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# BINUCLEAR COMPLEXES OF 1,4-DIAZA-3-METHYLBUTADIEN-2-YL-PALLADIUM(II) DERIVATIVES WITH PALLADIUM(II) AND PLATINUM(II) CHLORIDES

BRUNO CROCIANI *,

*Centro Chimica Tecnologia Composti Metallorganici Elementi Transizione C.N.R., Istituto di Chimica Industriale, Via Marzolo 9, Padova (Italy)*

MARINO NICOLINI

*Istituto di Chimica Generale, University of Padova (Italy)*

and ANTONIO MANTOVANI

*Cattedra di Chimica, Facoltà di Ingegneria, University of Padova (Italy)*

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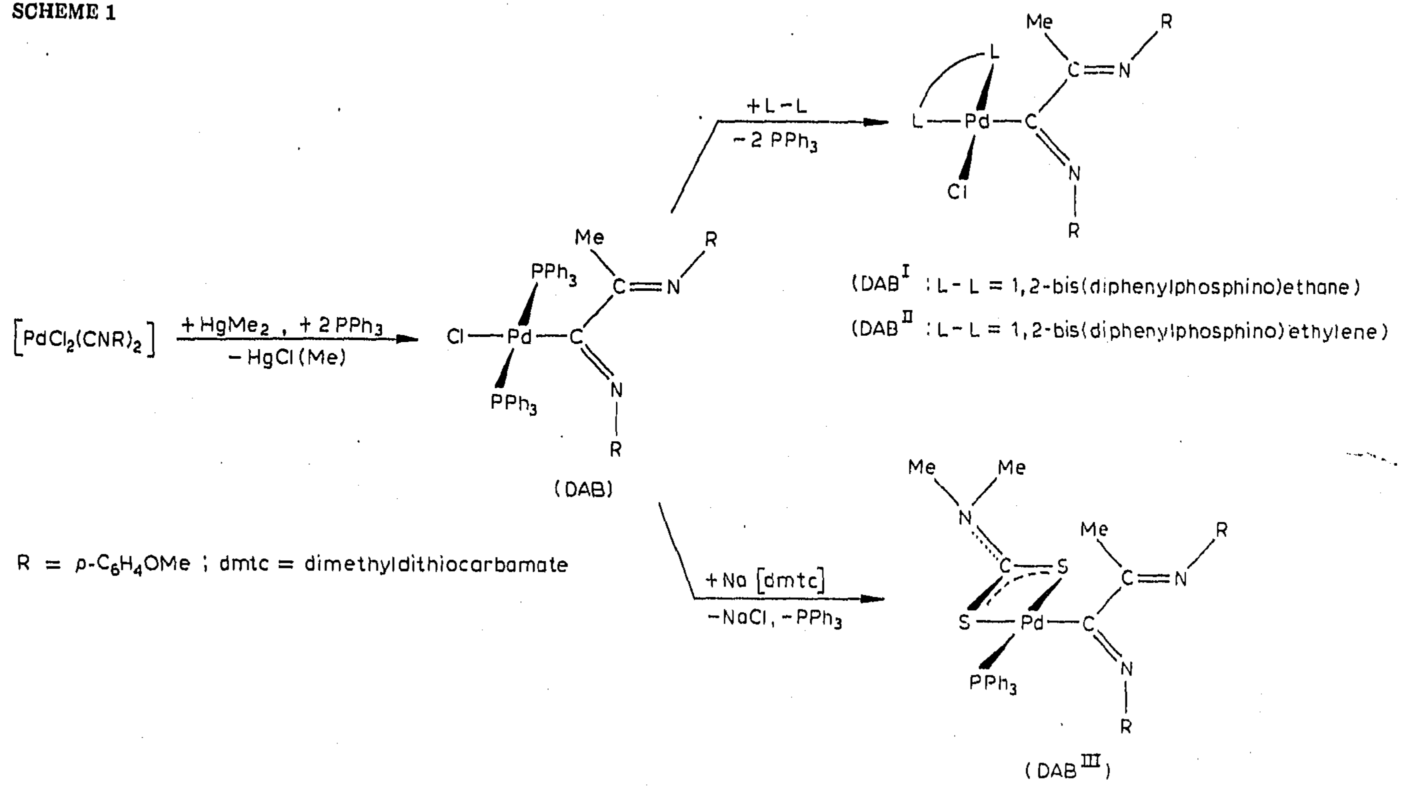
## Summary

The organometallic 1,4-diazabutadienes, RN=C(R')C(Me)=NR [$R = p\text{-}C_6H_4OMe$, R' = *trans*-PdCl($PPh_3$)$_2$ (DAB); PdCl(L—L), L—L = 1,2-bis(diphenylphosphino)-ethane (DAB$^{I}$), L—L = *cis*-1,2-bis(diphenylphosphino)ethylene (DAB$^{II}$); Pd(dmtc)-($PPh_3$), dmtc = dimethyldithiocarbamate (DAB$^{III}$)] react with ethylene or nitrile derivatives of palladium(II) and platinum(II), [$PdCl_2(CH_2{=}CH_2)]_2$, K[$PtCl_3(CH_2{=}CH_2)$], [$PdCl_2(N{\equiv}CMe)_2$], [$PtCl_2(N{\equiv}CPh)_2$] usually to give binuclear complexes of the type [$MCl_2${RN=C(R')C(Me)=NR}] (M = Pd, Pt), in which the 1,4-diazabutadiene group acts as a chelating bidentate ligand. The stability of these compounds in hot 1,2-dichloroethane or acetonitrile markedly depends on the nature of the ancillary ligands on the palladium atom of the group R'. When a chelating diphosphine is present, as in the case of DAB$^{I}$ and DAB$^{II}$, the corresponding binuclear complexes are recovered unchanged even after long refluxing times. In the case of DAB and DAB$^{III}$ adducts, a transfer of $PPh_3$ and dmtc ligands from the Pd atom of R' to the metal atom M of the coordinated $MCl_2$ unit occurs with the formation of *trans*-[$MCl_2(PPh_3)_2$] and of the new bimetallic complexes, [M(dmtc){RN=C(R'')C(Me)=NR}] (R'' = *cis*-$PdCl_2(PPh_3)$ (DAB$^{IV}$)), respectively. The rates of ligand transfer for the $PdCl_2$ adducts are much higher than for the $PtCl_2$ analogues.

## Introduction

We have previously described the preparation of organometallic α-diimines

SCHEME 1



(DAB$^{I}$ : L − L = 1,2-bis(diphenylphosphino)ethane)

(DAB$^{II}$ : L − L = 1,2-bis(diphenylphosphino)ethylene)

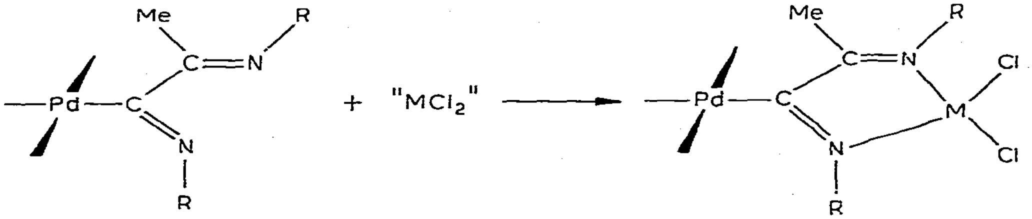
R = $p$-$C_6H_4OMe$ ; dmtc = dimethyldithiocarbamate containing the 1,4-diaza-3-methylbutadien-2-yl group * $\sigma$-bonded to palladium(II), $RN{=}C(R')C(Me){=}NR''$ [$R = R''$ = Ph, $p$-$C_6H_4OMe$, $C_6H_{11}$; $R = p$-$C_6H_4OMe$, $R''$ = Me; $R = C_6H_{11}$, $R'' = p$-$C_6H_4OMe$; $R'$ = *trans*-$PdCl(PPh_3)_2$, $PdCl(Ph_2PCH_2CH_2PPh_2)$] and their coordination reactions with metal ions of the first transition row [1—4]. In general, with anhydrous metal halides $MX_2$ (M = Fe, Co, Ni, Cu, Zn; X = Cl, Br) pseudo-tetrahedral complexes of the type $[MX_2\{RN{=}C(R')C(Me){=}NR''\}]$ are obtained. This investigation has been recently extended to examination of the coordinating abilities of this new type of *N*-bidentate ligands towards metal ions of the later transition series. In this paper we report a study on the reactions of chloro derivatives of palladium(II) and platinum(II), containing labile ligands such as ethylene or nitriles, with organometallic diazabutadienes having the same substituents on the imino nitrogen atoms ($R = R''$ = $p$-$C_6H_4OMe$) but different electronic and steric properties at the palladium centre of the group $R'$.

## Results and discussion

The diazabutadiene ligands were prepared by the reactions shown in Scheme 1.

In this way, a 1,4-diaza-3-methylbutadien-2-yl group with the same substituent R on both imino nitrogen atoms can be built into the DAB compound [1], from which the other derivatives, $DAB^{I}$—$DAB^{III}$, are easily obtained by substitution reactions at the palladium atom.

The reactions of these ligands with palladium(II) and platinum(II) chloro complexes containing coordinated ethylene or nitriles are depicted in eqn. 1.



(1)

DAB
$DAB^{I}$
$DAB^{II}$

$[MCl_2(DAB)]$
$[MCl_2(DAB^{I})]$
$[MCl_2(DAB^{II})]$

("$MCl_2$" = $1/2\,[PdCl_2(CH_2{=}CH_2)]_2$ ; $K[PtCl_3(CH_2{=}CH_2)]$ ; $[PdCl_2(N{\equiv}CMe)_2]$ ; $[PtCl_2(N{\equiv}CPh)_2]$ )

Ethylene is easily and rapidly displaced at room temperature, whereas the nitriles require heating, particularly in the case of $[PtCl_2(N{\equiv}CPh)_2]$. The adducts of ligand DAB, which has two mutually *trans* triphenylphosphines, are not very stable in halogenated solvents or acetonitrile, and even at room temperature slowly decompose to *trans*-$[MCl_2(PPh_3)_2]$. For this reason, they are better prepared from "$MCl_2$"—ethylene complexes and their solutions must be worked up as quickly as possible.

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* Alternative nomenclature: 1,2-bis(imino)propyl group [3].

The decomposition of $[PdCl_2(DAB)]$ in refluxing 1,2-dichloroethane occurs as shown in eqn. 2.

$$2[PdCl_2(DAB)] \rightarrow trans\text{-}[PdCl_2(PPh_3)_2] + \text{other products} \qquad (2)$$

The rate of decomposition of $[PtCl_2(DAB)]$ is much lower, and the amount of *trans*-$[PtCl_2(PPh_3)_2]$ formed never reaches the stoicheiometry of eqn. 2 of even after long refluxing times in 1,2-dichloroethane or acetonitrile. Although the mechanism of these reactions is not yet clearly understood, it appears from the nature of the decomposition products that the $PPh_3$ ligand migrates from the Pd atom of DAB to the metal atom of the $MCl_2$ unit. This is further supported by the formation of $[HgCl_2(PPh_3)]_2$ from the reaction of $HgCl_2$ with DAB (see Experimental).

At variance with $[MCl_2(DAB)]$, the adducts of ligands $DAB^{I}$ and $DAB^{II}$, containing a chelating diphosphine, are stable in boiling 1,2-dichloroethane or acetonitrile. Moreover, their UV spectra in the same solvents show that the

TABLE 1

ANALYTICAL AND PHYSICAL DATA

| Compound | Colour | Melting point (°C) [a] | C [b] (%) | H (%) | N (%) | Cl (%) | Molecular weight [b] |
|---|---|---|---|---|---|---|---|
| $[PdCl_2(DAB)]$ | Yellow-orange | 195—200 | 56.5<br>(56.58) | 4.3<br>(4.21) | 2.5<br>(2.49) | 9.4<br>(9.45) | 1152<br>(1125.0) |
| $[PtCl_2(DAB)]$ | Red-orange | 204 | 51.9<br>(52.44) | 4.1<br>(3.90) | 2.4<br>(2.31) | 8.8<br>(8.76) | 1176<br>(1213.7) |
| $[PdCl_2(DAB^{I})]$ | Yellow | 203—205 | 51.7<br>(51.70) | 4.0<br>(4.14) | 2.7<br>(2.80) | 10.8<br>(10.64) | 964<br>(998.9) |
| $[PtCl_2(DAB^{I})]$ | Orange-brown | 225 | 47.9<br>(47.48) | 3.8<br>(3.80) | 2.5<br>(2.58) | 9.8<br>(9.78) | 1065<br>(1087.6) |
| $DAB^{II}$ | Lemon-yellow | 190 | 63.7<br>(63.01) | 5.0<br>(4.79) | 3.3<br>(3.42) | 4.4<br>(4.32) | — [c]<br>(819.6) |
| $[PdCl_2(DAB^{II})]$ | Orange | 195 | 51.4<br>(51.80) | 3.8<br>(3.94) | 2.8<br>(2.81) | 10.3<br>(10.67) | 920<br>(996.9) |
| $[PtCl_2(DAB^{II})]$ | Orange-brown | 215 | 47.4<br>(47.57) | 3.5<br>(3.62) | 2.7<br>(2.58) | 9.7<br>(9.79) | 1100<br>(1085.6) |
| $DAB^{III}$ | Yellow | 147—150 | 59.2<br>(59.25) | 5.0<br>(4.97) | 5.4<br>(5.45) | | 753<br>(770.2) |
| $[PtCl_2(DAB^{III})]$ | Red-orange | 204 | 43.6<br>(44.04) | 3.80<br>(3.70) | 4.1<br>(4.06) | 7.0<br>(6.84) | 1061<br>(1036.2) |
| $[ZnCl_2(DAB^{III})]$ | Yellow | 250 | 50.2<br>(50.35) | 4.2<br>(4.22) | 4.5<br>(4.64) | 8.0<br>(7.82) | 891<br>(906.5) |
| $[CdCl_2(DAB^{III})]$ | Yellow-orange | 189 | 47.4<br>(47.86) | 3.9<br>(4.02) | 4.3<br>(4.41) | 7.6<br>(7.44) | 936<br>(953.5) |
| $[Pd(dmtc)(DAB^{IV})]$ | Orange | 201 | 47.6<br>(48.17) | 4.0<br>(4.04) | 4.4<br>(4.44) | 7.6<br>(7.48) | 957<br>(947.5) |
| $[Pt(dmtc)(DAB^{IV})]$ | Red | 216 | 43.6<br>(44.04) | 3.7<br>(3.70) | 4.1<br>(4.06) | 6.7<br>(6.84) | 1080<br>(1036.2) |

[a] Uncorrected values; all compounds decompose on melting. [b] The calculated values are reported in round brackets. [c] Not measured.

TABLE 2

CHARACTERISTIC IR BANDS ($\mathrm{cm}^{-1}$)

| Compound | $\nu(\mathrm{C{=}N})$ [a] | $\nu(\mathrm{Pd{-}Cl})$ | $\nu(\mathrm{M{-}Cl})$ | $\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{N})$ [b] | $\nu(\mathrm{Pd{-}S})$ [b] |
|---|---|---|---|---|---|
| DAB | 1616(sh); 1555m | 265m | | | |
| $[\mathrm{PdCl_2(DAB)}]$ | | 304m | 348ms; 335(sh) | | |
| $[\mathrm{PtCl_2(DAB)}]$ | | 310m | 344ms; 335(sh) | | |
| $\mathrm{DAB^{I}}$ | 1639s; 1620(sh); 1572s(br) | 294m or 283m | | | |
| $[\mathrm{PdCl_2(DAB^{I})}]$ | | 304m | 347m; 330m | | |
| $[\mathrm{PtCl_2(DAB^{I})}]$ | | 306m | 343ms; 331ms | | |
| $\mathrm{DAB^{II}}$ | 1635ms(br); 1564ms(br) | 295(sh) or 282m | | | |
| $[\mathrm{PdCl_2(DAB^{II})}]$ | | 300m | 342ms; 330(sh) | | |
| $[\mathrm{PtCl_2(DAB^{II})}]$ | | 303m | 338(sh); 330ms | | |
| $\mathrm{DAB^{III}}$ | 1623ms; 1572ms | | | 1520s | 364m |
| $[\mathrm{PtCl_2(DAB^{III})}]$ | | | 340ms; 335(sh) | 1543s(br) | 370m |
| $[\mathrm{ZnCl_2(DAB^{III})}]$ | | | 337ms; 316m | 1542s(br) | 369m |
| $[\mathrm{CdCl_2(DAB^{III})}]$ | | | 273ms; 217m | 1540s(br) | 370m |
| $[\mathrm{Pd(dmtc)(DAB^{IV})}]$ | | 301m; 282m | | 1570s(br) | 385m |
| $[\mathrm{Pt(dmtc)(DAB^{IV})}]$ | | 302m; 282m | | 1568s(br) | 390m [c] |

[a] In the coordinated diazabutadiene ligands the C=N stretching frequencies cannot be unambiguously detected because of the intense absorptions of the *para*-substituted phenyl rings at ca. 1600 and 1500 $\mathrm{cm}^{-1}$. [b] Bands of the coordinated dmtc group. [c] This band is assigned to $\nu(\mathrm{Pt{-}S})$.

Lambert-Beer law is obeyed at concentrations as low as $10^{-5}$ *M*.

All the products of reaction 1 are diamagnetic monomeric 1 : 1 adducts (see Table 1), in which the diazabutadiene moiety acts as a chelating bidentate ligand. The coordination is probably of the $\sigma,\sigma$ type through the N atoms, as we observed for allylic complexes of palladium(II) and platinum(II) with organic $\alpha$-diimines on the basis of their NMR spectra [5]. A $\sigma,\pi$ coordination was found only for complexes of zerovalent metals with organic diazabutadienes carrying bulky *N*-substituents such as s-propyl and t-butyl groups [6,7].

Two M—Cl stretching frequencies are observed in the range 348—330 $cm^{-1}$ of the IR spectra (see Table 2), in accord with a cis arrangement of the two chloride ligands in a square-planar geometry, as found for complexes of the type *cis*-$[MCl_2(L)_2]$ and $[MCl_2(L{-}L)]$ (M = Pd, Pt; L and L—L = monodentate and chelating bidentate nitrogen ligands, respectively) [8]. The position of the $\nu$(M—Cl) bands indicates a rather weak *trans*-influence for the 1,4-diaza-3-methylbutadien-2-yl group. Similar results have been obtained for the complex $[PdCl_2\{RN{=}C(Me)C(Me){=}NR\}]$ (R = *p*-$C_6H_4OMe$), the IR spectrum of which shows two $\nu$(PdCl) bands at 340 and 332 $cm^{-1}$ [9].

The free ligands DAB, $DAB^{I}$ and $DAB^{II}$ are characterized by the presence of two $\nu$(C=N) stretching vibrations in the range 1639—1555 $cm^{-1}$, which are shifted to lower frequency and markedly reduced in intensity upon coordination with metal ions of the first transition series [3,4]. In the binuclear complexes with $PdCl_2$ and $PtCl_2$ no $\nu$(C=N) band could be unambiguously detected, as they are probably masked by the strong absorptions of the *para*-substituted phenyl rings at ca. 1600 and 1500 $cm^{-1}$. In the DAB adducts, the Pd—Cl stretching vibration of the *trans*-$PdCl(PPh_3)_2$ group is ca. 40 $cm^{-1}$ higher than that of the free ligand, owing to the reduced *trans* influence of the $\sigma$-bonded 1,4-diaza-3-methylbutadien-2-yl group upon coordination [3,4]. On the other hand, $\nu$(Pd—Cl) of the ligands $DAB^{I}$ and $DAB^{II}$, in which the chloride is *trans* to a phosphorous atom of the chelating diphosphine, are much less influenced by coordination.

Only the complexes $[MCl_2(DAB)]$ are sufficiently soluble in halogenated solvents for $^1H$ NMR measurements. Their spectra (see Table 3) are similar to those of the compounds $[ZnX_2(DAB)]$ (X = Cl, Br) [3], suggesting that the coordinated diazabutadiene ligand has the same configuration in both types of derivatives. The only significant difference is due to the *ortho* protons of the *p*-$C_6H_4OMe$ group in position 1 of the diazabutadiene chain (see Fig. 1), which occur in the range 6.9—7.15 ppm for the square-planar $[MCl_2(DAB)]$, but at considerably lower field, 7.7—8.0 ppm, for the pseudo-tetrahedral zinc(II) complexes. The coordination of DAB to the Pt atom in $[PtCl_2(DAB)]$ is also confirmed by the presence of two $^{195}Pt$ satellites with a coupling constant $^4J$-(Pt—Me) 7.5 Hz for the signal of the methyl protons in position 3 on the diazabutadiene group.

The ligands $DAB^{I}$ and $DAB^{II}$ can be completely displaced from their adducts by reaction with $PPh_3$, according to eqn. 3 and 4.

$$[PdCl_2(DAB^{I})] + 2\ PPh_3 \rightarrow trans\text{-}[PdCl_2(PPh_3)_2] + DAB^{I} \qquad (3)$$

$$[PtCl_2(DAB^{II})] + 2\ PPh_3 \rightarrow cis\text{-}[PtCl_2(PPh_3)_2] + DAB^{II} \qquad (4)$$

TABLE 3

$^1$H NMR SPECTRA [a]

| Compound | Signal | | Assignment |
|---|---|---|---|
| $[PdCl_2(DAB)]$ | 2.19 s | [3] | C—$\underline{\mathrm{Me}}$ |
| | 3.70 s | [3] | O—$\underline{\mathrm{Me}}$ |
| | 3.79 s | [3] | O—$\underline{\mathrm{Me}}$ |
| | 6.20—6.40 m [b] | [2] | $-\underline{C_6H_4}-$ |
| | 6.40—6.80 m [c] | [4] | $-\underline{C_6H_4}-$ |
| | 6.95—7.15 m [b] | [2] | $-\underline{C_6H_4}-$ |
| | 7.0—7.8 m | [30] | P—$\underline{C_6H_5}$ |
| $[PtCl_2(DAB)]$ | 1.75 t<br>($^4J$(Pt—Me) 7.5 Hz) | [3] | C—$\underline{\mathrm{Me}}$ |
| | 3.72 s | [3] | O—$\underline{\mathrm{Me}}$ |
| | 3.81 s | [3] | O—$\underline{\mathrm{Me}}$ |
| | 6.25—6.45 m [b] | [2] | $-\underline{C_6H_4}-$ |
| | 6.45—6.85 m [c] | [4] | $-\underline{C_6H_4}-$ |
| | 6.90—7.10 m [b] | [2] | $-\underline{C_6H_4}-$ |
| | 7.1—7.7 m | [30] | P—$\underline{C_6H_5}$ |
| $DAB^{II}$ [d] | 1.85 s | [3] | C—$\underline{\mathrm{Me}}$ |
| | 3.70 s<br>3.72 s | [6] | O—$\underline{\mathrm{Me}}$<br>O—$\underline{\mathrm{Me}}$ |
| | 6.1—6.3 m | [2] [e] | $-\underline{C_6H_4}-$ |
| | 6.35—8.1 m | [28] | P—$\underline{C_6H_5}$ + P—$\underline{CH}$ = + $-\underline{C_6H_4}-$ |
| $DAB^{III}$ | 1.87 s | [3] | C—$\underline{\mathrm{Me}}$ |
| | 3.16 s | [3] | N—$\underline{\mathrm{Me}}$ |
| | 3.27 s | [3] | N—$\underline{\mathrm{Me}}$ |
| | 3.77 s<br>3.81 s | [6] | O—$\underline{\mathrm{Me}}$<br>O—$\underline{\mathrm{Me}}$ |
| | 6.4—6.6 m | [2] [e] | $-\underline{C_6H_4}-$ |
| | 6.65—6.95 m | [4] [c] | $-\underline{C_6H_4}-$ |
| | 7.1—7.8 m | [17] | P—$\underline{C_6H_5}$ + $-\underline{C_6H_4}-$ |
| $[PtCl_2(DAB^{III})]$ | 2.12 t<br>($^4J$(Pt—Me) 7.8 Hz) | [3] | C—$\underline{\mathrm{Me}}$ |
| | 3.11 s | [3] | N—$\underline{\mathrm{Me}}$ |
| | 3.30 s | [3] | N—$\underline{\mathrm{Me}}$ |
| | 3.77 s<br>3.79 s | [6] | O—$\underline{\mathrm{Me}}$<br>O—$\underline{\mathrm{Me}}$ |
| | 6.4—7.6 m | [23] | P—$\underline{C_6H_5}$ + $-\underline{C_6H_4}-$ |
| $[ZnCl_2(DAB^{III})]$ | 2.79 s | [3] | C—$\underline{\mathrm{Me}}$ |
| | 3.26 s | [3] | N—$\underline{\mathrm{Me}}$ |
| | 3.35 s | [3] | N—$\underline{\mathrm{Me}}$ |
| | 3.84 s | [6] | O—$\underline{\mathrm{Me}}$ |
| | 6.6—6.8 m [b] | [2] | $-\underline{C_6H_4}-$ |
| | 6.8—7.1 m [c] | [4] | $-\underline{C_6H_4}-$ |
| | 7.1—7.8 m | [15] | P—$\underline{C_6H_5}$ |
| | 7.9—8.1 m [b] | [2] | $-\underline{C_6H_4}-$ |

TABLE 3 (continued)

| Compound | Signal | | Assignment |
|---|---|---|---|
| $[CdCl_2(DAB^{III})]$ | 2.63 s | [3] | C—$\underline{\mathrm{Me}}$ |
| | 3.17 s | [3] | N—$\underline{\mathrm{Me}}$ |
| | 3.30 s | [3] | N—$\underline{\mathrm{Me}}$ |
| | 3.73 s<br>3.75 s | [6] | O—$\underline{\mathrm{Me}}$ |
| | 6.5—6.9 m [f] | [6] | —$\underline{C_6H_4}$— |
| | 7.0—7.9 m | [17] | P—$\underline{C_6H_5}$ + —$\underline{C_6H_4}$— |
| $[Pd(dmtc)(DAB^{IV})]$ | 2.88 s | [3] | C—$\underline{\mathrm{Me}}$ |
| | 3.04 s | [6] | N—$\underline{\mathrm{Me}}$ |
| | 3.77 s | [3] | O—$\underline{\mathrm{Me}}$ |
| | 3.83 s | [3] | O—$\underline{\mathrm{Me}}$ |
| | 6.6—7.0 m [f] | [6] | —$\underline{C_6H_4}$— |
| | 7.0—7.8 m | [17] | P—$\underline{C_6H_5}$ + —$\underline{C_6H_4}$— |
| $[Pt(dmtc)(DAB^{IV})]$ | 2.60 t<br>($^4J$(Pt—Me) $<$ 6 Hz) | [3] | C—$\underline{\mathrm{Me}}$ |
| | 2.97 s | [6] | N—$\underline{\mathrm{Me}}$ |
| | 3.72 s | [3] | O—$\underline{\mathrm{Me}}$ |
| | 3.78 s | [3] | O—$\underline{\mathrm{Me}}$ |
| | 6.6—6.9 m [f] | [6] | —$\underline{C_6H_4}$— |
| | 6.9—7.6 m | [17] | P—$\underline{C_6H_5}$ + —$\underline{C_6H_4}$— |

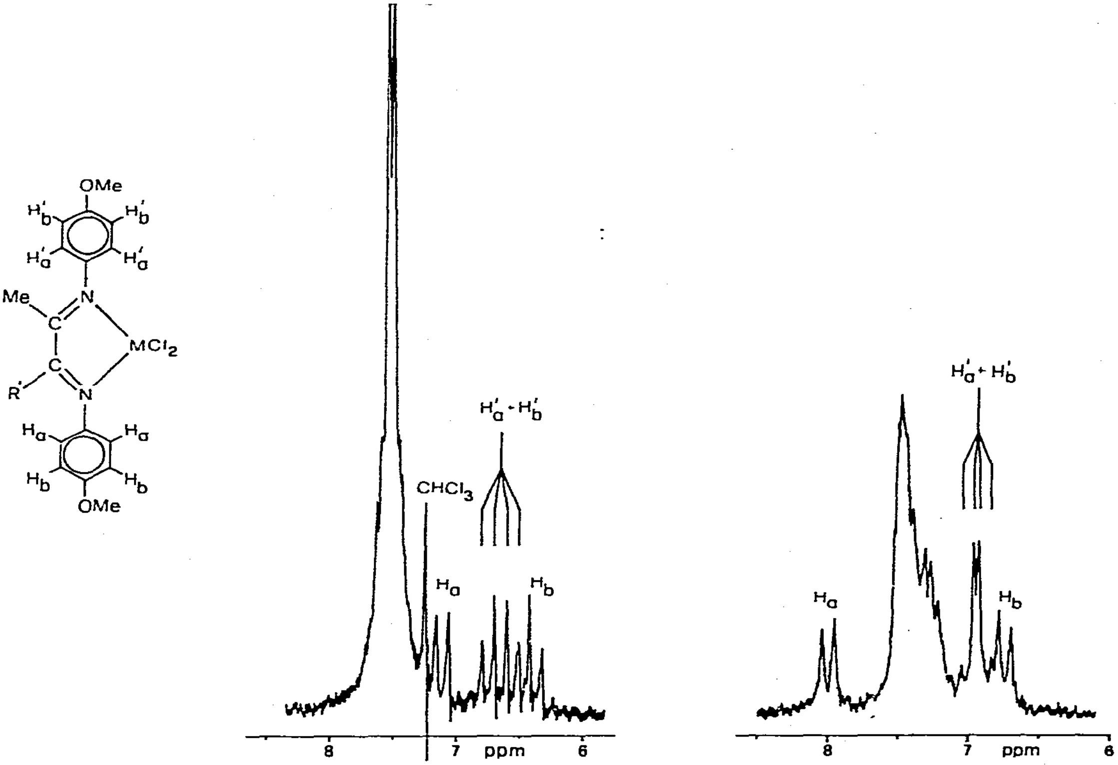
[a] $\delta$ values are in ppm from TMS as internal standard, in $CDCl_3$ solutions; integration values are given in square brackets; s singlet, m multiplet, t triplet. [b] Symmetrical sides of an *AA'BB'* signal of the $p$-$C_6H_4OMe$ group in position 1 (see Fig. 1). [c] *AA'BB'* signal of the $p$-$C_6H_4OMe$ group in position 4 (see Fig. 1). [d] Spectrum in $CD_2Cl_2$ solution. [e] Side of an *AA'BB'* signal; the other side is masked by the strong $PPh_3$ signals. [f] Overlapping *AA'BB'* signals.

Reaction 3 is very fast, whereas reaction 4 takes about two hours for completion. Each product can be isolated in almost quantitative yield and identified by comparing its IR and $^1H$ NMR spectra with those of authentic samples (see Experimental). These reactions provide chemical evidence of the nature of the binuclear complexes and in particular of the presence of the $MCl_2$ unit, since the $DAB^I$ and $DAB^{II}$ ligands are not affected by $PPh_3$ (see also the preparation method in Scheme 1).

The reactions of the ligand $DAB^{III}$ are shown in Scheme 2.

The reaction with the Zeise's salt yields a product, $[PtCl_2(DAB^{III})]$, analogous to those obtained from reaction 1. The presence of the coordinated $PtCl_2$ unit can be easily recognized by the appearance of two $\nu$(Pt—Cl) bands at 340 and 335 cm$^{-1}$ in the IR spectrum. When this compound is kept at 50°C in acetonitrile a slow reaction takes place, which involves migration of ligands between the two metallic centers of the binuclear complex. The final product, formulated as $[Pt(dmtc)(DAB^{IV})]$, is a structural isomer of $[PtCl_2(DAB^{III})]$, both compounds having the same elemental analysis and molecular weight, but different spectral properties.

The reaction of $DAB^{III}$ with the palladium(II) derivatives, "$PdCl_2$", is very



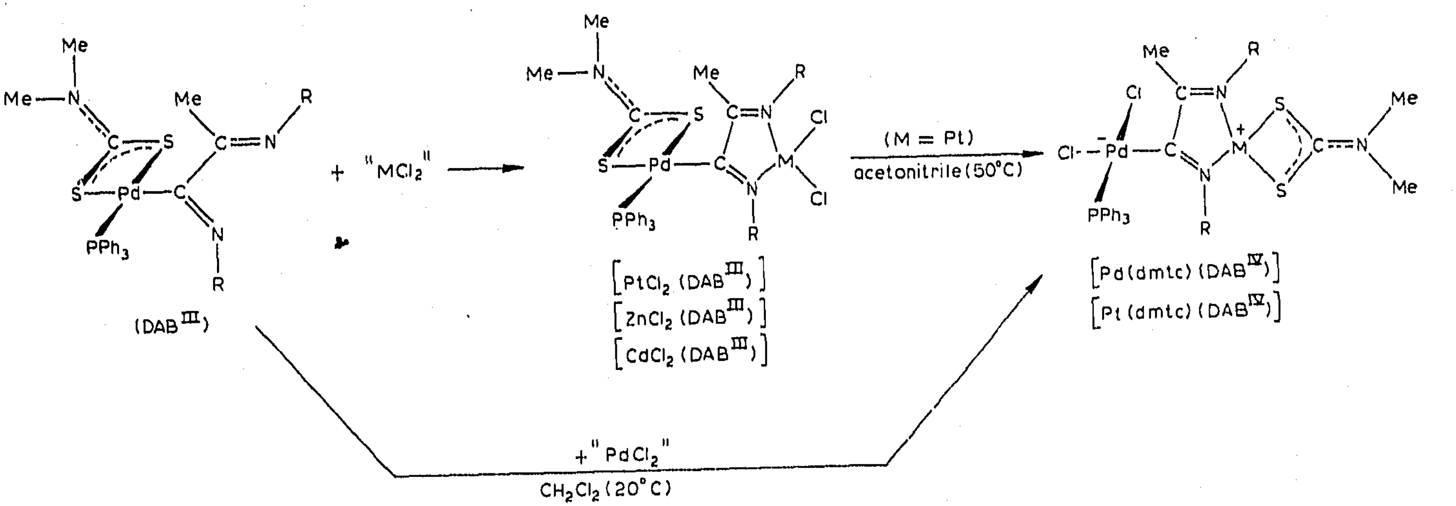
M = Pd: R' = trans-PdCl(PPh$_3$)$_2$ M = Zn: R' = Pd(dmtc)(PPh$_3$)

Fig. 1. $^1$H NMR spectra in the phenyl protons region of [PdCl$_2$(DAB)] and [ZnCl$_2$(DAB$^{III}$)] in CDCl$_3$.

fast and leads directly to the formation of the complex [Pd(dmtc)(DAB$^{IV}$)]. Although no intermediate species of the type [PdCl$_2$(DAB$^{III}$)] can be observed in the IR spectrum of the reaction mixture in CH$_2$Cl$_2$ immediately after mixing the reactants, it is likely that this reaction occurs with a stepwise mechanism as described above for the platinum(II) analogue.

The reactions with ZnCl$_2$ and CdCl$_2$ are also shown in Scheme 2 as they both yield 1 : 1 adducts without exchange of the dimethyldithiocarbamate and chloride ligands. The IR spectrum of [ZnCl$_2$(DAB$^{III}$)] shows two Zn—Cl stretching vibrations at 337 and 316 cm$^{-1}$, indicating the same pseudo-tetrahedral configuration around the Zn atom as previously observed for the corresponding diazabutadiene compounds [ZnCl$_2$(DAB)] and [ZnCl$_2$(DAB$^{I}$)], for which the $\nu$(Zn—Cl) bands fall in the range 336—315 cm$^{-1}$ [3]. The different position (273 and 217 cm$^{-1}$) of the two $\nu$(Cd—Cl) bands for [CdCl$_2$(DAB$^{III}$)] is ascribed to the presence of terminal and bridging chlorides in the solid state, i.e., to associated polymeric structure in which the Cd atom has a coordination number higher than four [10]. Distorted octahedral configurations with bridging chlorides have been proposed for the complexes of the type [CdCl$_2$(L—L)] (L—L = 2,2'-bipyridine and 1,10-phenantroline) for which the $\nu$(Cd—Cl) bands fall at ca. 220 cm$^{-1}$ [11]. However, the chloro bridges in [CdCl$_2$(DAB$^{III}$)] are not so strong as to prevent dissociation in solution: in fact this compound behaves as

SCHEME 2



"MCl$_2$" = K[PtCl$_3$(CH$_2$=CH$_2$)]; ZnCl$_2$ ; CdCl$_2$

"PdCl$_2$" = 1/2 [PdCl$_2$(CH$_2$=CH$_2$)]$_2$ , [PdCl$_2$(N≡CMe)$_2$]

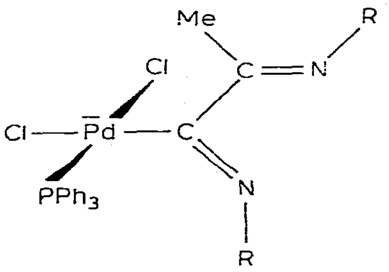
a monomer in 1,2-dichloroethane (see Table 1). The assignment of $\nu$(M—Cl) bands in the binuclear complexes [$MCl_2(DAB^{III})$] (M = Zn, Cd) is also confirmed by the far IR spectra of the mononuclear compounds [$MCl_2\{RN{=}C(Me)C(Me){=}NR\}$] (M = Zn, Cd; R = $p$-$C_6H_4OMe$), which show the stretching vibrations Zn—Cl at 331, 313 $cm^{-1}$ and Cd—Cl at 273, 216 $cm^{-1}$ [9].

The formulation of the complex [$ZnCl_2(DAB^{III})$] is further supported by its reaction with 2,2′-bipyridine (bipy):

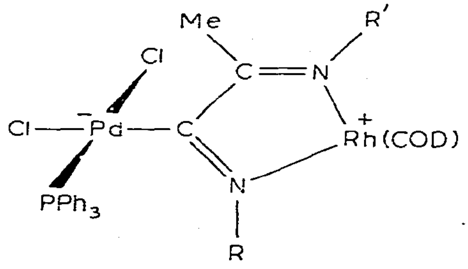
$$[ZnCl_2(DAB^{III})] + 4\ \text{bipy} \rightarrow [ZnCl_2(\text{bipy})] + DAB^{III} \qquad (5)$$

An excess of bipy is required in order to drive the reaction to completion. Both products were isolated in nearly quantitative yield, and easily identified from their IR spectra.

The products [$M(dmtc)(DAB^{IV})$] (M = Pd, Pt) are non-conducting monomeric compounds. Their formulation is mainly based on the far IR spectra and chemical reactions. The spectra in the metal—chloride stretching frequencies region are characterized by two medium intensity bands at ca. 300 and 280 $cm^{-1}$, that we assign to the $\nu$(Pd—Cl) stretching vibrations of the coordinated anionic ligand $DAB^{IV}$. The number and the low frequency values of these bands can be accounted for by the presence of two mutually *cis* chlorides in *trans* position to ligands of high *trans* influence, such as $PPh_3$ and the coordinated 1,4-diaza-3-methylbutadien-2-yl group [3,4]. Such a spectral feature seems to be diagnostic for derivatives of the anionic ligand $DAB^{IV}$, as found in rhodium complexes [12]. It is also present in the IR spectra of the binuclear compounds



($DAB^{IV}$)



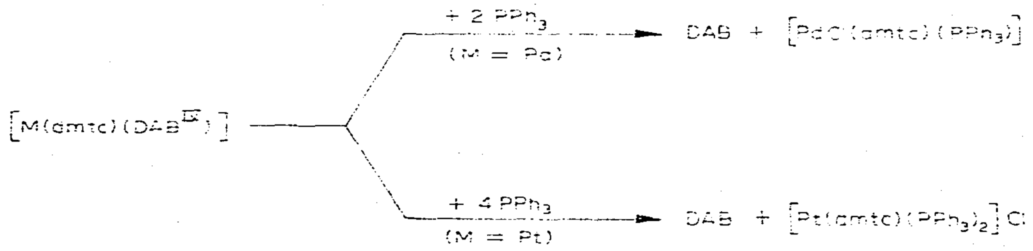
R = R′ = $p$-$C_6H_4OMe$

R = $p$-$C_6H_4OMe$; R′ = Me

COD = 1,5-cyclooctadiene

[Pd($\eta^3$-allyl) (DAB$^{IV}$)] and [Pd(acac)(DAB$^{IV}$)], which are now under investigation.

The coordination of the dmtc ligand to the metal M in [M(dmtc)(DAB$^{IV}$)] is indicated by the nature of the products formed according to reactions 6a and

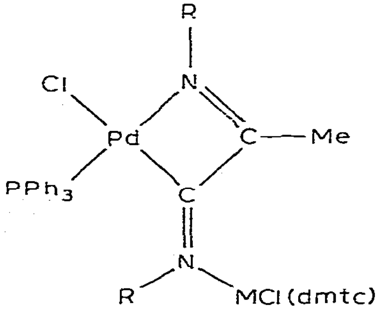


(6a)

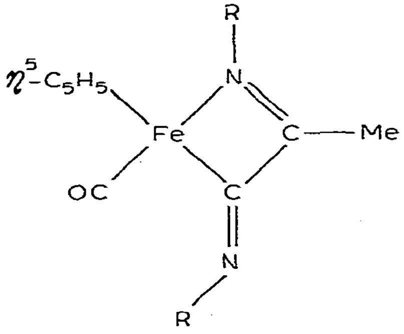
(6b)

6b. The M(dmtc) unit is completely displaced from the diazabutadiene ligand to yield the neutral complex [PdCl(dmtc)(PPh$_3$)] when M = Pd, and the cationic complex [Pt(dmtc)(PPh$_3$)$_2$]Cl when M = Pt, the formation of the latter being due to the presence of an excess of PPh$_3$ in reaction 6b. One molecule of PPh$_3$ reacts also at the palladium atom of DAB$^{IV}$ to give the neutral diazabutadiene derivative DAB in both reactions.

The binuclear complexes [M(dmtc)(DAB$^{IV}$)] can also be formulated in an alternative way (7). This structure does not require any separation of electrical charges and can be compared to the structures of other compounds containing a four-membered ring, viz. those of the type shown in (8) [13]. However, we prefer the zwitterionic structure shown in Scheme 2 in the light of the tendency of diazabutadienes to act as chelating ligands and of the greater stability of the five-membered ring.



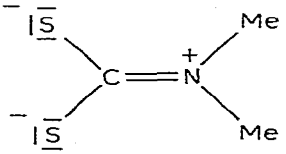
(7)



(8)

The dimethyldithiocarbamate group of $\mathrm{DAB^{III}}$ is scarcely influenced by the coordination of the diazabutadiene moiety in the adducts $[\mathrm{MCl_2(DAB^{III})}]$ (M = Pt, Zn, Cd). This group in $\mathrm{DAB^{III}}$ is characterized by a $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ band at 1520 $\mathrm{cm^{-1}}$ and by a $\nu$(Pd—S) band at 364 $\mathrm{cm^{-1}}$, which are only a little shifted to higher frequency (ca. 20 and 5 $\mathrm{cm^{-1}}$, respectively) in $[\mathrm{MCl_2(DAB^{III})}]$. Moreover, in the $^1$H NMR spectrum of $\mathrm{DAB^{III}}$ the N—Me protons of dmtc appear as two singlets of equal intensity at 3.16 and 3.27 ppm, the positions of which do not significantly vary (3.11—3.35 ppm) in the binuclear compounds $[\mathrm{MCl_2(DAB^{III})}]$.

In the complexes $[\mathrm{M(dmtc)(DAB^{IV})}]$ (M = Pd, Pt), the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ band of dmtc occurs at rather higher frequency (ca. 1570 $\mathrm{cm^{-1}}$), indicating a greater contribution of the limiting formula (9) in accord with a higher positive charge on the M atoms in this type of compounds. In the $^1$H NMR spectra the *N*-Me protons appear as only one singlet at ca. 3 ppm, even at —60° C, as though the two methyl groups of dmtc were not affected by the asymmetric nature of ligand $\mathrm{DAB^{IV}}$.



(9)

As already described for the complexes of DAB, $\mathrm{DAB^{I}}$ [3,4] and $\mathrm{DAB^{II}}$, the effects of coordination are much more pronounced in the spectral features of the 1,4-diaza-3-methylbutadien-2-yl group of $\mathrm{DAB^{III}}$. In the binuclear compounds no C=N stretching frequency can be assigned with certainty (see Table 2). The $^1$H NMR signal of the 3-methyl protons in the complexes $[\mathrm{MCl_2(DAB^{III})}]$ is shifted down-field relative to that of the free ligand. In $[\mathrm{PtCl_2(DAB^{III})}]$ this signal is at 2.12 ppm with a coupling constant $^4J$(Pt—Me) 7.8 Hz, while in $[\mathrm{Pt(dmtc)(DAB^{IV})}]$ it is found at 2.60 ppm with $^4J$(Pt—Me) $<$ 6 Hz. The different chemical shifts and different coupling constants are clearly related to the different structures of these isomers. In particular, the lower field position of $\delta$(C—Me) in the latter compound may also be due to the higher positive charge on the Pt atom. A marked down-field shift of the *ortho* protons resonances of the $p$-$\mathrm{C_6H_4OMe}$ substituent in position 1 is observed in the $^1$H NMR spectrum of the pseudo-tetrahedral complex $[\mathrm{ZnCl_2(DAB^{III})}]$ (see Fig. 1).

The features of the electronic spectra of the adducts $[\mathrm{PtCl_2(DAB)}]$, $[\mathrm{PtCl_2(DAB^{III})}]$ and $[\mathrm{Pt(dmtc)(DAB^{IV})}]$ in $\mathrm{CH_2Cl_2}$ solution are summarized in Fig. 2. The bands in the region 500—300 nm are probably due to electronic transitions between the metal $d$ levels and the antibonding orbitals of the conjugated double bonds system of the coordinated 1,4-diaza-3-methylbutadien-2-yl group (CT bands). Metal → ligand CT bands in the same region have been observed for the cationic derivatives $[\mathrm{M}(\eta^3\text{-allyl})\{\mathrm{RN{=}C(Me)C(Me){=}NR}\}]^+$ (M = Pd, Pt; R = $p$-$\mathrm{C_6H_4OMe}$) [5]. Although these bands have been extensively studied for several organic diazabutadiene complexes [14,15], in this case a detailed assignment is complicated by the low symmetry of the binuclear compounds and by the presence of two metallic centres in the same molecule. Except the strong band at 309 nm, the complexes $[\mathrm{PtCl_2(DAB)}]$ and $[\mathrm{PtCl_2(DAB^{III})}]$, both containing the coordinated $\mathrm{PtCl_2}$ unit, have electronic spectra

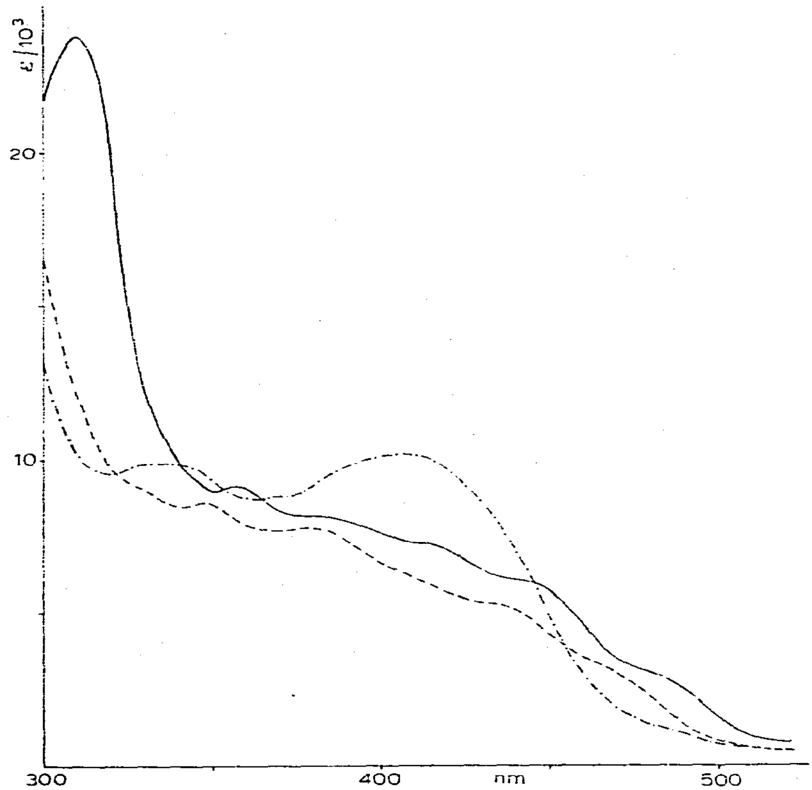


Fig. 2. Electronic spectra (300—500 nm) of [$PtCl_2$(DAB)] (———), [$PtCl_2$($DAB^{III}$)] (- - - - -) and [Pt(dmtc)($DAB^{IV}$)] (· — · — ·) in $CH_2Cl_2$.

similar to each other but different from that of [Pt(dmtc)($DAB^{IV}$)]. The bands in the range 350—500 nm appear to be much more influenced by a change in the ligands at the Pt atom rather than by the change of ligands at the Pd atom of the organometallic diazabutadienes.

## Experimental

The complexes [$PdCl_2(N{\equiv}CMe)_2$], [$PdCl_2(CH_2{=}CH_2)]_2$, [$PtCl_2(N{\equiv}CPh)_2$], K[$PtCl_3(CH_2{=}CH_2)$] were prepared by standard methods. The diazabutadiene derivatives RN=C(Me)C(R′)=NR (R = $p$-$C_6H_4OMe$; R′ = *trans*-$PdCl(PPh_3)_2$(DAB); R′ = PdCl(diphos) ($DAB^I$) were prepared and purified by published methods [1,3]. 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 solution were recorded with a Bausch-Lomb Spectronic 210 UV spectrophotometer in the range 700—250 nm at 25° C, using quartz cells of 1 cm path length. $^1H$ NMR spectra were recorded with a Varian EM-390 90 MHz instrument at room temperature with TMS as internal standard. 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 RN=C(Me)C(R')=NR (R = p-$C_6H_4OMe$)*

*(a) R' = PdCl(L—L); L—L = cis-1,2-bis(diphenylphosphino)ethylene ($DAB^{II}$).* The diazabutadiene derivative DAB (1.42 g, 1.5 mmol) was dissolved in 80 ml of $CH_2Cl_2$ and treated with 0.75 g (1.8 mmol) of *cis*-1,2-bis(diphenylphosphino)-ethylene (95% purity). The mixture was stirred for 6 h, then charcoal was added. After filtration, the clear orange solution was concentrated to small volume at reduced pressure and the product, $DAB^{II}$, was precipitated with diethyl ether. This compound was redissolved in a $CH_2Cl_2$/benzene (1/1, v/v) mixture and reprecipitated with diethyl ether after concentration of the solution (yield 1.16 g, 95%).

*(b) R' = Pd(dmtc)($PPh_3$) ($DAB^{III}$).* The diazabutadiene derivative DAB (0.948 g g, 1 mmol) in 80 ml of $CH_2Cl_2$ was treated with Na[dmtc] · 2 $H_2O$ (0.215 g, 1.2 mmol) in 10 ml of MeOH; NaCl separated immediately. After stirring for 15 min the mixture was taken to dryness and the solid residue treated with benzene and charcoal. After filtration the clear solution was concentrated to small volume at reduced pressure and the product precipitated with n-pentane. It was purified by reprecipitation from the same solvents (yield 0.62 g, 80%).

*Preparation of [$PdCl_2$(DAB)]*

The ligand DAB (0.474 g, 0.5 mmol) dissolved in 50 ml of $CH_2Cl_2$ was treated with [$PdCl_2(CH_2{=}CH_2)$]$_2$ (0.108 g, 0.25 mmol). The colour of the mixture changed immediately to red-orange. A small amount (ca. 10 mg) of a yellow precipitate was also formed; this was filtered off and identified as *trans*-[$PdCl_2(PPh_3)_2$] from its IR spectrum ($\nu$(Pd—Cl) 358 $cm^{-1}$). The resulting solution was concentrated to small volume and the product precipitated with diethyl ether.

This yellow-orange compound can be reprecipitated from the same solvents, but the $CH_2Cl_2$ solution must be worked up as quick as possible because of decomposition to *trans*-[$PdCl_2(PPh_3)_2$] (yield 0.42 g, 75%).

*Preparation of [$PtCl_2$(DAB)]*

The ligand DAB (0.316 g, 0.33 mmol) in 50 ml of $CH_2Cl_2$ was added to a MeOH solution (ca. 10 ml) of K[$PtCl_3(CH_2{=}CH_2)$] (0.130 g, 0.35 mmol). The colour of the solution changed immediately from yellow to deep-red. After 15 min stirring the mixture was taken to dryness and the solid residue was treated with $CH_2Cl_2$ and charcoal. After filtration the red solution was concentrated to small volume at reduced pressure and the red product was precipitated with diethyl ether. It was purified by reprecipitation from the same solvents (yield 0.330 g, 82%).

This compound is more stable in $CH_2Cl_2$ solution at room temperature than the analogue [$PdCl_2$(DAB)].

*Decomposition of [$MCl_2$(DAB)] (M = Pd, Pt)*

(a) A solution of [$PdCl_2$(DAB)] (0.56 g, 0.5 mmol) in 50 ml of 1,2-dichloroethane was refluxed for 4 h and then concentrated at reduced pressure to ca. 20 ml. On standing, yellow crystals of *trans*-$[PdCl_2(PPh_3)_2]$ appeared. The precipitation was completed by adding 10 ml of diethyl ether, to give a final crop of 0.171 g (0.243 mmol.).

This reaction was repeated three times with different amounts of $[PdCl_2(DAB)]$ and in one experiment acetonitrile was used as solvent. In all cases the molar ratio between the starting compound and the final product, $[PdCl_2(DAB)]/[PdCl_2(PPh_3)_2]$, was found to be very close to 2/1.

(b) A solution of $[PtCl_2(DAB)]$ (0.364 g, 0.3 mmol) in 50 ml of 1,2-dichloroethane was refluxed for 8 h and then treated in the way described above for the palladium(II) analogue. A pale-yellow product (0.060 g) was obtained, and was identified as *trans*-$[PtCl_2(PPh_3)_2]$ from its IR spectrum ($\nu$(Pt—Cl) 343 $cm^{-1}$) [16] and elemental analysis (Found: C, 54.8; H, 3.9; Cl, 9.1 Calcd. for $C_{36}H_{30}Cl_2P_2Pt$: C, 54.69; H, 3.83; Cl, 8.97%). The residue was refluxed in the same solvent for another 4 h to give a further crop of *trans*-$[PtCl_2(PPh_3)_2]$ (0.020 g). This reaction was repeated with longer refluxing times and with a different solvent, such as acetonitrile, but in no case was a 2/1 molar ratio between the starting compound and the final product reached.

### *Reaction of DAB with* $HgCl_2$

The ligand DAB (0.474 g, 0.5 mmol) in 50 ml of $CH_2Cl_2$ was treated with $HgCl_2$ (0.136, 0.5 mmol). A clear red-orange solution was obtained, its IR spectrum in the range 1700—1500 $cm^{-1}$ indicated complete coordination of the 1,4-diaza-3-methylbutadien-2-yl group of DAB. (The two strong $\nu$(C=N) absorptions of the free DAB ligand at 1634 and 1556 $cm^{-1}$ disappeared as soon as the reactants were mixed.) After ca. 1 h a white product began to precipitate. After stirring for two days at room temperature, the mixture was concentrated to a volume of ca. 20 ml and diethyl ether (20 ml) was added to complete the precipitation. The resulting off-white compound (0.115 g) was identified as $[HgCl_2(PPh_3)]_2$ from its elemental analysis (Found: C, 39.8; H, 2.7; Cl, 13.6. Calcd. for $C_{18}H_{15}Cl_2HgP$: C, 40.50; H, 2.83; Cl, 13.28%) and from its IR spectrum, which was compared with that of an authentic sample [$\nu$(Hg—$Cl_{terminal}$) 288 $cm^{-1}$] [17].

### *Preparation of* $[MCl_2(DAB^I)]$ *and* $[MCl_2(DAB^{II})]$ *(M = Pd, Pt)*

(a) The ligand $DAB^I$ (0.411 g, 0.5 mmol) in ca. 100 ml of $CH_2Cl_2$ was treated with $[PdCl_2(N{\equiv}CMe)_2]$ (0.13 g, 0.5 mmol). The mixture was stirred for 1 h, then treated with charcoal and filtered. The clear filtrate was concentrated to small volume and the product precipitated with diethyl ether. It was purified by reprecipitation from the same solvents (yield 0.46 g, 92%). The complex $[PdCl_2(DAB^{II})]$ was prepared in the same way from $DAB^{II}$ and $[PdCl_2(N{\equiv}CMe)_2]$ (yield 90%).

(b) The ligand $DAB^I$ (0.411 g, 0.5 mmol) suspended in 80 ml of 1,2-dicloroethane was treated with $[PtCl_2(N{\equiv}CPh)_2]$ (0.236 g, 0.5 mmol). The mixture was refluxed for 1 h until the $\nu$(C≡N) band of the coordinated nitrile disappeared. After treatment with charcoal and filtration, the clear solution was concentrated at reduced pressure and the product precipitated with diethyl ether. It was purified by reprecipitation from the same solvents (yield 0.39 g, 72%). The complex

$[PtCl_2(DAB^{II})]$ was prepared in the same way from $DAB^{II}$ and $[PtCl_2(N{\equiv}CPh)_2]$ (yield 75%).

### *Reaction of $[PdCl_2(DAB^{I})]$ with $PPh_3$*

The binuclear complex $[PdCl_2(DAB^{I})]$ (0.25 g, 0.25 mmol) suspended in ca. 30 ml of $CH_2Cl_2$ was treated with $PPh_3$ (0.131 g, 0.5 mmol). A clear golden-yellow solution was immediately obtained. After a few minutes a yellow product began to precipitate. The IR spectrum of the solution showed the $\nu$(C=N) bands of free $DAB^{I}$ at 1630 and 1572 $cm^{-1}$. After 1 h diethyl ether (20 ml) was added to complete the precipitation of the yellow compound, which was filtered off and identified as *trans*-$[PdCl_2(PPh_3)_2]$ from its IR spectrum (yield 0.160 g).

The mother liquor was concentrated to small volume and n-hexane was added to give a yellow precipitate (0.175 g), the IR and $^1$H NMR spectra of which were identical to those of $DAB^{I}$.

### *Reaction of $[PtCl_2(DAB^{II})]$ with $PPh_3$*

The complex $[PtCl_2(DAB^{II})]$ (0.27 g, 0.25 mmol) dissolved in ca. 50 ml of $CH_2Cl_2$ was treated with $PPh_3$ (0.131 g, 0.5 mmol). The colour of the mixture slowly changed from deep-red to yellow-orange, while the IR spectrum showed a progressive increase of the $\nu$(C=N) bands of free $DAB^{II}$ at 1628 and 1570 $cm^{-1}$. After ca. 2 h no appreciable change in the spectrum was observed. The solution was concentrated to ca. 20 ml volume and diethyl ether (20 ml) was added to give an off-white precipitate (0.185 g), which was identified as *cis*-$[PtCl_2(PPh_3)_2]$ by comparison of its IR spectrum with that of an authentic sample ($\nu$(Pt—Cl) 321 and 298 $cm^{-1}$, 285(sh). From the mother liquor the free ligand $DAB^{II}$ was recovered in almost quantitative yield (0.190 g) by concentration to small volume and addition of n-hexane.

### *Preparation of $[PtCl_2(DAB^{III})]$*

A solution of the ligand $DAB^{III}$ (0.385 g, 0.5 mmol) in $CH_2Cl_2$ (50 ml) was added to a MeOH solution (ca. 10 ml) of $K[PtCl_3(CH_2{=}CH_2)]$ (0.185 g, 0.5 mmol). The red-brown reaction mixture was worked up as described for the preparation of $[PtCl_2(DAB)]$ (yield 0.43 g, 83%).

### *Preparation of $[MCl_2(DAB^{III})]$ (M = Zn, Cd)*

A solution of the ligand $DAB^{III}$ (0.5 mmol) in $CH_2Cl_2$ (50 ml) was added dropwise to a stirred solution of anhydrous $MCl_2$ (0.5 mmol) in anhydrous methanol (10 ml). After 30 min the mixture was treated with charcoal and filtered. The solution was evaporated at reduced pressure until the product began to precipitate. At this point the precipitation was completed by addition of diethyl ether. The binuclear complexes were purified by reprecipitation from the same solvents (yields 85—90%).

### *Reaction of $[ZnCl_2(DAB^{III})]$ with 2,2'-bipyridine*

The complex $[ZnCl_2(DAB^{III})]$ (0.30 g, 0.33 mmol) in $CH_2Cl_2$ (25 ml) was treated with an excess of 2,2'-bipyridine (0.206 g, 1.32 mmol). After 10 min white crystals began to precipitate and the colour of the solution turned from orange to yellow. The mixture was stirred for 1 h, then concentrated to ca. 10

ml volume. Diethyl ether (40 ml) was added to complete the precipitation of the white product (0.09 g), identified as [$ZnCl_2$(bipy)] by comparing its IR spectrum with that of an authentic sample ($\nu$(Zn—Cl) 331 and 323 $cm^{-1}$) [18]. From the mother liquor the free ligand $DAB^{III}$ was recovered in nearly quantitative yield (0.235 g) by concentration and addition of n-hexane.

*Preparation of [Pd(dmtc)($DAB^{IV}$)]*

The ligand $DAB^{III}$ (0.385 g, 0.5 mmol) in $CH_2Cl_2$ (50 ml) was treated with [$PdCl_2(N{\equiv}CMe)_2$] (0.13 g, 0.5 mmol). The mixture immediately became red-orange. After treatment with charcoal and filtration the clear solution was concentrated to small volume and the product precipitated by addition of diethyl ether. The crude orange compound was purified by reprecipitation from a $CH_2Cl_2$ solution with diethyl ether/methanol (3/1, v/v) (yield 0.35 g, 74%). The same product, [Pd(dmtc)($DAB^{IV}$)], was also prepared from the reaction of $DAB^{III}$ with [$PdCl_2(CH_2{=}CH_2)$]$_2$ (molar ratio 2/1) in $CH_2Cl_2$.

*Preparation of [Pt(dmtc)($DAB^{IV}$)]*

A solution of the binuclear complex [$PtCl_2$($DAB^{III}$)] (0.50 g, 0.48 mmol) in acetonitrile (ca. 60 ml) was kept at 50°C for 8 h and left overnight at room temperature. The solvent was evaporated at reduced pressure and the solid residue was precipitated twice from $CH_2Cl_2$ solution with diethyl ether (yield 0.35 g, 70%).

*Reactions of [M(dmtc)($DAB^{IV}$)] with $PPh_3$*

(a) The complex [Pd(dmtc)($DAB^{IV}$)] (0.258 g, 0.27 mmol) dissolved in $CH_2Cl_2$ (30 ml) was treated with $PPh_3$ (0.143 g, 0.54 mmol). The IR spectrum of the mixture showed the appearance of a $\nu$(C=N) band at 1622 $cm^{-1}$. After stirring for 15 min benzene (20 ml) was added and the solution was concentrated to small volume at reduced pressure. Addition of diethyl ether gave a yellow precipitate (0.33 g), which consisted of an almost equimolar mixture of DAB and [PdCl(dmtc)($PPh_3$)] from IR and $^1H$ NMR spectral data. An authentic sample of [PdCl(dmtc)($PPh_3$)] was prepared from the reaction of the chloro bridged dimer [$PdCl_2(PPh_3)$]$_2$ with Na[dmtc] · $2H_2O$ (molar ratio Pd/dmtc 1/1.1) in a $CH_2Cl_2$/MeOH mixture (4/1, v/v). This compound was characterized by elemental analysis (Found: C, 47.8; H, 4.1; Cl, 6.7; N, 2.7. Calcd. for $C_{21}H_{21}ClNPPdS_2$: C, 48.10; H, 4.04; Cl, 6.76; N, 2.67.), and by IR and $^1H$ NMR spectra ($\nu$(C$\cdots$N) 1550vs, $\nu$(Pd—S) 378 m, $\nu$(Pd—Cl) 305 m; $\delta$(N—Me) 3.02 and 3.15 ppm in $CDCl_3$).

(b) A solution of the complex [Pt(dmtc)($DAB^{IV}$)] (0.124 g, 0.12 mmol) in $CH_2Cl_2$ (10 ml) was treated with an excess of $PPh_3$ (0.126 g, 0.48 mmol). The colour turned slowly from red to yellow-orange, while the IR spectrum showed a progressive increase of a $\nu$(C=N) band at 1622 $cm^{-1}$. After ca. 2 h no further appreciable change in the spectrum was observed. Diethyl ether (30 ml) was added and the mixture was set aside overnight. A pale-yellow precipitate (0.08 g) was obtained, and was identified as [Pt(dmtc)($PPh_3$)$_2$]Cl by comparison with an authentic sample. The mother liquor was concentrated and a diethyl ether/n-hexane (1/1, v/v) mixture was added to give a yellow precipitate (0.09 g) identified as DAB.

An authentic sample of [Pt(dmtc)$(PPh_3)_2$]Cl was prepared from the reaction of cis-[$PtCl_2(PPh_3)_2$] with Na[dmtc] · 2 $H_2O$ (molar ratio 1/1.1) in a $CH_2Cl_2$/MeOH mixture (4/1, v/v). This compound was characterized by elemental analysis (Found: C, 53.0; H, 4.1; Cl, 4.2; N, 1.6. Calcd. for $C_{39}H_{36}ClNP_2S_2Pt$: C, 53.51; H, 4.15; Cl, 4.05; N, 1.60%), conductivity measurements ($\Lambda_M$ 69 $ohm^{-1}$ $cm^2$ $mol^{-1}$ for a MeOH solution $10^{-3}$ *M* at 20°C), and by IR and $^1H$ NMR spectra ($\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ 1570 vs, $\nu$(Pt—S) 380 m; $\delta$(N—Me) 3.17 ppm in $CDCl_3$).

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