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THE PREPARATION AND COORDINATION PROPERTIES OF 1,4-DIAZA-3-METHYLBUTADIENE-2-YLPALLADIUM(II) COMPLEXES WITH DIFFERENT SUBSTITUENTS ON THE IMINO NITROGEN ATOMS

BRUNO CROCIANI *
Centro Chimica Tecnologia Composti Metallorganici Elementi Transizione C.N.R., Istituto di Chimica Industriale, Via Marzolo, 9 Padova (Italy)
and RAYMOND L. RICHARDS
School of Molecular Sciences, University of Sussex, Brighton, BN1 9QJ (Great Britain)

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Summary

The complexes *trans*-$[PdCl\{\overline{C(=NR)C}(Me)=NR'\}(PPh_3)_2]$ (R = C_6H_{11}, *p*-C_6H_4OMe; R$'$ = *p*-C_6H_4OMe, Me) containing a σ-bonded 1,4-diaza-3-methylbutadiene-2-yl group with different substituents on the nitrogen atoms have been prepared by two routes. The first involves initial methylation of the mixed isonitrile complex $[PdCl_2(CNR)(CNR')]$ by $HgMe_2$, followed by reaction with PPh_3 (Pd/PPh_3 molar ratio 1/2). The second method involves condensation of primary aliphatic amines with the carbonyl group of the 1-azabut-1-en-3-one-2-yl moiety of the complex *trans*-$[PdCl\{\overline{C(=NR)C}(Me) = O\}(PPh_3)_2]$. The 1,4-diaza-3-methylbutadiene-2-yl derivatives act through their imino nitrogen atoms as chelating ligands towards anhydrous metal chlorides MCl_2 (M = Co, Ni, Cu, Zn). Magnetic moment measurements and the far-infrared and electronic spectra of these adducts indicate an essentially pseudo-tetrahedral configuration at M in the solid and in solution. With the $ZnCl_2$ adducts, the ^1H NMR pattern for the phenyl protons of the *p*-methoxyphenyl N-substituent depends upon the position of the substituent in the 1,4-diazabutadiene chain.

Introduction

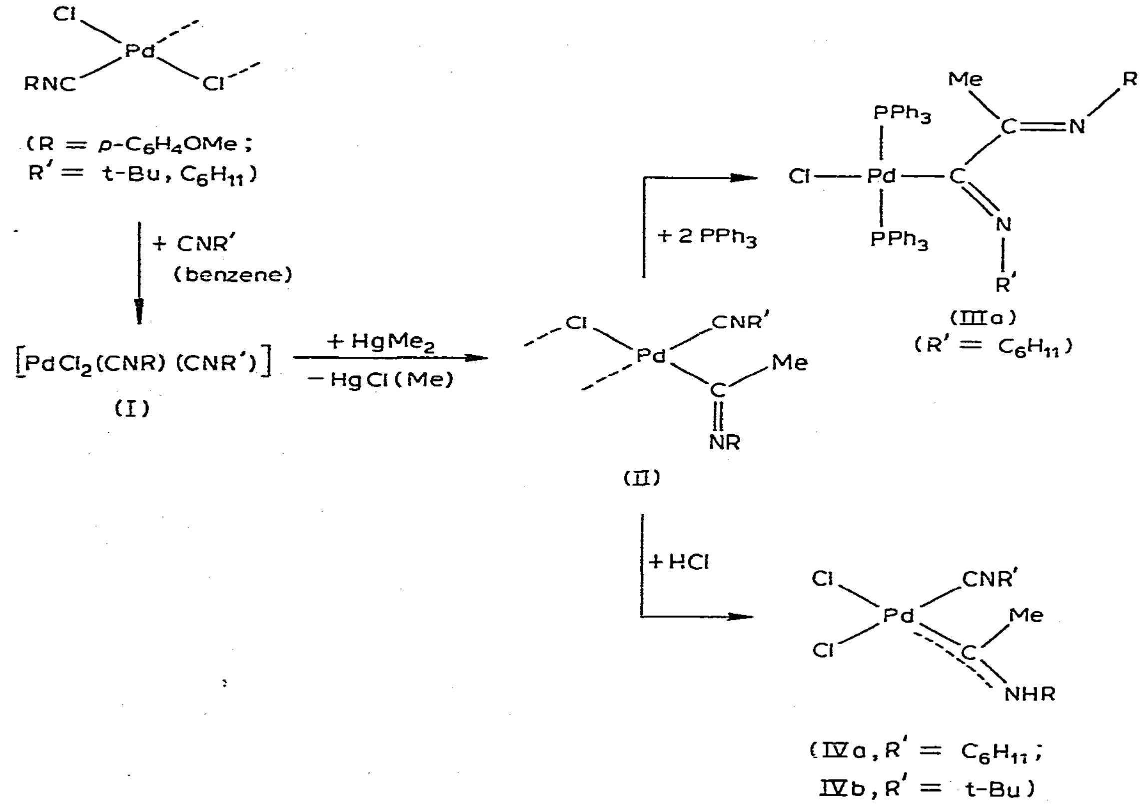
We previously described the preparation of 1,4-diaza-3-methylbutadiene-2-ylpalladium(II) complexes of the type *trans*-$[PdCl\{\overline{C(=NR)C}(Me)=NR\}(PPh_3)_2]$ having the same substituent R on both imino nitrogen atoms [1], and also of their adducts with anhydrous metal halides of the first transition series [2]. The ligating ability of such an organic moiety and the physico-chemical properties of the resulting binuclear compounds are affected by the electronic and steric requirements of the N-substituents [2b]. To examine the extent of these effects we have extended our study to the preparation of the related complexes, *trans*-$[PdCl\{C(=NR)C(Me)=NR'\}(PPh_3)_2]$, with different substituents on the nitrogen atoms. These compounds, obtained by two distinct synthetic routes, together with some of their coordination reactions, are reported in this paper.

Results and discussion

Preparation of diazabutadiene ligands

The first preparative method for 1,4-diaza-3-methylbutadiene-2-ylpalladium(II) derivatives with different N-substituents is shown in Scheme 1.

SCHEME 1



The chloro-bridged binuclear complex $[PdCl_2(CN\text{-}p\text{-}C_6H_4OMe)]_2$ easily reacts with the stoichiometric amount of the aliphatic isonitrile, CNR', to give the mixed-ligand compounds I as the major product [3]. These compounds were treated in situ with a benzene solution of $HgMe_2$ to yield the imino derivatives II, a reaction analogous to that reported for the complexes *cis*-$[PdCl_2(CNAr)L]$ ($L = PPh_3$, CNAr; Ar = Ph, $p\text{-}C_6H_4Me$, $p\text{-}C_6H_4OMe$) [1,4]. The methylation has been shown to occur at the more electron deficient aromatic isonitrile carbon atom by conversion of II with gaseous HCl [4] to the methyl(p-methoxyphenylamino)carbene complexes IV, whose IR and ^1H NMR spectra show that the aliphatic isonitrile (CNR′) has not undergone any reaction with $HgMe_2$. Furthermore, when treated with an excess of PPh_3 the aliphatic isonitrile ligand is partially displaced and is easily identified in the reaction mixture by IR spectroscopy (In benzene solution the stretching vibration (C≡N) of the free isonitriles occurs at 2140 and 2138 cm^{-1} for CNC_6H_{11} and CNBu-t respectively, while for CN-*p*-C_6H_4-OMe it occurs at significantly lower frequency (2125 cm^{-1})).

The reaction of II (R′ = C_6H_{11}) with PPh_3 yields the 1-cyclohexyl-4-*p*-methoxphenyl)-1,4-diaza-3-methylbutadiene-2-yl derivative IIIa. The imino intermediate II (R′ = C_6H_{11}) is characterized in benzene solution by a strong ν(C≡N) IR band of coordinated isonitrile at 2215 cm^{-1}. This band shifts to 2205 cm^{-1} as soon as PPh_3 is added to the reaction mixture, because of a fast chloro-bridge splitting reaction. The intensity of the latter band decreases with time as the insertion of the coordinated cyclohexylisocyanide into the Pd—C σ-bond of II progresses, until it completely disappears, ca. 90 min after initial PPh_3 addition. A similar reaction time was also observed for the same reaction with R = R′ = C_6H_{11}, whereas for R = R′ = *p*-C_6H_4OMe the insertion was completed after ca. 15 min [2b]. Probably the different electrophilic character of the terminal carbon of the coordinated isonitrile CNR′ in the imino intermediates II is responsible for the variation in reaction rate [5].

The product IIIa obtained from the first precipitation (see Experimental) contains a small amount (ca. 10%, as measured from its ^{1}H NMR spectrum) of the complex *trans*-$[PdCl\{C(=NR)C(Me)=NR\}(PPh_3)_2]$ (R = *p*-C_6H_4OMe). Since this compound can be prepared by a reaction sequence analogous to that shown in Scheme 1 starting from *cis*-$[PdCl_2(CN\text{-}p\text{-}C_6H_4OME)_2]$ [1] its presence in the product IIIa prompted us to study in some detail the reaction of $[PdCl_2(CN\text{-}p\text{-}C_6H_4OMe)]_2$ with CNC_6H_{11} (1/2 molar ratio) in benzene solution. The IR spectrum of the reaction mixture shows two very strong ν(C≡N) bands at 2240 and 2225 cm^{-1} with two unresolved shoulders at 2250 and 2218 cm^{-1} respectively. The ^{1}H NMR spectrum of the same mixture in C_6D_6 shows four OMe signals in the region 3.3—3.0 ppm (see Fig. 1).

The species giving rise to the main signal at δ 3.28 ppm is considered to be *cis*-$[PdCl_2(CNC_6H_{11})(CN\text{-}p\text{-}C_6H_4OMe)]$ because the IR spectrum of the reaction solution shows the two very strong ν(C≡N) bands expected for such a complex. An analogous compound, *cis*-$[PdCl_2(CNC_6H_{11})(CN\text{-}p\text{-}C_6H_4Me)]$, was obtained in ca. 60% yield from the reaction of $[PdCl_2(CN\text{-}p\text{-}C_6H_4Me)]_2$ with CNC_6H_{11} in tetrahydrofuran [3]. The signals at δ 3.17 and 3.08 ppm respectively are due to a small amount of $[PdCl_2(CN\text{-}p\text{-}C_6H_4OMe)_2]$, probably present as both *cis* and *trans* isomers.

This assignment was confirmed by the ^{1}H NMR spectrum of an authentic sample of $[PdCl_2(CN\text{-}p\text{-}C_6H_4OMe)_2]$ in a C_6D_6 solution to which some $[PdCl_2(CNC_6H_{11})_2]$ was added in order to increase the solubility. The remaining signal at δ 3.19 ppm is very likely due to the isomer *trans*-$[PdCl_2(CNC_6H_{11})(CN\text{-}p\text{-}C_6H_4OMe)]$.

The two broad signals at ca. 3.9 and 3.0 ppm shown in Fig. 1 are due to N—CH of the cyclohexyl groups.

These various species may arise from a redistribution reaction of the type:

$$[PdCl_2(CNR)]_2 + 2\,CNR' \rightarrow$$

$$2[PdCl_2(CNR)(CNR')] \rightleftharpoons [PdCl_2(CNR)_2] + [PdCl_2(CNR')_2]$$

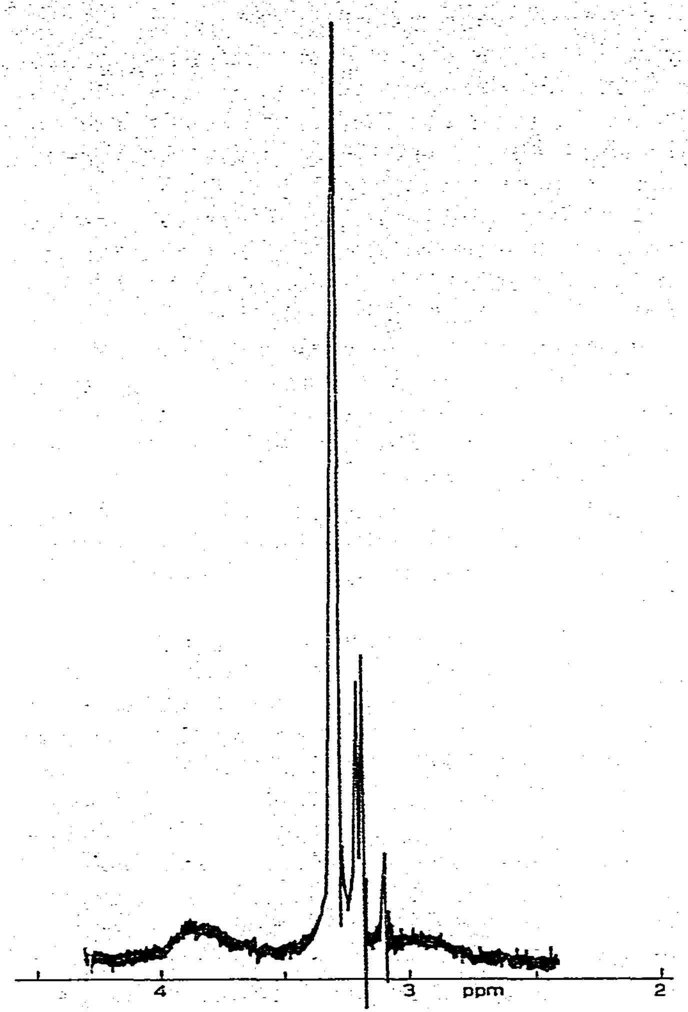


Fig. 1. ^{1}H NMR spectrum in the range 4.3—2.5 ppm for the reaction $[PdCl_2(CN\text{-}p\text{-}C_6H_4OMe)]_2$ + 2 CNC_6H_{11} in C_6D_6.

in which each palladium compound is present in both *cis* and *trans* isomers.

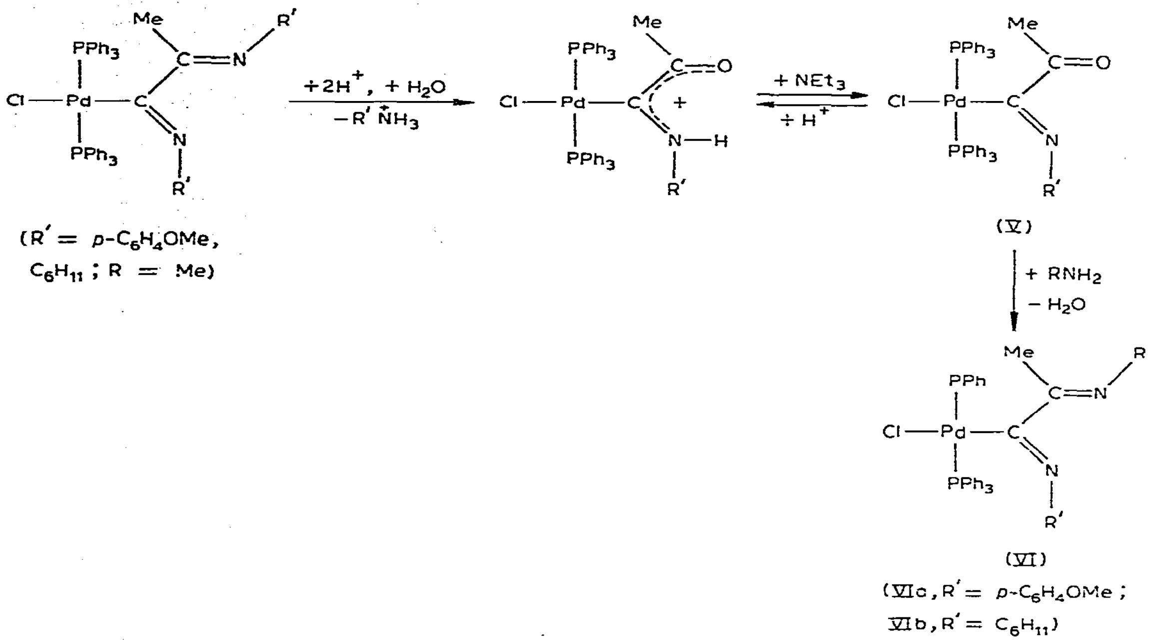
Treatment of the complexes $[PdCl_2(CNR)_2]$ and $[PdCl_2(CNR')_2]$ with $HgMe_2$ (Scheme 1) eventually leads to 1,4-diazabutadiene-2-yl derivatives with the same substituents on both imino-nitrogen atoms, the less soluble of which (i.e. the compound with R = p-C_6H_4OMe [2b]) precipitates during the isolation of IIIa.

The second preparative method for 1,4-diaza-3-methylbutadiene-2-ylpalladium(II) derivatives with different N-substituents is shown in Scheme 2.

The course of the hydrolysis and deprotonation reactions leading to the 1-azabut-1-ene-3-one-2-yl derivative V, and the nature of the products involved, have been already reported and discussed [6].

This compound is a useful intermediate since it can undergo a condensation

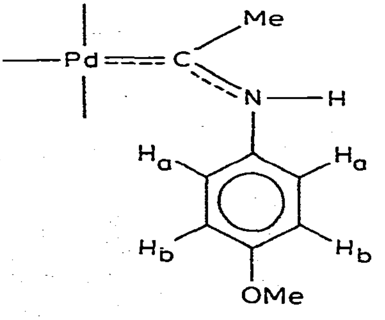
SCHEME 2



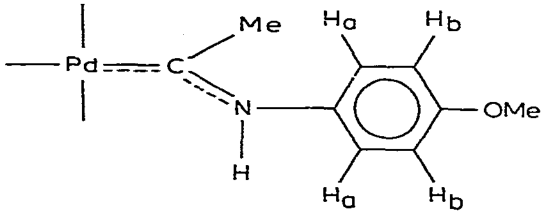
reaction at the carbonyl group with primary amines yielding 1,4-diazabutadiene-2-yl complexes of the type VI.

We report here only the reaction with MeNH$_2$, but preliminary tests have shown that V can react in a similar way with a variety of primary aliphatic amines carrying other functional groups, such as ethanolamine, ethylenediamine or diethylenetriamine, to give tridentate or tetradentate organometallic ligands.

The carbene derivatives IV have a *cis* configuration as indicated by the presence of two ν(Pd—Cl) bands in the range 317—281 cm^{-1}. The N—H and $C\overset{\cdots}{-}N$ stretching frequencies are very close to those reported for related complexes [4,7]. Restricted rotation around the $C\overset{\cdots}{-}N$ bond of the methyl(*p*-methoxyphenylamino)carbene group could give two isomers, A or B.



(A)



(B)

The ^{1}H NMR spectrum of *cis*-[PdCl$_2${C(NH-*p*-C$_6$H$_4$OMe)Me}(CNBu-t)] (IVb) at room temperature, shows that only one isomer is present in CDCl$_3$ solution, to which structure A is assigned since the *ortho* protons H_a are shifted to low

TABLE 1

ANALYTICAL AND PHYSICAL DATA

Compound	Colour	Melting points (°C) [a]	Analysis (Found (calcd.) (%))				Molecular weights (found (calcd.))	μ_{eff} [b] (BM)
			C	H	N	Cl		
$[PdCl\{\overline{C(=NC_6H_{11})C}(Me){=}N\text{-}p\text{-}C_6H_4OMe\}(PPh_3)_2]$ (IIIa)	pale-yellow	134	68.0 (67.81)	5.5 (5.56)	3.0 (3.03)	3.9 (3.84)	873 (928.7)	
$[PdCl_2\{C(NH\text{-}p\text{-}C_6H_4OMe)Me\}(CNC_6H_{11})]$ (IVa)	pale-yellow	175—180	43.8 (44.11)	5.0 (5.00)	6.4 (6.43)	16.4 (16.27)		
$[PdCl_2\{C(NH\text{-}p\text{-}C_6H_4OMe)Me\}(CNBu\text{-}t)]$ (IVb)	cream-yellow	210	41.3 (41.05)	4.8 (4.92)	6.8 (6.84)	17.0 (17.31)		
$[PdCl\{\overline{C(=N\text{-}p\text{-}C_6H_4OMe)C}(Me){=}NMe\}(PPh_3)_2]$ (VIa)	yellow	148—155	65.7 (65.97)	4.9 (5.07)	3.3 (3.27)	4.2 (4.14)	894 (855.6)	
$[PdCl\{\overline{C(=NC_6H_{11})C}(Me){=}NMe\}(PPh_3)_2]$ (VIb)	pale-yellow	144—147	66.1 (66.43)	5.6 (5.70)	3.4 (3.37)	4.3 (4.26)	800 (831.6)	
$[CoCl_2$—IIIa$]$	green	200	59.3 (59.28)	4.9 (4.88)	2.7 (2.66)	10.2 (10.10)	1024 (1053.6)	4.44 [4.39]
$[NiCl_2$—IIIa$]$	red-brick	205—211	59.1 (59.29)	4.8 (4.88)	2.7 (2.66)	10.2 (10.09)	1180 (1053.4)	3.64 [3.50]
$[CuCl_2$—IIIa$]$	dark-brown	178—181	59.1 (59.02)	4.8 (4.86)	2.7 (2.65)	10.2 (10.05)	1087 (1058.2)	2.20 [1.81]
$[ZnCl_2$—IIIa$]$	deep-yellow	181—185	59.2 (58.92)	4.7 (4.85)	2.6 (2.64)	10.2 (10.03)	1055 (1060)	
$[CoCl_2$—VIa$]$	pale-green	202	56.9 (57.28)	4.3 (4.40)	2.8 (2.84)	10.9 (10.79)	1006 (985.5)	4.61 [4.70]
$[CuCl_2$—VIa$]$	brown	180	56.9 (57.01)	4.4 (4.37)	2.8 (2.83)	10.9 (10.74)	973 (990)	2.14 [1.85]
$[ZnCl_2$—VIa$]$	yellow	200	56.7 (56.90)	4.3 (4.37)	2.8 (2.82)	10.8 (10.72)	1003 (991.9)	

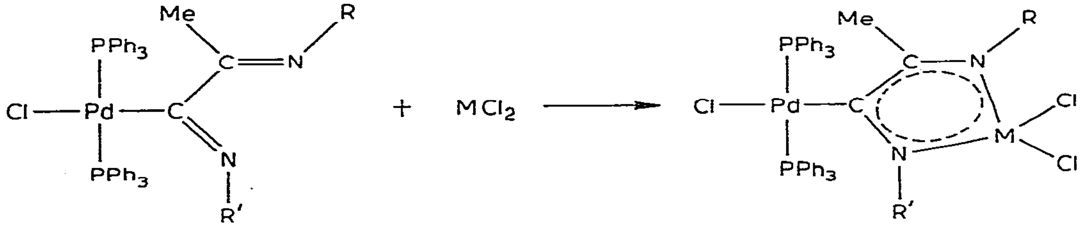
[a] Uncorrected values; all compounds decompose on melting. [b] The figures in square brackets refer to magnetic moment measured in CH_2Cl_2 solutions 10^{-2} *M* at 25°C; the magnetic moment in the solid state has been measured at 20°C.

field due to interaction with the metallic centre which is only possible for isomer A [7,8]. The complex *cis*-$[PdCl_2\{C(NH\text{-}p\text{-}C_6H_4OMe)Me(CNC_6H_{11})\}]$ (IVa) shows both A and B isomers in 4/1 ratio, the minor isomer B having δ(C—Me) at 2.82, δ(O—Me) at 3.87 and δ(N—H) at 11.0 ppm (see Table 4). The C_6H_4 signals occur in the range 7.3—6.7 ppm and are partially overlapped by the more intense resonances of the *meta* protons H_b of isomer A.

Coordination properties of diazabutadiene ligands

The 1,4-diaza-3-methylbutadiene-2-yl derivatives (IIIa and VIa) act as chelating bidentate ligands towards anhydrous metal chlorides of the first transition series according to Scheme 3.

SCHEME 3



(IIIa, R = p-C_6H_4OMe ; R' = C_6H_{11};
VIa, R = Me ; R' = p-C_6H_4OMe)

$[MCl_2$ - IIIa$]$
$[MCl_2$ - VIa$]$
(M = Co, Ni, Cu, Zn)

Derivatives IIIa and VI and the corresponding binuclear adducts are monomers in 1,2-dichloroethane solution (see Table 1). Only the complex $[NiCl_2$—IIIa$]$ has a molecular weight slightly higher than the calculated one as found also for other related nickel(II) binuclear compounds [2], and probably these complexes are partially associated in solution [9].

The adducts with $CoCl_2$, $NiCl_2$ and $CuCl_2$ are high-spin paramagnetic compounds with 3, 2 and 1 unpaired electrons respectively. The solid-state values of μ_{eff} for the cobalt(II) and nickel(II) derivatives are close to those measured in CH_2Cl_2 solution, whereas for the analogous copper(II) complexes, the magnetic moments in solution are significantly lower (by 0.3—0.4 BM).

The IR spectra of IIIa, VIa and VIb show two strong ν(C=N) bands in the range 1633—1563 cm^{-1} and one ν(Pd—Cl) band at rather low frequencies (255—247 cm^{-1}, see Table 2), an indication of the high *trans*-influence of the σ-bonded 1,4-diazabutadiene-2-yl group [1,2b].

Upon coordination, the (C=N) bands of complex IIIa are shifted to lower frequencies and reduced in intensity. In the adducts of VIa only one low intensity band is observed in the range 1520—1515 cm^{-1}.

This might be due to the formation of a delocalised π-electron system on the 5-membered ring by interaction of the C=N double bonds and *d* orbitals of appropriate symmetry of the metal M, similar to that deduced to occur in complexes of purely organic 1,4-diazabutadiene ligands on the basis of IR and NMR studies and force constants calculations [10,11]. Another typical effect of coordi-

TABLE 2

CHARACTERISTIC IR BANDS (cm^{-1})

Compound	ν(N—H)	ν(C$\equiv$N)	ν(C=N)	ν(Pd—Cl)	ν(M—Cl)
IIIa			1629ms, 1571ms	250ms	
IVa	3220(sh), 3180m 3150(sh)	2235s	1573ms	361ms, 282ms	
IVb	3220(sh), 3180m 3140(sh)	2220s	1569ms	317ms, 281ms	
VIa			1630s, 1563s	255m	
VIb			1633s, 1583s	247m	
[$CoCl_2$—IIIa]			1585m, 1522ms	298ms	350s, 332ms
[$NiCl_2$—IIIa]			1586m, 1516ms	298ms	343s, 335(sh)
[$CuCl_2$—IIIa]			1584m, 1519m	296ms or 305(sh)	322m, 305(sh) or 296ms
[$ZnCl_2$—IIIa]			1592m, 1532ms	300ms	337s, 320m
[$CoCl_2$—VIa]			1515(sh)	292m	346ms, 334ms
[$CuCl_2$—VIa]			1515(sh)	297m	321m, 297m
[$ZnCl_2$—VIa]			1520(sh)	297(sh)	330s, 318s

nation is to shift the (Pd—Cl) band to higher frequencies by 40—50 cm^{-1}, due to the reduced *trans*-influence of the chelated 1,4-diazabutadiene-2-yl moiety [1,2b].

All the binuclear complexes exhibit two M—Cl stretching vibrations in ranges typical of non-associated pseudo-tetrahedral compounds [$MCl_2(L)_2$] and [MCl_2(L—L)] (M = Co, Ni, Cu, Zn), where L and L—L are monodentate and chelating bidentate N-donor ligands [2,12,13]. A pseudo-tetrahedral configuration in the solid is also indicated by the magnetic moment values [14,17]. For example, magnetic moments in the range 2.06—2.13 BM have been found for the copper derivatives [CuX_2(L—L)] (X = Cl, Br, L—L = C- and N-substituted ethylenediamines) in which tetrahedral geometry is favoured by the steric requirements of the bulky bidentate ligands [18,19].

The binuclear complexes also have a distorted tetrahedral configuration at the metal centre M in CH_2Cl_2 solution as indicated by their electronic spectra in the range 25000—5000 cm^{-1} (Table 3). A typical feature of these spectra is the presence of a strong metal→ligand charge-transfer band with a maximum at frequencies higher than 25000 cm^{-1}, the position of which depends on the nature of the coordinated metal M and particularly on the N-substituents of the 1,4-diazabutadiene-2-yl ligands [2b,20—22]. In certain cases this band tails considera-

TABLE 3

ELECTRONIC SPECTRA IN THE VISIBLE AND NEAR-INFRARED REGION [a]

[$CoCl_2$—IIIa]	16807(162); 15270(sh); 14815(392)	9804(32); 7300(87); 6130(sh)
[$CoCl_2$—VIa]	16950(155); 15270(sh); 14815(445)	9434(16); 7380(77); 6130(sh)
[$NiCl_2$—IIIa]	m [b]	11560(41); 9850(63); 8330(sh)
[$CuCl_2$—IIIa]		10640(br) (128)
[$CuCl_2$—VIa]		12190(br)(166)

[a] The band maxima are in cm^{-1}; the molar extinction coefficients ϵ are in parentheses. [b] Masked by the charge-transfer band tail (see text).

bly into the visible region of the spectrum, masking some of the *d*—*d* transition of the metal M and becoming partially responsible for the colours of the complexes [2b]. This effect is particularly evident in the spectrum of the adduct [$NiCl_2$—IIIa], in which the region 25000—14300 cm^{-1} is completely hidden. Although molecular weight measurements indicate a slight association in solution for this compound, the position and the intensity of the observable *d*—*d* bands suggest that the pseudotetrahedral species predominates [9,13,16,19]. The green colour of the cobalt derivatives, [$CoCl_2$—IIIa] and [$CoCl_2$—VIa],

TABLE 4

^{1}H NMR SPECTRA [a]

Compound	Signals	Assignment
IIIa	0.8—1.8 M(br)	$(CH_2)_5$
	1.32 S	C—Me
	3.77 S	O—Me
	4.65 M(br)	N—CH
	5.55—5.85 M [b]	C_6H_4
	6.5—6.8 M [b]	C_6H_4
	7.0—8.0 M	P—C_6H_5
IVa [c]	0.8—2.3 M(br)	$(CH_2)_5$
	2.82 S, 3.11 S	C—Me
	3.7 M(br)	N—CH
	3.87 S, 3.90 S	O—Me
	6.7—7.3 M [b]	C_6H_4
	8.1—8.5 M [b]	C_6H_4
	11.0 br, 12.8 br	NH
IVb	1.31 S	t-Bu
	3.12 S	C—Me
	3.88 S	O—Me
	6.8—7.2 M [b]	C_6H_4
	8.1—8.5 M [b]	C_6H_4
	13.6(br)	NH
VIa	1.01 S	C—Me
	3.02 S	N—Me
	3.84 S	O—Me
	6.6—6.9 M [d]	C_6H_4
	7.0—8.2 M	P—C_6H_5, C_6H_4
VIb	0.8—1.9 M(br)	$(CH_2)_5$
	0.97 S	C—Me
	2.75 S	N—Me
	4.65 M(br)	N—CH
	7.1—8.2 M	P—C_6H_5
[$ZnCl_2$—IIIa]	0.7—2.2 M (br)	$(CH_2)_5$
	1.92 S	C—Me
	3.76 S	O—Me
	5.15 M(br)	N—CH
	6.3—6.9 M	C_6H_4
	7.0—8.0 M	P—C_6H_5
[$ZnCl_2$—VIa]	1.97 S	C—Me
	2.73 S	N—Me
	3.83 S	O—Me
	6.4—6.6 M [b]	C_6H_4
	7.3—7.6 M	P—C_6H_5
	7.6—7.9 M [b]	C_6H_4

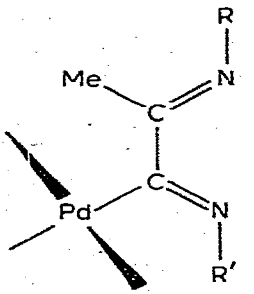
[a] Values in ppm from TMS as internal standard; S, singlet; M, multiplet; (br), broad. [b] Symmetrical sides of an AA'BB' signal. [c] Two isomers are present (see text). [d] Side of an AA'BB' signal; the other side is masked by the strong PPh_3 signals.

probably results from the combination of the charge-transfer band tail and the typical *d—d* bands of these pseudo-tetrahedral complexes [9,13,19,23].

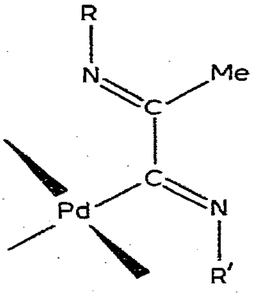
A distorted tetrahedral configuration can also be assigned to the $CuCl_2$ adducts in solution [13b,18,19]. The higher frequency position of the *d—d* band in the spectrum of [$CuCl_2$—VIa] suggests a more flattened tetrahedral structure for this compound, which may result from the reduced steric hindrance of the ligand VIa compared to that of IIIa [18]. The lower magnetic moment values of the complexes [$CuCl_2$—IIIa] and [$CuCl_2$—VIa] in CH_2Cl_2 solution relative to those in the solid state may also be explained by an increased flattening of the tetrahedral geometry at the copper atom in solution [18].

The ^1H NMR spectra of the 1,4-diaza-3-methylbutadiene-2-yl ligands, IIIa, VIa and VIb (see Table 4) suggests that only one of the various configurations, which can arise from restricted rotation in the conjugated double bond system, is present in $CDCl_3$ solution. This appears to be a general feature of all complexes of this type that have been studied so far [1,2b,24]. The structure of the only observed isomer is mainly influenced by steric factors, as has been observed in other bulky molecules such as palladium(II) and platinum(II) carbene complexes [25].

According to models the configurations with the least steric hindrance are C and D.



(C)



(D)

Structure C clearly must be assumed when these compounds act as chelating ligands.

In the $ZnCl_2$ adducts the signals of the methyl groups in position 3 of the diazabutadienyl ligand (C—Me in Table 4) are shifted downfield for both ligands IIIa and VIa. A downfield shift is also observed for the α proton resonance (N—CH$<$) of the cyclohexyl group at position 1 of ligand IIIa, while the signal of the methyl group at position 4 of ligand VIa (N—Me) moves upfield by 0.29 ppm. This opposite effect on the N—CH protons is probably related to a change of configuration in the 1,4-diazabutadiene-2-yl moiety upon coordination.

The aromatic protons of the p-C_6H_4OMe group appear as AA'BB' symmetrical multiplets which have different patterns and chemical shifts according to the position of this group on the diazabutadiene chain. This is clearly shown by the spectra of [$ZnCl_2$—VIa] and [$ZnCl_2$—IIIa] (Fig. 2 and Fig. 3, respectively).

In the spectrum of the complex [$ZnCl_2$—VIa] the signals at rather low-field (7.6—7.9 ppm in Fig. 2) are assigned to the *ortho* protons H_a because of the

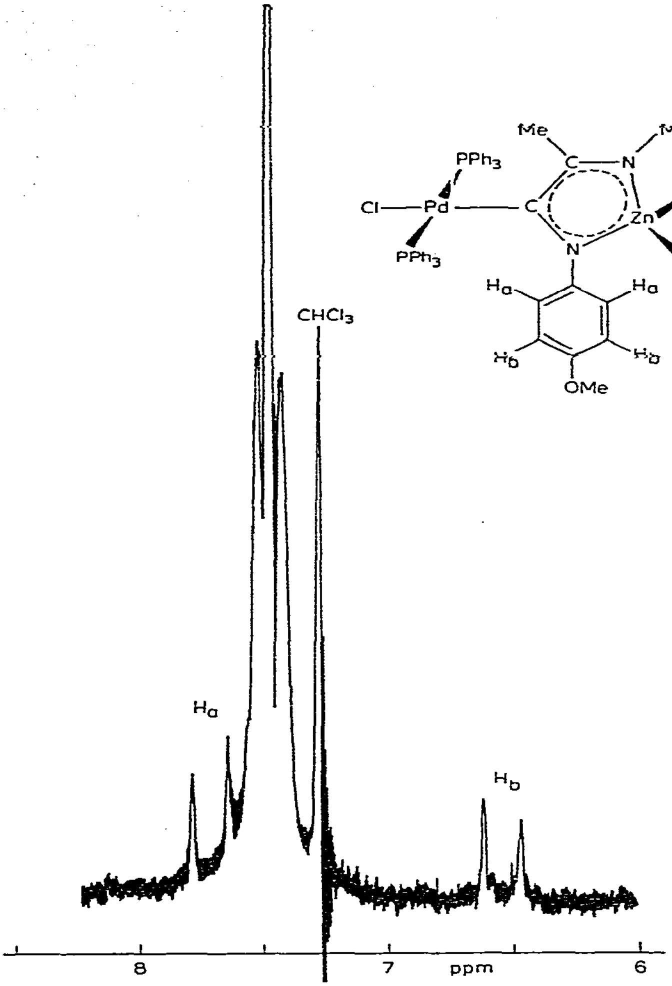


Fig. 2. ^{1}H NMR spectrum of the complex [$ZnCl_2$—VIa] in $CDCl_3$ solution in the phenyl region.

deshielding effect of the palladium atom in close proximity [7,8]. Similar low-field resonances for the p-C_6H_4OMe substituent at position 1 have been observed in the related compounds *trans*-[PdX{$\overline{\mathrm{C({=}N\text{-}}p\mathrm{\text{-}C_6H_4OMe)C}}$(Me)=N-$p$-$C_6H_4OMe$}-$(PPh_3)_2$] (X = Cl, Br) [2b] and in the methyl(p-methoxyphenylamino)carbene derivatives IV. In the free ligand VIa the *ortho* protons H_a are masked by the intense PPh_3 resoannce (see Table 4).

In the spectrum of the complex [$ZnCl_2$—IIIa] (Fig. 3) the H_a and H_b protons of the p-C_6H_4OMe group in position 4 appear in the narrow range 6.9—6.3 ppm, while in the free ligand they give rise to two more widely spaced symmetrical signals in the ranges 6.8—6.5 and 5.85—5.55 ppm.

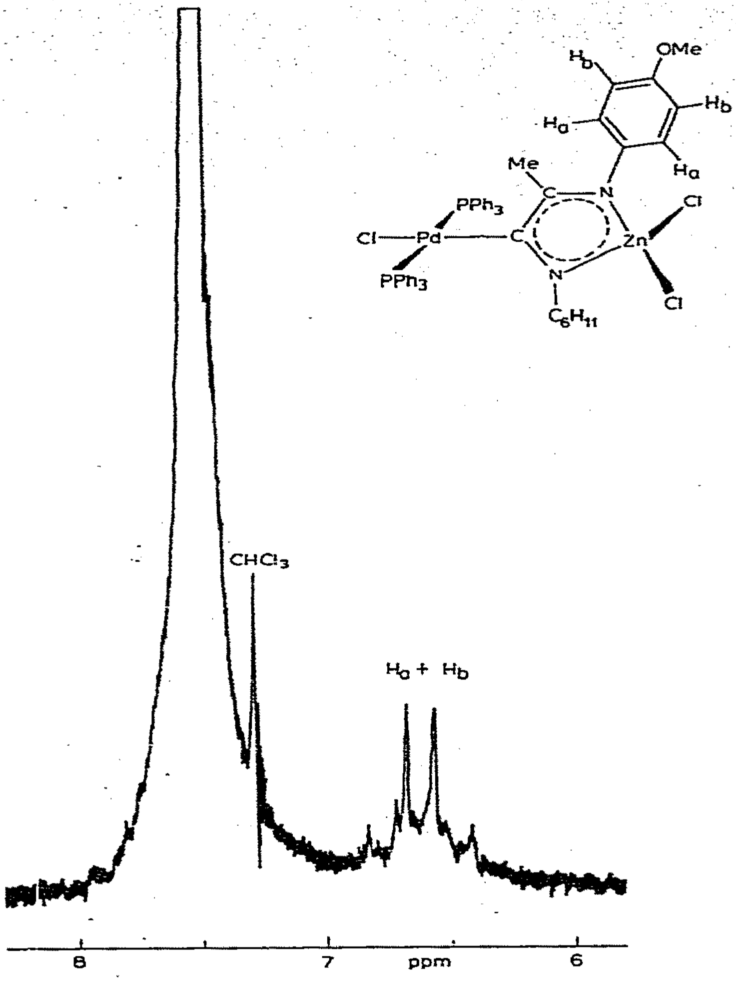


Fig. 3. ^{1}H NMR spectrum of the complex [ZnCl$_2$—IIIa] in CDCl$_3$ solution in the phenyl region.

Experimental

Isonitriles [26] and the palladium complexes, $[PdCl_2(CNR)]_2$ [3], *trans*-$[PdCl\{\overline{C(=NR)C}(Me)=NR\}(PPh_3)_2]$ [1,2b] and *trans*-$[PdCl\{\overline{C(=NR)C}(Me)=O\}(PPh_3)_2]$ [6] (R = *p*-C_6H_4OMe, C_6H_{11}), were prepared and purified by published methods. All other chemicals were reagent grade, and used without further purification. Infrared spectra were recorded with Perkin—Elmer 457 (4000—250 cm^{-1}) and Beckman IR 11 (400—120 cm^{-1}) instruments. Hexachlorobutadiene mulls and NaCl plates were used in the range 4000—1300 cm^{-1} and Nujol mulls and CsI or thin polythene discs in the range 1700—120 cm^{-1}. Electronic spectra in CH_2Cl_2 solution were recorded with a Cary model 14 Recording spectrophotometer in the range 25000—5000 cm^{-1} at room temperature, using quartz cells of 1 cm path length. ^{1}H NMR spectra were recorded with a Varian NV-14 60 MHz instrument at room temperature with $SiMe_4$ as internal reference. Magnetic moments were measured in the solid state with a Bruker Magnet BM6 instrument at 20°C.

Magnetic moments in CH_2Cl_2 solution were measured by published methods [27]. Molecular weights were measured with a Mechrolab osmometer at 37°C in 1,2-dichloroethane. Elemental analyses were made by A. Berton and G. Biasioli of the Microanalytical Laboratory, Laboratorio Radioelementi C.N.R., Padova.

Preparation of trans-$[PdCl\{\overline{C(=NC_6H_{11})C}(Me)=N\text{-}p\text{-}C_6H_4OMe\}(PPh_3)_2]$*, (IIIa)*

The complex $[PdCl_2(CN\text{-}p\text{-}C_6H_4OMe)]_2$ (1.24 g, 2 mmol) was suspended in benzene (100 cm^3) and treated with CNC_6H_{11} (0.44 g, 4 mmol) with stirring. The resulting clear yellow solution was treated with $HgMe_2$ (10 cm^3 of a benzene solution, 6.15×10^{-1} *M*). The reaction was complete in about 5—6 h at room temperature. During this time some decomposition also occurs, as indicated by the formation of metallic palladium. The reaction mixture was then treated with PPh_3 (2.1 g, 8 mmol) and stirred for 2 h. This reaction was complete in about 90 min as shown by IR spectroscopy of the solution (see text). Addition of charcoal and filtration gave a pale-yellow solution, which was concentrated to small volume at reduced pressure.

Some yellow-greenish product began to precipitate during the concentration. The precipitation was competed by addition of ethyl ether/n-hexane mixture (2/1, v/v). The small amount of Hg(Me)Cl still present in the compound was removed by sublimation (80°C, 10^{-2} mmHg, 4 h). The ^1H NMR spectrum of the resulting product showed the presence of about 10% of *trans*-$[PdCl\{\overline{C(=N\text{-}p\text{-}C_6H_4OMe)C}(Me)=N\text{-}p\text{-}C_6H_4OMe\}(PPh_3)_2]$, which was eliminated by fractional precipitations from the same solvents.

The yield of pure complex IIIa is about 40%.

Preparation of cis-$[PdCl_2\{C(NHR)Me\}(CNR')]$ *(R =* $p\text{-}C_6H_4OMe$*; R' =* C_6H_{11} *or t-Bu)*

The complex $[PdCl_2(CN\text{-}p\text{-}C_6H_4OMe)]_2$ (0.62 g, 1 mmol) was treated with the isonitrile CNR' (R' = C_6H_{11} or t-Bu, 2 mmol) and then with $HgMe_2$ (Pd/Hg molar ratio 1/1.5) as described above. Gaseous HCl was bubbled through the resulting benzene solution giving an immediate yellowish precipitate. After stirring for 10 min the mixture was taken to dryness at reduced pressure and the solid residue treated with $CHCl_3$ and charcoal. After filtration the clear yellow solution was concentrated to small volume (5—6 cm^3) and the product was precipitated with ethyl ether. Any trace of Hg(Me)Cl still present was removed by sublimation (80—100°C, 10^{-2} mmHg, 3 h). Analytically pure samples were obtained after two successive precipitations from the same solvents (yields 50—60%).

These compounds are stable when solid but tend to decompose in $CHCl_3$ solution.

Preparation of trans-$[PdCl\{\overline{C(=NR')C}(Me)=NMe\}(PPh_3)_2]$ *(R' =* $p\text{-}C_6H_4OMe$ *(VIa); R' =* C_6H_{11} *(VIb))*

Gaseous $MeNH_2$ was bubbled for 10 min through a solution of *trans*-$[PdCl\{\overline{C(=NR')C}(Me)=O\}(PPh_3)_2]$ (1 mmol) in CH_2Cl_2 (80 cm^3). The reaction mixture was stirred for 24 h in the presence of anhydrous Na_2SO_4. During this time the progress of the condensation reaction was monitored in solution for the C=O and C=N stretching frequencies (1750—1550 cm^{-1}). After filtration, the solvent was evaporated and the solid residue washed 4—5 times with distilled water.

The resulting crude product was dried in vacuo and then redissolved in CH_2Cl_2 (for R′ = p-C_6H_4OMe). After treatment with charcoal, filtration, and concentration to a small volume, the yellow crystalline product was precipitated by addition of ethyl ether (yield ≃60%).

In the case of R′ = C_6H_{11}, after being washed with water and dried in vacuo the crude product was redissolved in benzene and precipitated with n-hexane (yield ≃50%).

Preparation of [MCl_2—IIIa] and [MCl_2—VIa] (M = Co, Ni, Cu, Zn)

The 1,4-diazabutadiene-2-yl ligand (IIIa or VIa, 0.5 mmol), dissolved in CH_2Cl_2 (50 cm^3) was added dropwise to a stirred solution of anhydrous MCl_2 (0.5 mmol) in absolute ethanol (10 cm^3). After 30 min the reaction mixture was treated with charcoal and filtered. The resulting solution was evaporated at reduced pressure until the product began to precipitate. At this point the precipitation was completed by addition of ethyl ether. The binuclear complexes were purified by re-precipitation from CH_2Cl_2 solution with either ethyl ether or a mixture of ethyl ether/ethanol (3/1, v/v). The yields were 70—80% for [MCl_2—IIIa] and 80—90% for [MCl_2—VIa].

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