻¹ M⁻¹. These bands are essentially

due to metal → DAB CT transitions, as indicated by their dependence on the nature of the central metal and of the diazabutadiene ligands, as well as by solvatochromic effects [6, 13, 14].

An increasing substitution of protons by methyl groups at the imino carbon atoms in DAB ligands shifts the band maxima to higher frequency and reduces their intensities, as shown by the MeOH solution spectra of the complexes: $[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{I}})]\text{ClO}_4$, λ_{max} 21,550 cm⁻¹ (ϵ 14,000 cm⁻¹ M⁻¹); $[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{II}})]\text{ClO}_4$, 23,920 (8000); $[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{III}})]\text{ClO}_4$, 24,510 (4600). A higher frequency shift is also observed in more polar solvents as reported in Fig. 2 for $[\text{Pt}(\eta^3\text{-all})(\text{DAB}^{\text{III}})]\text{ClO}_4$ spectra in 1,2-dichloroethane *vs.* methanol solutions.

In the latter solvents the Lambert-Beer law is generally observed, whereas in acetonitrile a dissociation equilibrium occurs according to eqn. 2:

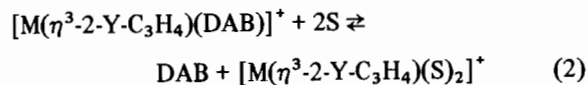


TABLE II. ^1H NMR Spectra.^a

Compound	DAB Ligand		η^3 -Allyl Group ^b		Solvent
DAB ^I	3.77 S 6.8–7.4 M ^c 8.35 S	O–Me –C ₆ H ₄ – N=CH			CDCl ₃
[Pd(all)(DAB ^I)] ClO ₄	3.83 S 6.9–6.6 M ^c 8.47 S	O–Me –C ₆ H ₄ – N=CH	3.54 D ³ J _{H–Y} = 12.0 4.06 D ³ J _{H–Y} = 6.9 5.82 M	H ₂ , H ₃ H ₁ , H ₄ Y = H	CD ₂ Cl ₂
[Pd(Meall)(DAB ^I)] ClO ₄	3.87 S 6.9–7.5 M ^c 8.50 S	O–Me –C ₆ H ₄ – N=CH	2.15 S 3.39 S 3.83 S	Y = Me H ₂ , H ₃ H ₁ , H ₄	CD ₂ Cl ₂
[Pt(all)(DAB ^I)] ClO ₄	3.89 S 6.8–7.8 M ^d 9.10 T ³ J _{Pt–H} = 74.4	O–Me –C ₆ H ₄ – N=CH	3.20 M ³ J _{H–Y} = 12.3 J _{syn–anti} = 2.1 ² J _{Pt–H} = 73.2 4.04 M ³ J _{H–Y} = 7.5 J _{syn–anti} = 2.1 ² J _{Pt–H} = 24 5.22 M	H ₂ , H ₃ H ₁ , H ₄ Y = H	CD ₂ Cl ₂
DAB ^{II}	2.15 S 3.72 S 6.6–7.4 M ^e 8.15 S	C–Me O–Me –C ₆ H ₄ – N=CH			CDCl ₃
[Pd(all)(DAB ^{II})] ClO ₄	2.36 S 3.79 S 6.8–7.6 M ^e 8.35 S	C–Me O–Me –C ₆ H ₄ – N=CH	3.31 D ³ J _{H–Y} = 12.6 3.66 D ³ J _{H–Y} = 6.6 5.68 M	H ₂ , H ₃ H ₁ , H ₄ Y = H	CDCl ₃
[Pd(Meall)(DAB ^{II})] ClO ₄	2.37 S 3.78 S 3.80 S 6.8–7.6 M ^e 8.37 S	C–Me O–Me O–Me –C ₆ H ₄ – N=CH	2.05 S 3.16 S 3.42 S	Y = Me H ₂ , H ₃ H ₁ , H ₄	CDCl ₃
DAB ^{III}	2.10 S 3.75 S 6.6–6.9 M ^c	C–Me O–Me –C ₆ H ₄ –			CDCl ₃
[Pd(all)(DAB ^{III})] ClO ₄	2.33 S 3.83 S 6.8–7.2 M ^c	C–Me O–Me –C ₆ H ₄ –	3.17 D ³ J _{H–Y} = 12.6 3.38 D	H ₂ , H ₃ H ₁ , H ₄	CD ₂ Cl ₂

(continued on facing page)

TABLE II. (continued)

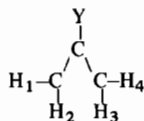
Compound	DAB Ligand		η^3 -Allyl Group ^b		Solvent	
			$^3J_{H-Y} = 6.9$ 5.65 M	Y = H		
[Pd(Meall)(DAB ^{III})]ClO ₄	2.33 S (2.30) ^f	C-Me	2.03 S (1.98) ^f	Y = Me	CD ₂ Cl ₂	
	3.83 S (3.79) ^f	O-Me	3.02 S (2.94) ^f	H ₂ , H ₃		
	6.9–7.2 M ^c (6.8–7.2) ^f	–C ₆ H ₄ –	3.17 S (3.05) ^f	H ₁ , H ₄		
[Pt(all)(DAB ^{III})]ClO ₄	2.31 T $^4J_{Pt-H} = 7.9$	C-Me	2.80 M $^3J_{H-Y} = 12.7$	H ₂ , H ₃	CD ₂ Cl ₂	
	3.84 S 6.9–7.3 M ^d	O-Me	$J_{syn-anti} = 2.2$ $^2J_{Pt-H} = 75$			
		–C ₆ H ₄ –	3.35 M $^3J_{H-Y} = 6.8$	H ₁ , H ₄		
			$J_{syn-anti} = 2.2$ $^2J_{Pt-H} = 27$			
			4.92 M	Y = H		
DAB ^{IV}	1.29 S 7.93 S	C(Me) ₃ N=CH			CDCl ₃	
[Pd(all)(DAB ^{IV})]ClO ₄	1.37 S 8.44 S	C(Me) ₃ N=CH	3.36 D $^3J_{H-Y} = 12.6$ 4.47 D $^3J_{H-Y} = 7.2$	H ₂ , H ₃ H ₁ , H ₄ Y = H	CDCl ₃	
			5.69 M			
[Pd(Meall)(DAB ^{IV})]ClO ₄	1.38 S 8.45 S	C(Me) ₃ N=CH	2.12 S 3.21 S 4.20 S	Y = Me H ₂ , H ₃ H ₁ , H ₄	CDCl ₃	
[Pd(Meall)(bipy)]BF ₄	7.5–8.8 M	–NC ₅ H ₄	2.24 S 3.38 S 3.97 S	Y = Me H ₂ , H ₃ H ₁ , H ₄	CD ₂ Cl ₂	
{[PdCl(Meall)] ₂ (DAB ^I)}	3.80 S 6.8–7.6 M 8.78 S, br	[5H] ^g [4H] [1H]	O-Me –C ₆ H ₄ – N=CH	2.05 S [3H] 2.86 S [2H] 3.75 S [5H] ^g	Y = Me H ₂ , H ₃ H ₁ , H ₄	CDCl ₃
[PdCl(Meall)] ₂ + DAB ^{III}	2.49 S, br 3.80 S 6.8–7.4 M	[3H] [3H] [4H]	C-Me O-Me –C ₆ H ₄ –	2.01 S [3H] 2.86 br [2H] 3.50 br [2H]	Y = Me H ₂ , H ₃ H ₁ , H ₄	CDCl ₃
[PdCl(Meall)] ₂ + DAB ^{III} ^h	2.56 S, br	[6H]	C-Me	1.97 S [6H]	Y = Me	CDCl ₃

(continued overleaf)

TABLE II. (continued)

Compound	DAB Ligand			η^3 -Allyl Group ^b		Solvent
	3.76 S	[8H] ^g	O-Me	2.71 S	[2H]	H ₂ , H ₃ ⁱ
	6.8-7.3 M ^c	[8H]	-C ₆ H ₄ -	2.98 S	[2H]	H ₂ , H ₃ ^j
				3.07 S	[2H]	H ₁ , H ₄ ^j
				3.78 sh	[6H] ^g	H ₁ , H ₄ ⁱ
[PdCl(Meall)] ₂ (DAB ^{IV})	1.39 S	[9H]	C(Me) ₃	2.07 S	[3H]	Y = Me
	8.62 S, br	[1H]	N=CH	2.80 S	[2H]	H ₂ , H ₃
				3.81 S	[2H]	H ₁ , H ₄
[Pd(Meall)(bipy)] ⁺	7.5-8.9 M	[8H]	-NC ₅ H ₄	2.02 S	[3H]	Y = Me ⁱ
[PdCl ₂ (Meall)] ⁻				2.20 S	[3H]	Y = Me ^j
				2.75 S	[2H]	H ₂ , H ₃ ⁱ
				3.45 S,br	[2H]	H ₂ , H ₃ ^j
				3.76 S	[2H]	H ₁ , H ₄ ⁱ
				4.04 S,br	[2H]	H ₁ , H ₄ ^j
[PdCl ₂ (Meall)]AsPh ₄	7.4-7.9 M		C ₆ H ₅	2.01 S		Y = Me
				2.70 S		H ₂ , H ₃
				3.71 S		H ₁ , H ₄

^aSpectra recorded at 35 °C; δ values in ppm from TMS as internal standard; S singlet, D doublet, T triplet, M multiplet, sh shoulder, br broad. Coupling constants in Hz. Integration values are given in square brackets. ^bNumbering of allylic protons



^cAA'BB' symmetrical multiplet. ^dAA'BB' signal coupled with ¹⁹⁵Pt. ^eTwo overlapping AA'BB' signals. ^fSpectrum in CDCl₃ solution. ^gIntegration value of two overlapping signals. ^hSpectrum at -40 °C. ⁱSignals of the cationic species (see text). ^jSignals of anionic species [PdCl₂(Meall)]⁻.

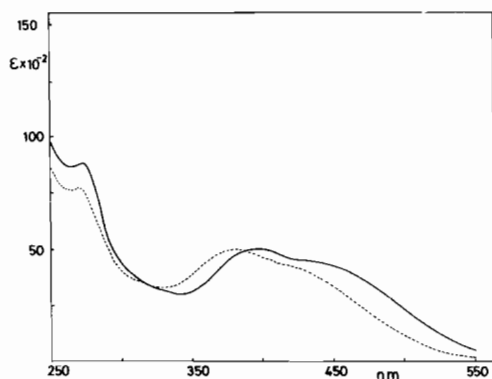


Fig. 2. Electronic spectra of [Pt(η^3 -all)(DAB^{III})]ClO₄ in 1,2-dichloroethane (—) and methanol (-----).

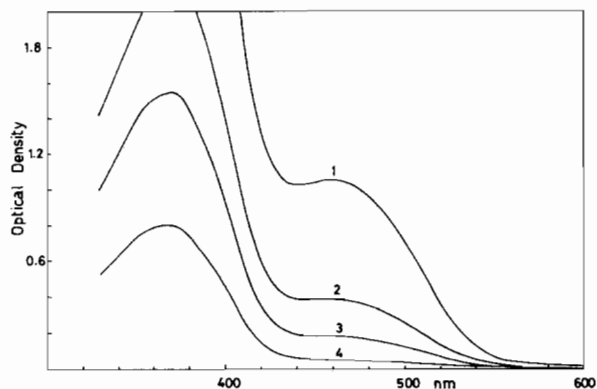


Fig. 3. Electronic spectra of [Pd(η^3 -Meall)(DAB^I)]ClO₄ in acetonitrile (25 °C) at the following concentrations (M): 1) 2.39×10^{-4} ; 2) 1.20×10^{-4} ; 3) 7.98×10^{-5} ; 4) 3.99×10^{-5} .

(M = Pd, Pt; Y = H, Me; S = MeCN)

As an example, Fig. 3 shows the electronic spectra of $[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{I}})]\text{ClO}_4$ at various concentrations at 25 °C.

The intense band at $27,030\text{ cm}^{-1}$ is due to the free DAB^{I} ligand, while the maximum at $21,740\text{ cm}^{-1}$ is assigned to the CT band system of the undissociated complex. *Abstract factor analysis* [15] of the spectral changes with dilution has shown the presence of only two absorbing species in the range $30,000\text{--}22,000\text{ cm}^{-1}$ (*viz.* the free ligand and the undissociated complex) whereas one single absorbing species (*i.e.* the undissociated substrate) is observed below $22,000\text{ cm}^{-1}$. As expected, increasing additions of free DAB^{I} will shift the equilibrium to the left, as indicated by the corresponding intensity increase of the maximum at $21,740\text{ cm}^{-1}$. The dissociation product $[\text{Pd}(\eta^3\text{-Meall})(\text{S})_2]^+$ can also be generated *in situ* by an alternative route, namely by treatment of an acetonitrile solution of $[\text{PdCl}(\eta^3\text{-Meall})]_2$ with AgClO_4 (Pd/Ag 1/1 molar ratio): after filtration of the AgCl precipitate, the resulting pale-yellow solution was found to be conducting and did not display any appreciable absorption in the frequency range in which the equilibrium 2 had been investigated. Consistently, appropriate additions of free DAB^{I} to such solution closely reproduced the electronic spectra corresponding to the dissociation of $[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{I}})]\text{ClO}_4$ under the same concentration conditions.

Non-linear regression analysis of the spectral changes with dilution, analogous to those of Fig. 3, was carried out according to the following model [16]:

$$\frac{[\text{M}][\text{L}]}{[\text{ML}]} = K_{\text{D}}$$

$$[\text{ML}] = \frac{1}{2} \{ (2a + K_{\text{D}}) - [(2a + K_{\text{D}})^2 - 4a^2]^{1/2} \}$$

$$A_{\lambda} = \epsilon_{\text{ML}}^{\lambda} [\text{ML}] + \epsilon_{\text{L}}^{\lambda} [\text{L}]$$

where:

$$\text{ML} = [\text{M}(\eta^3\text{-2-Y-C}_3\text{H}_4)(\text{DAB})]^+$$

$$\text{M} = [\text{M}(\eta^3\text{-2-Y-C}_3\text{H}_4)\text{S}_2]^+$$

$$\text{L} = \text{DAB}$$

a = total, analytical concentration of ML

A_{λ} = optical density of the solution at wavelength λ

ϵ_i^{λ} = extinction coefficients at λ

The function minimized was

$$\phi = \phi(\epsilon_i, K_{\text{D}}) = \sum w_i (A_{\text{obs}} - A_{\text{calcd}})^2$$

No weighting scheme was applied. The minimization was carried out by an optimized version of

Marquardt's algorithm [17] as implemented on a Tektronix 4052 Graphic System minicomputer with 64 Kbytes of memory. Good starting guesses for the parameter vector were obtained by a preliminary Nelder–Mead *Simplex* search [18]. The following dissociation constants $K_{\text{D}}(M)$ were obtained:

$[\text{Pd}(\eta^3\text{-all})(\text{DAB}^{\text{I}})]\text{ClO}_4$	$(3.0 \pm 0.4) \times 10^{-4}$
$[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{I}})]\text{ClO}_4$	$(3.4 \pm 0.5) \times 10^{-4}$
$[\text{Pd}(\eta^3\text{-all})(\text{DAB}^{\text{III}})]\text{ClO}_4$	$(1.7 \pm 0.7) \times 10^{-5}$
$[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{III}})]\text{ClO}_4$	$(3.4 \pm 0.4) \times 10^{-5}$
$[\text{Pt}(\eta^3\text{-all})(\text{DAB}^{\text{I}})]\text{ClO}_4$	$(3.0 \pm 0.8) \times 10^{-6}$

(averages of determinations at several wavelengths; errors quoted are averaged standard errors of estimate).

The complexes $[\text{Pt}(\eta^3\text{-all})(\text{DAB}^{\text{III}})]\text{ClO}_4$ and $[\text{Pd}(\eta^3\text{-Meall})(\text{bipy})]\text{ClO}_4$ are virtually undissociated and the Lambert–Beer law is obeyed even at rather high dilutions. The cationic derivatives of DAB^{II} and DAB^{IV} undergo extensive decomposition in acetonitrile, which prevents any equilibrium study.

The values of the dissociation constants show that the stability of the five-membered ring depends on the 1,4-diazabutadiene ligand and more markedly on the central metal in the orders:

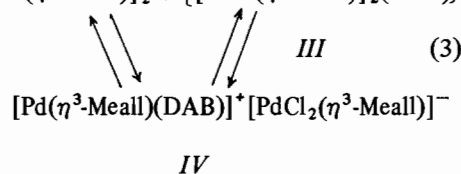
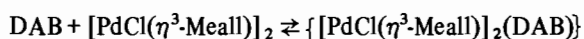


and



Reactions in the Absence of NaClO_4

When the dimer $[\text{PdCl}(\eta^3\text{-Meall})]_2$ is treated with the DAB ligands in various solvents, such as dichloromethane, chloroform, 1,2-dichloroethane, benzene, methanol, the following equilibria take place:



Although only the species that were isolated and characterized are reported in eqn. 3, labile compounds of type $[\text{PdCl}(\eta^3\text{-Meall})(\text{DAB})]$ containing the metal and the DAB ligand in a 1/1 molar ratio may also be present in solution [19, 20]. In any case, the ^1H NMR spectra of the reaction mixtures indicate that the allyl moiety is *trihapto* bonded in all the equilibrium components (*cf.* Table II, Fig. 5 and further discussion).

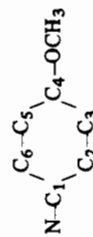
The particular product that can be precipitated off the equilibrium solution by addition of ethyl ether

TABLE III. ^{13}C NMR Spectra.^a

Compound	1,4-Diazabutadiene R-N=C(R')-C(R'')=N-R		η^3 -Allyl Group C ₁ -C ₂ (Y)-C ₃			
	C=N	N-R	R'	C _{1,III}	C ₂	Y
DAB ^I	158.43 DD	144.0 S (C ₁)				
	¹ J _{C-H} = 163.0	123.60 DD (C _{2,6})				
	² J _{C-H} = 10.1	¹ J _{C-H} = 160.2				
		² J _{C-H} = 5.5				
		115.16 DD (C _{3,5})				
		¹ J _{C-H} = 160.2				
		² J _{C-H} = 4.6				
		160.43 S (C ₄)				
		56.12 Q (OCH ₃)				
		¹ J _{C-H} = 144.6				
[Pd(allyl)(DAB ^I)]ClO ₄ ^b	161.70	142.40 (C ₁)		66.67	120.0	
		125.23 (C _{2,6})				
		115.64 (C _{3,5})				
		162.55 (C ₄)				
		56.59 (OCH ₃)				
[Pt(allyl)(DAB ^I)]ClO ₄ ^b	164.68 T	143.20 S ^c (C ₁)		50.96 T	109.52 T	
	² J _{Pt-C} = 16.5	125.60 T (C _{2,6})		¹ J _{Pt-C} = 232.6	¹ J _{Pt-C} = 73.2	
		³ J _{Pt-C} = 18.5				
		115.53 S (C _{3,5})				
		162.86 S (C ₄)				
		56.54 S (OCH ₃)				
DAB ^{III} b	169.0	144.9 (C ₁)	15.58 (CH ₃)			
		121.11 (C _{2,6})				
		114.86 (C _{3,5})				
		157.16 (C ₄)				
		56.01 (OCH ₃)				
[Pd(allyl)(DAB ^{III})]ClO ₄	177.24 S	143.20 S (C ₁)	20.31 Q (CH ₃)	64.98 T	120.50 D	
		123.11 DD (C _{2,6})	¹ J _{C-H} = 130.0	¹ J _{C-H} = 157.7	¹ J _{C-H} = 163.9	
		¹ J _{C-H} = 163.0				

		$^2J_{C-H} = 4.6$ 115.16 DD ($C_{3,s}$) $^1J_{C-H} = 162.0$ $^2J_{C-H} = 3.7$ 159.46 S (C_4) 56.23 Q (OCH ₃) $^1J_{C-H} = 144.7$							23.95 Q (CH ₃) $^1J_{C-H} = 131.8$
[Pd(Meall)(DAB ^{III})]ClO ₄	177.04 S	143.18 S (C_1) 123.05 DD ($C_{2,6}$) $^1J_{C-H} = 163.0$ $^2J_{C-H} = 5.1$ 115.10 DD ($C_{3,s}$) $^1J_{C-H} = 162.0$ $^2J_{C-H} = 4.6$ 159.44 S (C_4) 56.17 Q (OCH ₃) $^1J_{C-H} = 143.7$		20.25 Q (CH ₃) $^1J_{C-H} = 131.0$	63.46 T $^1J_{C-H} = 156.6$	136.80 S			
DAB ^{IV}	157.8 ^d (159.10) ^e	58.1 C(CH ₃) ₃ (61.13) 29.4 C(CH ₃) ₃ (23.32)							
[Pd(all)(DAB ^{IV})]ClO ₄ ^b	163.22	64.31 C(CH ₃) ₃ 29.36 C(CH ₃) ₃			64.68	116.56			
[Pd(Meall)(DAB ^{IV})]ClO ₄ ^b	163.04	64.07 C(CH ₃) ₃ 29.30 C(CH ₃) ₃			64.07	132.40			23.17 (CH ₃)

^aSpectra recorded in CD₂Cl₂; δ values in ppm from TMS at room temperature; the coupling constants are given in Hz (± 0.1); S singlet, D doublet, T triplet, Q quartet, DD doublet of doublets; the carbon atoms of the phenyl ring are numbered as follows:



^bProton decoupled spectra. ^cThe ¹⁹⁵Pt satellites are masked by the instrument noise. ^dSpectrum in CDCl₃ reported in ref. [5a]. ^eSpectrum in CDCl₃ reported in ref. [13].

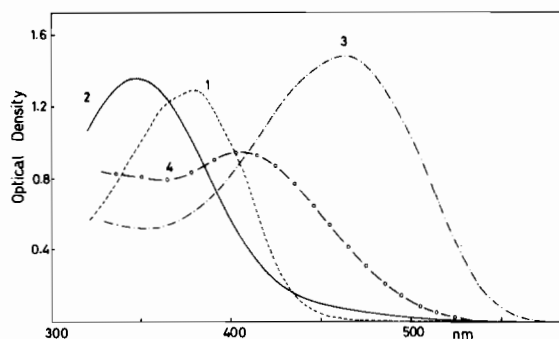


Fig. 4. Electronic spectra: 1) $\{[\text{PdCl}(\eta^3\text{-Meall})]_2(\text{DAB}^{\text{I}})\}$ in CHCl_3 , $5.06 \times 10^{-5} M$; 2) Reaction mixture $\text{DAB}^{\text{III}}/[\text{PdCl}(\eta^3\text{-Meall})]_2$ in CHCl_3 (molar ratio $\text{DAB}^{\text{III}}/\text{Pd}$ $\frac{1}{2}$, DAB^{III} $2 \times 10^{-4} M$); 3) $\{[\text{PdCl}(\eta^3\text{-Meall})]_2(\text{DAB}^{\text{I}})\}$ in MeOH , $1 \times 10^{-4} M$; 4) Reaction mixture $\text{DAB}^{\text{III}}/[\text{PdCl}(\eta^3\text{-Meall})]_2$ in MeOH (molar ratio $\text{DAB}^{\text{III}}/\text{Pd}$ $\frac{1}{2}$, DAB^{III} $2 \times 10^{-4} M$).

and/or light petroleum ether appears to depend only on the nature of DAB and neither on the molar ratio of reactants nor on the solvent. In fact, when DAB^{I} and DAB^{IV} , both having $\text{R}' = \text{R}'' = \text{H}$, are involved in eqn. 3, only products of type *III* can be isolated in the solid. With DAB^{III} , the isolation procedure leads back to the starting reactants, although the ^1H NMR spectrum of the reaction mixture in CDCl_3 at -40°C and the electronic spectrum in methanol both show the ionic compound *IV* to be the predominant species. When bipy is used, only the product *IV* is obtained. These findings occur whatever the Pd/DAB molar ratio in the range 1/1–2/1 in all solvents examined.

The product *III* containing DAB^{I} can also be obtained from the reaction of $[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{I}})]\text{-ClO}_4$ with $[\text{PdCl}_2(\eta^3\text{-Meall})]\text{AsPh}_4$ (molar ratio 1/1) in chlorinated solvents, after filtration of the insoluble $\text{AsPh}_4\text{ClO}_4$.

Complexes *III* are stable only in the solid state and represent the predominant species in highly concentrated solutions, such as those employed for NMR studies (*ca.* 0.1 *M*)*. The coordination of both imino nitrogens of DAB is confirmed by the low frequency shift of the $\nu(\text{C}=\text{N})$ bands as compared to the free ligands. Also, the down-field shifts of $\delta(\text{N}=\text{CH})$ signals in the ^1H NMR spectra (Table II) indicate a Pd–N σ type of bonding. Cleavage of chlorobridges of the starting dimeric allyl compound is suggested by the presence of only one $\nu(\text{Pd}-\text{Cl})$ band in *III* at *ca.* 277 cm^{-1} (Table I), a significantly higher frequency than $\nu(\text{Pd}-\text{Cl}_{\text{bridging}})$ in $[\text{PdCl}(\eta^3\text{-Meall})]_2$ (260 and 248 cm^{-1}). This is consistent with

*Analytical data and NMR integration values both indicate that in *III* a Pd/DAB ratio of 2:1 is present.

the $\nu(\text{Pd}-\text{Cl})$ values of the bridge-splitting products $[\text{PdCl}(\eta^3\text{-Meall})(\text{L})]$ ($\text{L} = \text{pyridine}$, $\nu(\text{Pd}-\text{Cl})$ 283; AsPh_3 , 280; PPh_3 , 276 cm^{-1}).

The far-IR spectra of *III* also rule out the presence of the anion $[\text{PdCl}_2(\eta^3\text{-Meall})]^-$ of compound *IV*, which is characterized by two strong $\nu(\text{Pd}-\text{Cl})$ bands at 270 and 257 cm^{-1} . The most probable formulation for *III* in the solid state involves a N-bidentate DAB ligand bridging two $\text{PdCl}(\eta^3\text{-Meall})$ units, similar to that reported for the binuclear complexes $\{[\text{RhCl}(\text{CO})_2]_2(\text{DAB}^{\text{IV}})\}$ [4b] and $\{[\text{trans-PtCl}_2(\text{PBu}_3)]_2(\text{DAB}^{\text{IV}})\}$ [19].

In dilute solutions complexes *III* are extensively dissociated as indicated by molecular weight, conductivity measurements and electronic spectra. The M.W. value in 1,2-dichloroethane for the DAB^{I} derivative is found to be 325 (calcd. 662.2), whereas for the DAB^{IV} species the observed value is 298 as compared to the theoretical value of 562.2. Dissociation in methanol solution yields ionic products: conductivity measurements for $10^{-3} M$ solutions give the following Λ_{M} values ($\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$): 37 and 74 for DAB^{IV} and DAB^{I} compounds, respectively. In benzene and chlorinated solvents (10^{-3} – $5 \times 10^{-5} M$) the complex $\{[\text{PdCl}(\eta^3\text{-Meall})]_2(\text{DAB}^{\text{I}})\}$ is almost quantitatively dissociated into $[\text{PdCl}(\eta^3\text{-Meall})]_2$ the free DAB^{I} ligand, the latter being characterized by spectrum 1 in Fig. 4, while the former was isolated by crystallisation from a dilute solution of $\{[\text{PdCl}(\eta^3\text{-Meall})]_2(\text{DAB}^{\text{IV}})\}$ in benzene/*n*-pentane.

In dilute methanol solution the dissociation of DAB^{I} derivative yields quantitatively the ionic compound *IV*, the cation of which imparts a red colouration to the solution due to its intense CT band at $21,550\text{ cm}^{-1}$ (spectrum 3 in Fig. 4).

The electronic spectra of the reaction mixture $\text{DAB}^{\text{III}}/[\text{PdCl}(\eta^3\text{-Meall})]_2$ (molar ratio $\text{DAB}^{\text{III}}/\text{Pd}$ $\frac{1}{2}$; concentration range 10^{-3} – $10^{-4} M$) in chlorinated solvents clearly indicate that in this case also the predominant absorbing species is the free ligand (spectrum 2 in Fig. 4), whereas in methanol the equilibria 3 are almost completely shifted towards species *IV*, as shown by conductivity measurements and by the strong CT bands of the cation $[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{III}})]^+$ with a maximum at $24,500\text{ cm}^{-1}$ (spectrum 4 in Fig. 4).

The reaction 3 with 2,2'-bipyridine yields quantitatively the ionic product *IV*, $[\text{Pd}(\eta^3\text{-Meall})(\text{bipy})]^+[\text{PdCl}_2(\eta^3\text{-Meall})]^-$ ($\Lambda_{\text{M}} = 84\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ in $10^{-3} M$ methanol solution; $\nu(\text{Pd}-\text{Cl}) = 270, 256\text{ cm}^{-1}$). The electronic spectra in chloroform and methanol closely match those of $[\text{Pd}(\eta^3\text{-Meall})(\text{bipy})]\text{BF}_4$ in the same solvents.

The ^1H NMR spectrum of $\{[\text{PdCl}(\eta^3\text{-Meall})]_2(\text{DAB}^{\text{I}})\}$ in CDCl_3 at 35°C is reported in Table II and in Fig. 5a. An identical spectrum is obtained for the reaction mixtures: (i) $\text{DAB}^{\text{I}}/[\text{PdCl}(\eta^3\text{-Meall})]_2$ (molar ratio $\text{DAB}^{\text{I}}/\text{Pd}$ $\frac{1}{2}$), (ii) $[\text{Pd}(\eta^3\text{-Meall})]_2$ (molar ratio $\text{DAB}^{\text{I}}/\text{Pd}$ $\frac{1}{2}$), (iii) $[\text{Pd}(\eta^3\text{-Meall})]_2$ (molar ratio $\text{DAB}^{\text{I}}/\text{Pd}$ $\frac{1}{2}$).

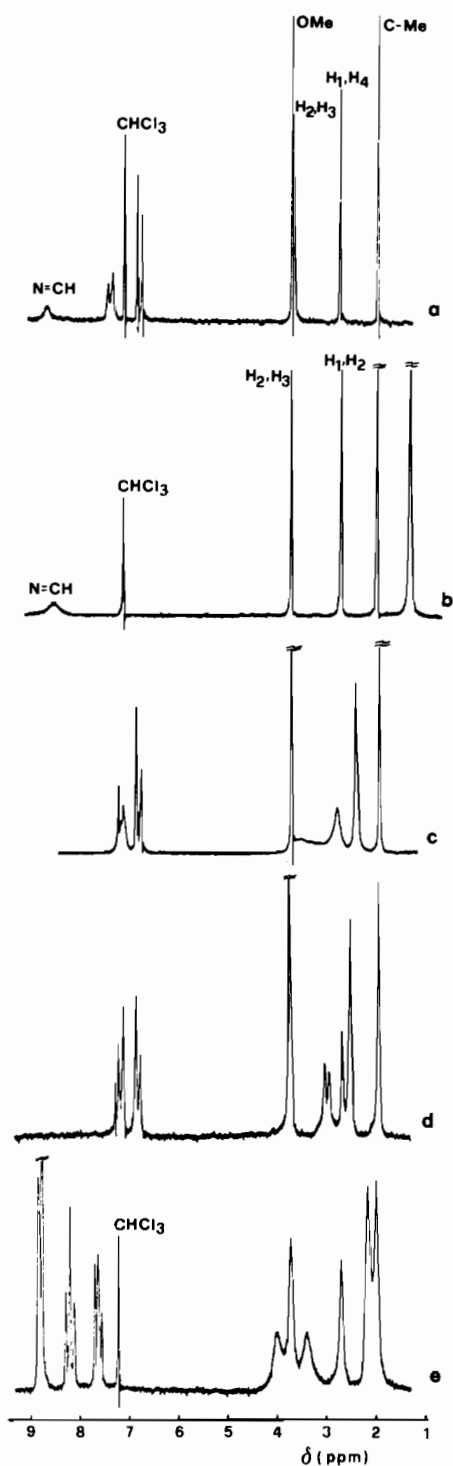


Fig. 5. ^1H NMR spectra in CDCl_3 : $\{[\text{PdCl}_2(\eta^3\text{-Meall})]_2(\text{DAB}^{\text{I}})\}$ at 35°C (a); $\{[\text{PdCl}(\eta^3\text{-Meall})]_2(\text{DAB}^{\text{IV}})\}$ at 35°C (b); Reaction mixture $\text{DAB}^{\text{III}}/[\text{PdCl}(\eta^3\text{-Meall})]_2$ (molar ratio $\text{DAB}^{\text{III}}/\text{Pd } 1/2$) at 35°C (c) and at -40°C (d); $[\text{Pd}(\eta^3\text{-Meall})(\text{bipy})][\text{PdCl}_2(\eta^3\text{-Meall})]$ at 35°C (e).

$\text{Meall}(\text{DAB}^{\text{I}})]\text{ClO}_4/[\text{PdCl}_2(\eta^3\text{-Meall})]\text{AsPh}_4$ (molar ratio 1/1). This spectrum is characterized by a broad $\delta(\text{N}=\text{C}-\text{H})$ signal at 8.78 ppm and two sharp singlets at 3.75 and 2.86 ppm, due to the *syn* (H_1 , H_4) and *anti* (H_2 , H_3) allylic protons, respectively. This is a strong evidence that a fast *syn-anti*, *anti* exchange takes place in this system at 35°C , caused by the rapid (on the NMR time scale) establishment of equilibria 3, which entails scrambling of the $\text{Pd}(\eta^3\text{-Meall})$ unit among the different allyl complexes involved. A similar spectrum is displayed by $\{[\text{PdCl}(\eta^3\text{-Meall})]_2(\text{DAB}^{\text{IV}})\}$ (Fig. 5b and Table II). The broad $\delta(\text{N}=\text{C}-\text{H})$ signal at 8.62 ppm and the sharp $\delta(\text{H}_2$, $\text{H}_3)$, $\delta(\text{H}_1$, $\text{H}_4)$ and $\delta(\text{CMe}_3)$ singlets at 2.80, 3.81 and 1.39 ppm, respectively, are each resolved into four non-equivalent signals at -50°C . Although a detailed study was not attempted, the features of the low temperature spectrum suggest the presence of various conformers of III, since no $\delta(\text{N}=\text{C}-\text{H})$ resonance attributable to free DAB^{IV} and/or $[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{IV}})]^+$ was detected.

The ^1H NMR spectrum in CDCl_3 at 35°C of the reaction mixture $\text{DAB}^{\text{III}}/[\text{PdCl}(\eta^3\text{-Meall})]_2$ (molar ratio $\text{DAB}^{\text{III}}/\text{Pd } 1/2$) is reported in Fig. 5c. In this case the allylic proton signals appear as broad resonances centered at 2.86 and 3.50 ppm (Table II), which indicates a markedly lower exchange rate as compared to the previous systems. Lowering the temperature to -40°C (Fig. 5d) leads to an almost complete freezing of the exchange, whereupon the allylic protons give rise to four singlets. Two of these (at 2.98 and 3.07 ppm) are assigned to the *anti* and *syn* protons of the cationic species $[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{III}})]^+$ respectively (cf. the spectrum of $[\text{Pd}(\eta^3\text{-Meall})(\text{DAB}^{\text{III}})]\text{ClO}_4$ in CDCl_3). The other two singlets at 2.71 and 3.78 ppm are assigned to the *anti* and *syn* protons of the anion $[\text{PdCl}_2(\eta^3\text{-Meall})]^-$ respectively (cf. the spectrum of $[\text{PdCl}_2(\eta^3\text{-Meall})]\text{-AsPh}_4$ in CDCl_3). The 3.78 ppm signal is partially masked by the stronger resonance of the OMe group at 3.76 ppm.

The ^1H NMR spectrum of product IV, $[\text{Pd}(\eta^3\text{-Meall})(\text{bipy})][\text{PdCl}_2(\eta^3\text{-Meall})]$, in CDCl_3 also appears as a superposition of the spectra of $[\text{Pd}(\eta^3\text{-Meall})(\text{bipy})]\text{BF}_4$ and $[\text{PdCl}_2(\eta^3\text{-Meall})]\text{AsPh}_4$ even at 35°C (see Table II and Fig. 5e). The broadness of the four allylic proton singlets indicates that the *syn-syn* and *anti-anti* exchange upon anion-cation interaction is still operating at this temperature, albeit at a much lower rate than the other systems.

From the above discussion it follows that the exchange rate depends on the nature of diazabutadiene ligands in the order



which is the reverse order of stability of the cationic complexes $[\text{Pd}(\eta^3\text{-Meall})(\text{DAB})]^+$ resulting from the equilibrium studies in acetonitrile.

References

- 1 K. Vrieze, 'Fluxional Allyl Complexes', in 'Dynamic Nuclear Magnetic Resonance Spectroscopy', L. M. Jackman and F. A. Cotton, Eds., Academic Press, New York (1975) and references therein.
- 2 G. Carturan, A. Scrivanti, U. Belluco and F. Morandini, *Inorg. Chim. Acta*, **27**, 37 (1978), and references therein.
- 3 B. Crociani, G. Bandoli and D. A. Clemente, *J. Organometal. Chem.*, **184**, 269 (1980) and references therein.
- 4 a) H. tom Dieck and M. Svoboda, *Chem. Ber.*, **109**, 1657 (1976);
b) H. van der Poel, G. van Koten and K. Vrieze, *J. Organometal. Chem.*, **135**, C63 (1977);
c) *Idem*, *Inorg. Chem.*, **19**, 1145 (1980).
- 5 a) D. Leibfritz and H. tom Dieck, *J. Organometal. Chem.*, **105**, 255 (1976);
b) L. H. Staal, A. Oskam and K. Vrieze, *J. Organometal. Chem.*, **145**, C7 (1978).
- 6 H. tom Dieck and I. W. Renk, *Chem. Ber.*, **104**, 110 (1971).
- 7 F. R. Hartley and S. R. Jones, *J. Organometal. Chem.*, **66**, 465 (1974).
- 8 J. Lukas, B. E. Morris and A. Clementi, *Inorg. Synt.*, **15**, 79 (1974).
- 9 B. Crociani and R. L. Richards, *J. Chem. Soc. Dalton Trans.*, 693 (1974).
- 10 I. D. Rae, B. E. Reichert and B. O. West, *J. Organometal. Chem.*, **81**, 227 (1974) and references therein.
- 11 A. J. Deeming, I. P. Rothwell, M. B. Hursthouse and K. M. Abdul Malik, *J. Chem. Soc. Dalton Trans.*, 1899 (1979).
- 12 J. B. Stothers, 'Carbon-13 NMR Spectroscopy', Academic Press, New York and London (1972).
- 13 R. W. Balk, D. J. Stufkens and A. Oskam, *Inorg. Chim. Acta*, **28**, 133 (1978).
- 14 L. H. Staal, D. J. Stufkens and A. Oskam, *ibid.*, **26**, 255 (1978).
- 15 a) E. R. Malinowski, *Anal. Chem.*, **49**, 602, 612 (1977);
b) P. Uguagliati *et al.*, *Anal. Chim. Acta, Computer Techn. and Optim.*, in press.
- 16 W. E. Wentworth, W. Hirsch and E. Chen, *J. Phys. Chem.*, **71**, 218 (1967).
- 17 D. W. Marquardt, *JSIAM*, **2**, 431 (1963); T. Tabata and R. Ito, *Computer J.*, **18**, 250 (1975).
- 18 D. M. Olsson and L. S. Nelson, *Technometrics*, **17**, 45 (1975).
- 19 H. van der Poel, G. van Koten, K. Vrieze, M. Kokkes and C. H. Stam, *Inorg. Chim. Acta*, **39**, 197 (1980).
- 20 G. van Koten, personal communication.