

*Journal of Organometallic Chemistry*, 233 (1982) 387–402  
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

## PREPARATION AND REACTIVITY OF 1,2-BIS(IMINO)ETHYLPALLADIUM(II) COMPLEXES

BRUNO CROCIANI <sup>\*</sup>,

*Istituto di Chimica Generale, Via Archirafi 26, University of Palermo (Italy)*

ANTONIO MANTOVANI

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

and ALBERTO SCRIVANTI

*Centro di Chimica Tecnologia Composti Metallorganici Elementi Transizione, C.N.R. Padova (Italy)*

(Received February 10th, 1982)

### Summary

The 1,2-bis(imino)ethylpalladium complex, *trans*-[PdCl{ $\overline{C(=NR)CH=NR}$ }- $(PPh_3)_2$ ] (R = *p*-C<sub>6</sub>H<sub>4</sub>OMe, DAB<sup>I</sup>) can be prepared by treatment of [Pd(PPh<sub>3</sub>)<sub>4</sub>] with two equivalents of CNC<sub>6</sub>H<sub>4</sub>OMe-*p* followed by slow addition of HCl at -70° C. The  $\sigma$ -bonded 1,2-bis(imino) group can be easily monoprotinated and undergoes acid hydrolysis to give the  $\alpha$ -aldehydoimidoyl derivative *trans*-[PdCl{ $\overline{C(=NR)CH=O}$ }- $(PPh_3)_2$ ]. Condensation of the aldehydic carbonyl group with methylamine yields the product *trans*-[PdCl{ $\overline{C(=NC_6H_4OMe-p)CH=NMe}$ }- $(PPh_3)_2$ ], DAB<sup>II</sup>, with different substituents on the *N*-imino atoms. Substitution of ancillary ligands at the palladium center of DAB<sup>I</sup> by dimethyldithiocarbamate anion (dmtc) affords the complex [Pd(dmtc){ $\overline{C(=NR)CH=NR}$ }- $(PPh_3)$ ], DAB<sup>III</sup>. The DAB<sup>I</sup>, DAB<sup>II</sup> and DAB<sup>III</sup> derivatives react with anhydrous metal chlorides, MCl<sub>2</sub> (M = Co, Ni, Cu, Zn) to give 1/1 adducts in which the 1,2-bis(imino)ethyl group acts as a chelating bidentate ligand. Magnetic moment measurements and the far-infrared and electronic spectra of these binuclear compounds indicate an essentially pseudo-tetrahedral configuration at M. The reaction of DAB<sup>I</sup> with [PdCl( $\eta^3$ -2-MeC<sub>3</sub>H<sub>4</sub>)]<sub>2</sub>, or [PtCl(C<sub>3</sub>H<sub>5</sub>)]<sub>4</sub>, (DAB<sup>I</sup>/Pd or Pt ratio, 1/2) involves the exchange of Cl<sup>-</sup> and PPh<sub>3</sub> ligands, which leads to the formation of the zwitterionic binuclear derivatives [Pd( $\eta^3$ -2-MeC<sub>3</sub>H<sub>4</sub>)(DAB<sup>IV</sup>)], or [Pt( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(DAB<sup>IV</sup>)] (DAB<sup>IV</sup> = *cis*-PdCl<sub>2</sub>{ $\overline{C(=NR)CH=NR}$ }- $(PPh_3)$ ), and [PdCl( $\eta^3$ -2-MeC<sub>3</sub>H<sub>4</sub>)(PPh<sub>3</sub>)], or [PtCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(PPh<sub>3</sub>)].

## Introduction

Complexes of palladium(II) with C-bonded 1,2-bis(imino)propyl\* groups are generally prepared by "double" insertion reaction of two isocyanide molecules into a Pd—Me  $\sigma$  bond, which can be either present in the starting compound (e.g., in *trans*-[PdI(Me)(L)<sub>2</sub>] (L = tertiary phosphine) [1] or be formed in situ through the action of a methylating agent (e.g., in the reaction of [PdX<sub>2</sub>(CNR)<sub>2</sub>] (X = Cl, I) with HgMe<sub>2</sub> followed by addition of two equivalents of PPh<sub>3</sub> [2]).

Owing to our interest in the chemistry of these compounds, which can be regarded as C-palladated  $\alpha$ -diimines, we have studied various synthetic routes for the preparation of the analogous 1,2-bis(imino)ethylpalladium(II) derivatives. Among the reactions investigated only the oxidative addition of HCl at low temperature to the system [Pd(PPh<sub>3</sub>)<sub>4</sub>]/CNR (R = *p*-C<sub>6</sub>H<sub>4</sub>OMe; Pd/CNR ratio, 1/2) gave a satisfactory yield of *trans*-[PdCl{C(=NC<sub>6</sub>H<sub>4</sub>OMe-*p*)CH=NC<sub>6</sub>H<sub>4</sub>OMe-*p*} (PPh<sub>3</sub>)<sub>2</sub>], as briefly described in a preliminary communication [3]. We want to report here the complete characterization of this product through reactions involving either the palladium center or, in particular, the  $\sigma$ -bonded 1,2-bis(imino)ethyl\*\* group.

## Results and discussion

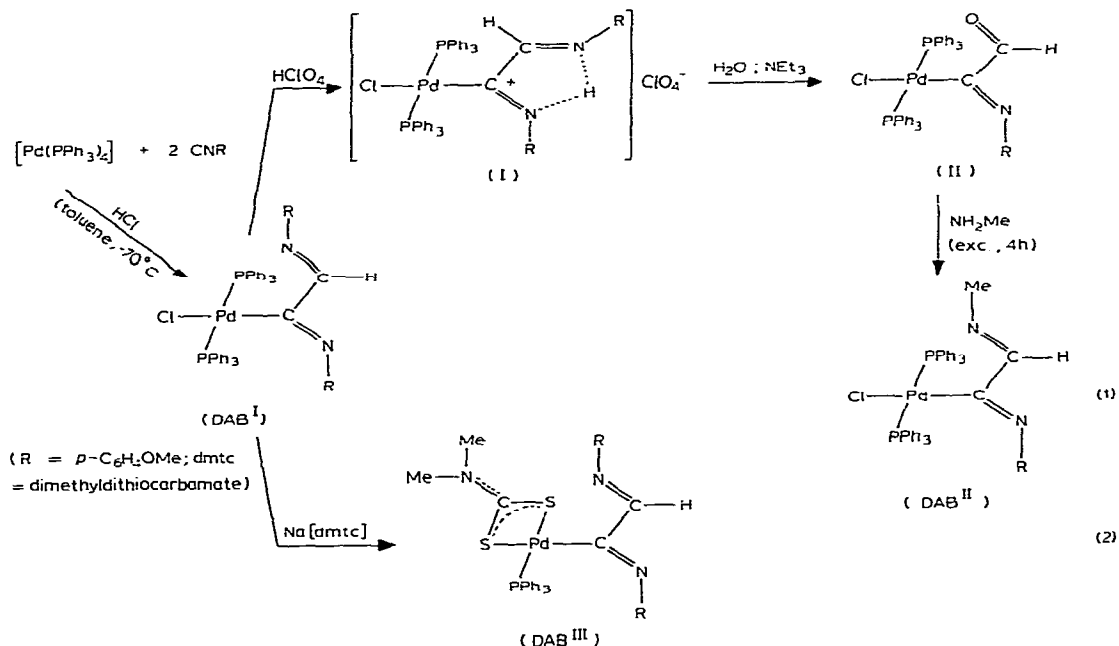
### Preparation of the 1,2-bis(imino)ethylpalladium(II) complexes

All our attempts to prepare compounds of this type involve reactions in which a Pd—H bond may be initially formed in substrates containing isocyanide ligands (Pd/CNR ratio, 1/2). This approach is based on the well-known ability of isocyanides to insert into M—H bonds [4] and on the tendency of palladium(II) complexes to undergo successive insertion of two isocyanide molecules into the Pd—C  $\sigma$  bond [1,2]. However, because of the high reactivity of palladium-hydrido species, side reactions, such as the reductive elimination of HCl from [PdCl(H)(L)<sub>2</sub>] intermediates in the presence of a base or the evolution of H<sub>2</sub> in the reaction with protic acids, may successfully compete with the insertion reaction to give a reduced or even negligible yield of the expected 1,2-bis(imino)-ethyl product. In fact, the reaction of *cis*-[PdCl<sub>2</sub>(CNR)<sub>2</sub>] (R = aryl group) with hydrides (LiH, NaBH<sub>4</sub>, LiAlH<sub>4</sub>) yields only palladium(0) derivatives [5]. On the other hand, slow addition of HCl to the [Pd(PPh<sub>3</sub>)<sub>4</sub>]/CNC<sub>6</sub>H<sub>4</sub>OMe-*p* mixture at -70°C (the only successful method found), as in Scheme 1, gives the product DAB<sup>I</sup> in a moderate yield (50–55%), because of the concomitant formation of [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]. If the reaction sequence is changed, with the isocyanide being added to the mixture resulting from the initial reaction of HCl with [Pd(PPh<sub>3</sub>)<sub>4</sub>] at low temperature, the yield of DAB<sup>I</sup> is even lower (ca. 16%, see Experimental). In our search we also examined other systems, such as "Pd(CNR)<sub>2</sub>" / HCl / 2PPh<sub>3</sub>, [Pd(*p*-quinone)(PPh<sub>3</sub>)<sub>2</sub>] / 2CNR / HCl, 1/2[Pd<sub>2</sub>(dibenzylideneacetone)<sub>3</sub>] / 2PPh<sub>3</sub> / 2CNR / HCl (R = *p*-C<sub>6</sub>H<sub>4</sub>OMe), but in no case did we obtain appreciable amounts of DAB<sup>I</sup>.

\* Alternative nomenclature: 1,4-diaza-3-methylbutadien-2-yl group.

\*\* Alternative nomenclature: 1,4-diaza-1,3-butadien-2-yl group.

SCHEME 1



The steps involved in the formation of  $DAB^I$  have been previously discussed in terms of successive insertion reactions of two isocyanide molecules, the first one into a Pd—H bond formed in situ by oxidative addition of HCl to palladium(0) species of the equilibrium mixture  $[Pd(PPh_3)_4]/2CNC_6H_4OMe-p$  [3].

The 1,2-bis(*p*-methoxyphenylimino)ethyl moiety of  $DAB^I$  can be easily monoprotonated by strong acids to give the cationic derivative I, which in the presence of water undergoes hydrolysis at the imino group not directly bound to the palladium center [6]. Subsequent deprotonation with  $NEt_3$  yields complex II containing an  $\alpha$ -aldehydoimidoyl group, which in turn reacts with methylamine to give the 1-(*p*-methoxyphenylimino)-2-(methylimino)ethyl derivative  $DAB^{II}$ . The same condensation reaction also occurs for the  $\alpha$ -ketoimidoyl complex, *trans*- $[PdCl\{C(=NC_6H_4OMe-p)C(Me)=O\}(PPh_3)_2]$ , although at a lower rate (ca. 24 h) under comparable experimental conditions [2b]. Substitution at the palladium center of  $DAB^I$  by the dimethyldithiocarbamate anion leads to the compound  $DAB^{III}$  with a chelating dmtc ligand [7].

The complexes  $DAB^I$ , II,  $DAB^{II}$  and  $DAB^{III}$  are non-conducting in polar solvents, such as methanol or acetonitrile, and are monomeric in 1,2-dichloroethane (see Table 1). The protonated compound I behaves as uni-univalent electrolyte in methanol ( $\Lambda_M = 78.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  for a  $10^{-3} M$  solution at  $20^\circ C$ ).

The formulation of  $DAB^I$ ,  $DAB^{II}$  and  $DAB^{III}$  is supported by the IR spectra, which show two  $\nu(C=N)$  stretching vibrations in the range  $1643\text{--}1539 \text{ cm}^{-1}$  (Table 1). Complex  $DAB^{III}$  exhibits the typical bands of coordinated dmtc ligand:  $\nu(Pd-S)$ , 363 and  $\nu(C\equiv N)$ ,  $1515 \text{ cm}^{-1}$  [8]. The  $\alpha$ -aldehydoimidoyl group of II is characterized by a  $\nu(C=N)$  band at  $1532 \text{ cm}^{-1}$  and by intense  $\nu(C=O)$  and  $\nu(C-H)$  absorptions at 1693 and  $2785 \text{ cm}^{-1}$  respectively, which are typical of the aldehydo function [9]. For complex I three weak  $\nu(N-H)$

TABLE 1  
ANALYTICAL, PHYSICAL, AND CHARACTERISTIC IR BANDS ( $\text{cm}^{-1}$ )

Compound	Colour	Melting point ( $^{\circ}\text{C}$ ) <sup>a</sup>	Analyses (Found (calcd.) (%))			
			C	H	N	Cl
DAB <sup>I</sup>	Yellow	182— 186	66.2 (66.89)	4.7 (4.86)	3.0 (3.00)	3.9 (3.80)
[(DAB <sup>I</sup> )H]ClO <sub>4</sub> (I)	Yellow-orange	234	60.6 (60.39)	4.4 (4.48)	2.8 (2.71)	6.9 (6.85)
[PdCl{C(=NC <sub>6</sub> H <sub>4</sub> OMe- <i>p</i> )CH=O}(PPh <sub>3</sub> ) <sub>2</sub> ] (II)	Pale-yellow	137	66.5 (65.23)	4.5 (4.62)	1.7 (1.69)	4.4 (4.28)
DAB <sup>II</sup>	Pale-yellow	152	66.1 (65.64)	5.0 (4.91)	3.2 (3.33)	4.2 (4.21)
DAB <sup>III</sup>	Yellow-orange	145	59.2 (58.76)	4.8 (4.80)	5.6 (5.56)	
[ZnCl <sub>2</sub> (DAB <sup>I</sup> )]	Yellow	218	58.5 (58.37)	4.1 (4.24)	2.7 (2.62)	10.1 (9.94)
[ZnCl <sub>2</sub> (DAB <sup>II</sup> )]	Deep-yellow	188— 192	56.2 (56.50)	4.2 (4.23)	2.7 (2.86)	10.8 (10.87)
[ZnCl <sub>2</sub> (DAB <sup>III</sup> )]	Yellow-orange	183	49.2 (49.79)	4.1 (4.07)	4.6 (4.71)	8.0 (7.94)
[CoCl <sub>2</sub> (DAB <sup>I</sup> )]	Dark-brown	192	58.8 (58.72)	4.1 (4.26)	2.7 (2.63)	9.8 (10.00)
[NiCl <sub>2</sub> (DAB <sup>I</sup> )]	Yellow-brown	243	58.9 (58.73)	4.4 (4.27)	2.6 (2.63)	10.1 (10.00)
[CuCl <sub>2</sub> (DAB <sup>I</sup> )]	Dark-brown	138	58.5 (58.47)	4.1 (4.25)	2.6 (2.62)	9.9 (9.96)
[Pt( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )(DAB <sup>IV</sup> )]	Orange	180	46.8 (47.12)	3.6 (3.74)	2.8 (2.97)	7.6 (7.52)

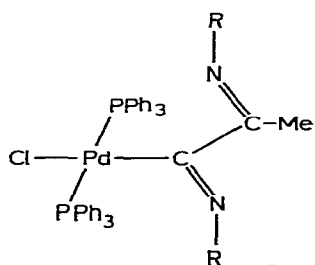
<sup>a</sup> Uncorrected values: all compounds decompose on melting. <sup>b</sup> Bands of the dimethyldithiocarbamate ligand. <sup>c</sup> The  $\nu(\text{Pd}-\text{Cl})$  band is masked by the  $\nu(\text{M}-\text{Cl})$  absorptions. <sup>d</sup> The compound decomposes in solution (see Text).

and three strong  $\nu(\text{Cl}-\text{O})$  bands are detected around 3200 and 1100  $\text{cm}^{-1}$ , respectively. The splitting of  $\nu(\text{Cl}-\text{O})$  of the tetrahedral  $\text{ClO}_4^-$  anion is indicative of symmetry reduction due to either solid state effects or, more likely, to the occurrence of hydrogen bonding (this would also account for the number of the observed  $\nu(\text{N}-\text{H})$  vibrations). The  $\nu(\text{Pd}-\text{Cl})$  bands of DAB<sup>I</sup> and DAB<sup>II</sup> are found at rather low frequency (274 and 263  $\text{cm}^{-1}$ , respectively) owing to the high *trans* influence of the  $\sigma$ -bonded 1,2-bis(imino)alkyl groups [2,10].

The <sup>1</sup>H NMR spectra of DAB<sup>I</sup>, DAB<sup>II</sup> and DAB<sup>III</sup> (Table 2) indicate that in solution the 1,2-bis(imino)ethyl moiety assumes only one of its possible configurations resulting from *cis* or *trans* arrangement of the two conjugated double bonds C=N and from the different position of imino-nitrogen substituents.

It is likely that the configuration in solution corresponds to that observed in the solid for the 1,2-bis(imino)propyl group of the complex DAB, for which the single-crystal X-ray analysis showed that the N=C-C=N unit is virtually planar, its plane making an angle of 82.1° with the mean coordination plane, with a *trans* arrangement of the C=N double bonds and with nitrogen substituents in *anti* position [10]. On the other hand, this is also the preferential configuration

Molecular weight (Found (calcd.))	$\nu(\text{C}=\text{N})$	$\nu(\text{Pd}-\text{Cl})$	$\nu(\text{M}-\text{Cl})$	Other bands
924 (933.7)	1613m; 1539m 1620mw; 1540m	274m 325m		3250w; 3205w; 3180w [ $\nu(\text{N}-\text{H})$ ]; 1140s; 1115vs; 1060s [ $\nu(\text{Cl}-\text{O})$ ]; 624s [ $\delta(\text{Cl}-\text{O})$ ]
829 (828.6)	1532ms	293m or 275m		2785ms [ $\nu(\text{C}-\text{H})$ ]; 1693s [ $\nu(\text{C}=\text{O})$ ]
836 (841.6)	1643(sh); 1635m; 1564s	263m		
710 (756.2)	1610ms; 1547ms			1515(sh) [ $\nu(\text{C}=\text{N})$ ] <sup>b</sup> ; 363m [ $\nu(\text{Pd}-\text{S})$ ] <sup>b</sup>
1079 (1070.0)	1565ms	n.o.	335ms; 312ms,br <sup>c</sup>	
927 (977.9)	1580m; 1519m	n.o.	335ms; 312ms,br <sup>c</sup>	
887 (892.4)	1567m		337ms; 310ms	1548ms,br [ $\nu(\text{C}=\text{N})$ ] <sup>b</sup> 370m [ $\nu(\text{Pd}-\text{S})$ ] <sup>b</sup>
1078 (1063.5)	1553m	303m	352m; 332ms	
1076 (1063.3)	1555m	305m or 285m	340(sh); 327ms	
<sup>d</sup>	1550m	n.o.	325m; 310(sh); 297ms <sup>c</sup>	
1017 (943.0)	1551m	304ms; 280ms		



(R = *p*-C<sub>6</sub>H<sub>4</sub>OMe; DAB)

of organic  $\alpha$ -diimines in solution [11]. In complex I, a cyclic structure with a bridging proton is assigned to the protonated ligand on the basis of analogous structures proposed for mono-protonated  $\alpha$ -diimines [12]. In the <sup>1</sup>H NMR spectrum of I at 35°C no  $\delta(\text{N}-\text{H})$  signal was observed due to the high rate of proton exchange (probably with solvent [2a]). The chemical shift of the imino or aldehydo proton,  $\text{Z}=\text{C}-\text{H}$ , is markedly influenced by the electronic properties of Z group. When Z = NC<sub>6</sub>H<sub>4</sub>OMe, as in the case of DAB<sup>I</sup>, DAB<sup>III</sup> and I, the  $\delta(\text{N}=\text{C}-\text{H})$  signal is masked by the intense phenyl protons resonances of PPh<sub>3</sub> ligands and of *p*-C<sub>6</sub>H<sub>4</sub>OMe groups in the ranges 6.5–7.8 ppm. When Z is the more electronegative oxygen atom of complex II,  $\delta(\text{O}=\text{C}-\text{H})$  appears at lower

TABLE 2  
<sup>1</sup>H NMR SPECTRA <sup>a</sup>

Compound	Signal	Assignment
DAB <sup>I</sup>	3.76 S [3] 3.80 S [3] 6.5—6.8 M <sup>b</sup> [8] 7.0—7.7 M [31]	O—Me O—Me H <sub>a</sub> + H <sub>b</sub> + H <sub>a'</sub> + H <sub>b'</sub> PPh <sub>3</sub> + N=C—H
[(DAB <sup>I</sup> )H]ClO <sub>4</sub> (I)	3.79 S } [6] 3.80 S } 6.7—7.0 M [4] 7.0—7.8 M [33] 8.3—8.5 M [2]	O—Me H <sub>b</sub> + H <sub>b'</sub> PPh <sub>3</sub> + N=C—H + H <sub>a'</sub> H <sub>a</sub>
[PdCl{ $\overbrace{C(=NC_6H_4OMe-p)}^{(II)}$ CH=O}(PPh <sub>3</sub> ) <sub>2</sub> ]	3.81 S [3] 6.6—6.8 M [2] 7.0—7.7 M [32] 7.89 T [1] <sup>4</sup> J(P—H) 2.4	O—Me H <sub>b</sub> PPh <sub>3</sub> + H <sub>a</sub> O=C—H
DAB <sup>II</sup>	2.98 D [3] <sup>4</sup> J(H—Me) 1.5 3.77 S [3] 6.39 M <sup>c</sup> [1] <sup>4</sup> J(H—Me) 1.5 <sup>4</sup> J(P—H) 1.8	N—Me O—Me N=C—H
DAB <sup>III</sup>	6.5—6.7 M [2] 6.9—7.8 M [32] 3.14 S [3] 3.20 S [3] 3.75 S } [6] 3.78 S }	H <sub>b</sub> PPh <sub>3</sub> + H <sub>a</sub> N—Me <sup>d</sup> N—Me <sup>d</sup> O—Me
[ZnCl <sub>2</sub> (DAB <sup>I</sup> )]	6.7—7.0 M [6] 7.0—7.8 M [18] 3.76 S [3] 3.80 S [3] 6.5—7.0 M [6] 7.2—7.5 M } [31] 7.58 S }	H <sub>a'</sub> + H <sub>b'</sub> + H <sub>b</sub> PPh <sub>3</sub> + H <sub>a</sub> + N=C—H O—Me O—Me H <sub>a'</sub> + H <sub>b'</sub> + H <sub>b</sub> PPh <sub>3</sub> N=C—H
[ZnCl <sub>2</sub> (DAB <sup>II</sup> )]	7.65—7.8 M [2] 2.72 D [3] <sup>4</sup> J(H—Me) 1.5 3.78 S [3]	H <sub>a</sub> N—Me O—Me
[ZnCl <sub>2</sub> (DAB <sup>III</sup> )]	6.5—6.7 M [2] 7.1—7.6 M [31] 7.6—7.8 M [2] 3.18 S [3] 3.22 S [3] 3.74 S } [6] 3.76 S }	H <sub>b</sub> PPh <sub>3</sub> + N=C—H H <sub>a</sub> N—Me <sup>d</sup> N—Me <sup>d</sup> O—Me
[Pt(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )(DAB <sup>IV</sup> )] <sup>e</sup>	6.6—6.9 M [4] 7.1—7.5 M [17] 7.9—8.1 M [2] 8.58 S [1] 3.88 S 3.94 S 6.7—7.1 M 7.1—7.8 M 9.15 T <sup>3</sup> J(Pt—H) 74.0 4.3—4.9 M 2.54 D 2.76 D <sup>3</sup> J(H—H) 12.5 3.16 D 3.53 D <sup>3</sup> J(H—H) 7.0	H <sub>b</sub> + H <sub>b'</sub> PPh <sub>3</sub> + H <sub>a'</sub> H <sub>a</sub> N=C—H O—Me O—Me H <sub>b</sub> + H <sub>b'</sub> PPh <sub>3</sub> + H <sub>a</sub> + H <sub>a'</sub> N=C—H H <sub>central</sub> <sup>f</sup> H <sub>anti</sub> <sup>f</sup> H <sub>syn</sub> <sup>f</sup>

field, 7.89 ppm, as a triplet due to coupling with the two equivalent  $^{31}\text{P}$  nuclei of the  $\text{trans-PdCl}(\text{PPh}_3)_2$  unit ( $^4J(\text{P-H})$  2.4 Hz). When  $\text{Z} = \text{N-Me}$ , as in  $\text{DAB}^{\text{II}}$ , the  $\delta(\text{N=C-H})$  signal is shifted up-field at 6.39 ppm, because of the higher

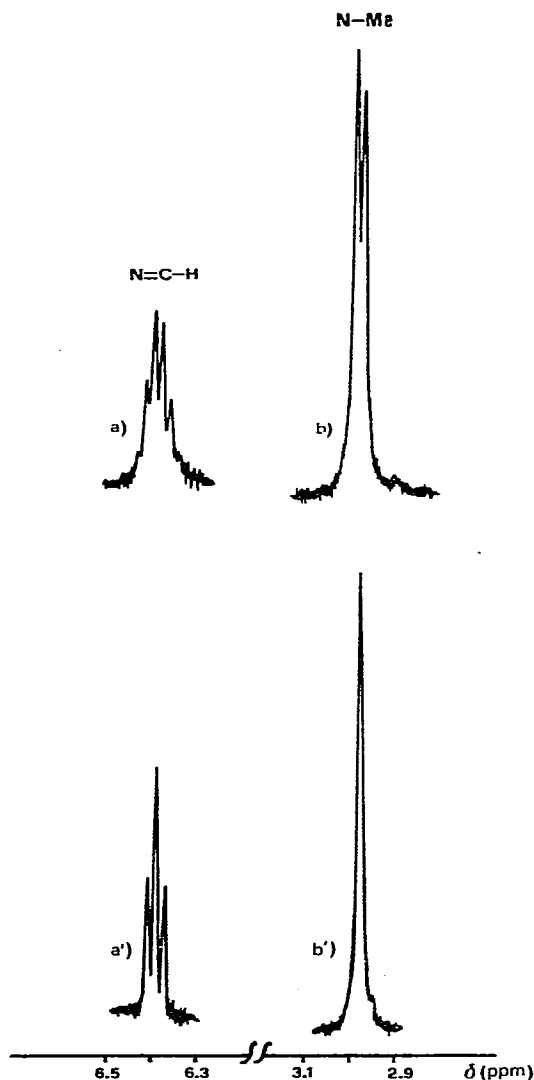


Fig. 1.  $^1\text{H}$  NMR spectrum of complex  $\text{DAB}^{\text{II}}$  in the ranges 6.5–6.3 and 3.1–2.9 ppm: (a)  $\delta(\text{N=C-H})$  signal, (a') the same signal upon irradiation at 2.98 ppm; (b)  $\delta(\text{N-Me})$  signal, (b') the same signal upon irradiation at 6.39 ppm.

<sup>a</sup> Spectra recorded in  $\text{CDCl}_3$  solution at  $35^\circ\text{C}$ ;  $\delta$  values in ppm from TMS as internal standard; coupling constants in Hz; integration values in square brackets; S = singlet, D = doublet, T = triplet, M = multiplet.

<sup>b</sup> The phenyl protons of  $p\text{-C}_6\text{H}_4\text{OMe}$  substituents appear as symmetrical  $\text{AA}'\text{BB}'$  signals; the  $\text{H}_\text{a}$  and  $\text{H}_\text{b}$  symbols indicate the *ortho* and *meta* protons of the  $p\text{-C}_6\text{H}_4\text{OMe}$  substituent on the 1-imino group; the  $\text{H}_\text{a}'$  and  $\text{H}_\text{b}'$  symbols indicate the *ortho* and *meta* protons of the  $p\text{-C}_6\text{H}_4\text{OMe}$  substituent on the 2-imino group. (For the labelling scheme, see ref. 2b and 7). <sup>c</sup> For the resolution of this signal, see Text. <sup>d</sup> Signals of *dmfc* ligand. <sup>e</sup> Spectrum recorded at  $-40^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ . <sup>f</sup> Signals of the allyl protons, the  $^{195}\text{Pt}$  satellites being masked by partial overlapping of bands.

electron-releasing ability of the methyl substituent. In this case, a rather complex resonance is observed, resulting from coupling with N—Me protons and with  $^{31}\text{P}$  nuclei, as shown in Fig. 1.

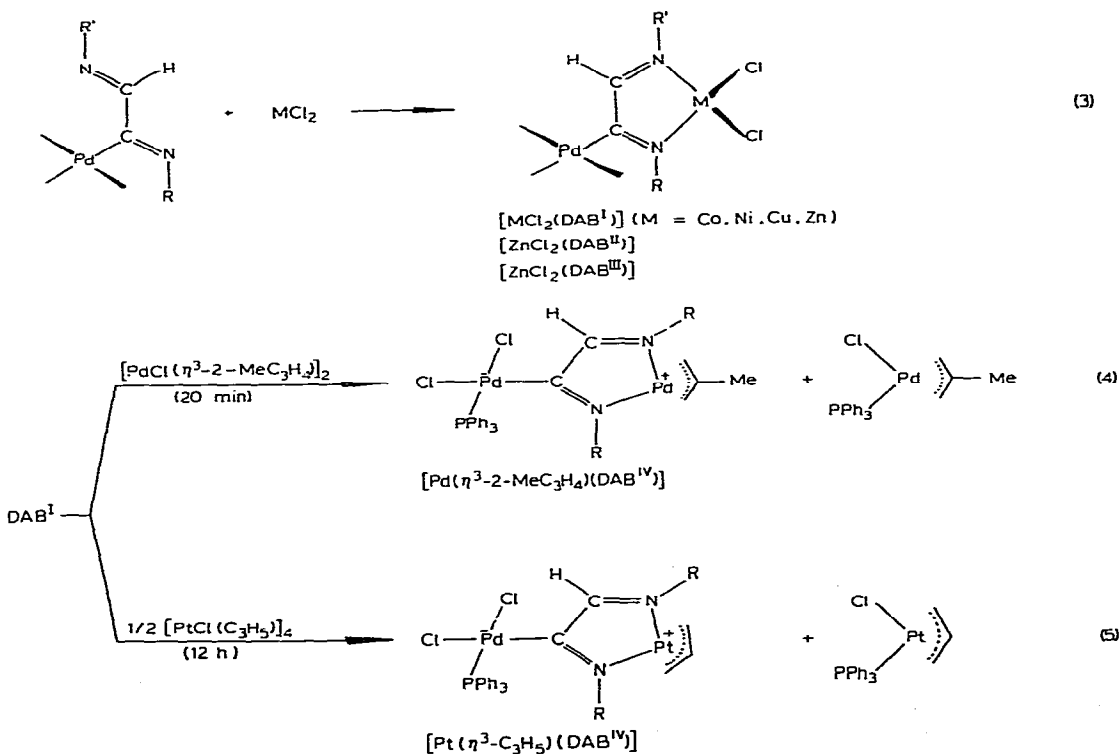
The coupling between the imino proton and the N—Me group is indicated by the appearance of  $\delta(\text{N—Me})$  as a doublet at 2.98 ppm with a  $^4J(\text{H—Me})$  value of 1.5 Hz, and further confirmed by spin decoupling experiments. Upon irradiation at a frequency corresponding to 2.98 ppm the  $\delta(\text{N=C—H})$  signal becomes a triplet, since the imino proton is now coupled only with the two equivalent  $^{31}\text{P}$  nuclei ( $^4J(\text{P—H})$  1.8 Hz). As expected, the  $\delta(\text{N—Me})$  resonance becomes a singlet upon irradiation at 6.39 ppm.

In addition to the influence of the Z group (which is essentially inductive in nature), the imino proton chemical shift is also affected by the *trans*-PdCl(PPh<sub>3</sub>)<sub>2</sub> unit, as shown by a comparison with  $\delta(\text{N=C—H})$  values of the  $\alpha$ -di-imines RN=C(R')—C(R'')=NR (R = *p*-C<sub>6</sub>H<sub>4</sub>OMe, R' = R'' = H:  $\delta(\text{N=C—H})$  8.35 ppm; R = *p*-C<sub>6</sub>H<sub>4</sub>OMe, R' = H, R'' = Me 8.15 ppm; R = CMe<sub>3</sub>, R' = R'' = H 7.93 ppm) [13]. The up-field shift of  $\delta(\text{N=C—H})$  in DAB<sup>I</sup> and DAB<sup>II</sup> may be reasonably accounted for by the through-space shielding effect of the phenyl ring currents of the two mutually *trans*-PPh<sub>3</sub> ligands, previously observed in 1,2-bis(imino)propyl derivatives of DAB type [10].

### Coordination properties

Some representative coordination reactions of 1,2-bis(imino)ethyl complexes are shown in Scheme 2.

SCHEME 2





The complex  $\text{DAB}^{\text{I}}$  gives 1/1 adducts with all  $\text{MCl}_2$  chlorides examined. For  $\text{DAB}^{\text{II}}$  and  $\text{DAB}^{\text{III}}$  we have studied only the reactions with  $\text{ZnCl}_2$ , which yield the diamagnetic compounds  $[\text{ZnCl}_2(\text{DAB}^{\text{II}})]$  and  $[\text{ZnCl}_2(\text{DAB}^{\text{III}})]$ , susceptible to  $^1\text{H}$  NMR investigation. The binuclear products of reaction 3 are monomers in 1,2-dichloroethane solution. The  $[\text{CuCl}_2(\text{DAB}^{\text{I}})]$  adduct undergoes a slow decomposition in solution which prevents any accurate measurement of molecular weight and electronic spectrum (the decomposition in methanol is indicated by progressive increase in electrical conductivity and slow precipitation of  $[\text{PdCl}_2(\text{PPh}_3)_2]$ ). For  $[\text{MCl}_2(\text{DAB}^{\text{I}})]$  ( $\text{M} = \text{Co}, \text{Ni}$ ), the presence of typical  $d-d$  bands in the visible and near IR spectra (Fig. 2), the values of magnetic moment in the solid ( $\mu_{\text{eff}}$  4.83 and 3.25 BM for  $\text{M} = \text{Co}$  and  $\text{Ni}$ , respectively), and the position and number of  $\nu(\text{M}-\text{Cl})$  vibrations (Table 1) are in accord with a pseudo-tetrahedral configuration around the metal  $\text{M}$ , analogous to that proposed for the corresponding  $[\text{MCl}_2(\text{DAB})]$  derivatives [2c]. A distorted pseudo-tetrahedral structure is probably present in  $[\text{CuCl}_2(\text{DAB}^{\text{I}})]$ , as can be inferred from the X-ray structural data for  $[\text{CuCl}_2(\text{DAB})]$  [14]. For the  $\text{ZnCl}_2$  adducts, the  $\nu(\text{Zn}-\text{Cl})$  bands fall in the range  $337-310\text{ cm}^{-1}$  in good agreement with the corresponding vibrations in the tetrahedral complex  $[\text{ZnCl}_2(2,2'\text{-bipyridine})]$  [15] and in other binuclear 1,2-bis(imino)propylpalladium(II)/ $\text{ZnCl}_2$  derivatives [2b, 2c]. Upon coordination,  $\nu(\text{Pd}-\text{Cl})$  of  $\text{DAB}^{\text{I}}$  and  $\text{DAB}^{\text{II}}$  shifts to higher frequencies, due to the reduced *trans*-influence of the  $\sigma$ -bonded organic moieties [2b, 2c, 7, 14], and in some cases is masked by the more intense  $\nu(\text{M}-\text{Cl})$  vibrations. Conversely, the  $\nu(\text{C}=\text{N})$  absorptions move to lower frequencies by ca.  $50-60\text{ cm}^{-1}$ . In most cases, only one  $\nu(\text{C}=\text{N})$  band is observed, the second infrared-active  $\text{C}=\text{N}$  stretching vibration being masked by

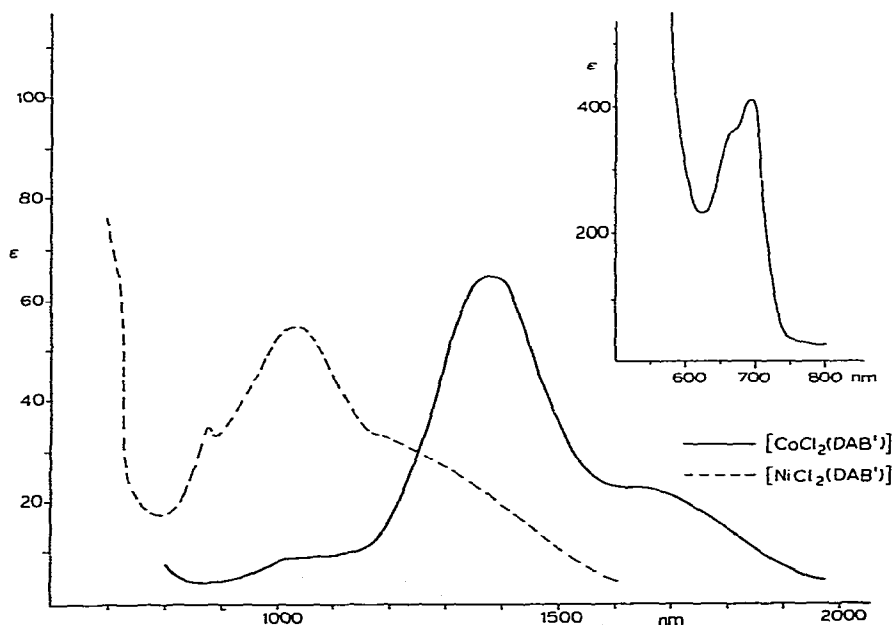
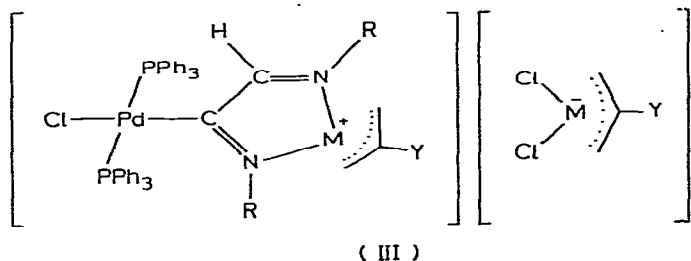


Fig. 2. Electronic spectra in  $\text{CH}_2\text{Cl}_2$  of  $[\text{CoCl}_2(\text{DAB}^{\text{I}})]$  (—) and  $[\text{NiCl}_2(\text{DAB}^{\text{I}})]$  (-----).

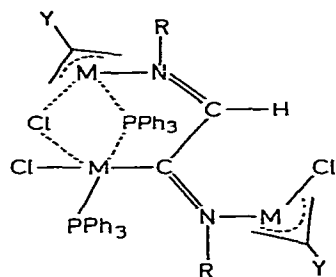
the strong absorptions of the *para*-substituted phenyl groups around  $1500\text{ cm}^{-1}$ .

From the  $^1\text{H}$  NMR spectra of Table 2 it appears that, in addition to the down-field shift of the *ortho* protons resonances of *p*- $\text{C}_6\text{H}_4\text{OMe}$  substituent on the 1-imino group [2a, 2b, 7], the coordination of the 1,2-bis(imino)ethyl moieties of  $\text{DAB}^{\text{I}}$ ,  $\text{DAB}^{\text{II}}$  and  $\text{DAB}^{\text{III}}$  brings about a deshielding of  $\delta(\text{N}=\text{C}-\text{H})$  signals, resulting from steric and electronic effects, such as change of configuration of the 1,2-bis(imino) ligand, inductive and ring current effects. In the case of  $\text{DAB}^{\text{II}}$  derivatives, the down-field shift of  $\delta(\text{N}=\text{C}-\text{H})$  (at 6.39 ppm in the free ligand) is such that in the adduct  $[\text{ZnCl}_2(\text{DAB}^{\text{II}})]$  the signal is masked by the intense  $\text{PPh}_3$  resonances in the range 7.1–7.6 ppm. Also for the zwitterionic binuclear products of reaction 4 and 5, the imino proton chemical shift occurs at rather low field (8.88 ppm for  $[\text{Pd}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{DAB}^{\text{IV}})]$  [16] and 9.15 ppm for  $[\text{Pt}(\eta^3\text{-C}_3\text{H}_5)(\text{DAB}^{\text{IV}})]$ ). In the binuclear derivatives,  $\delta(\text{N}=\text{C}-\text{H})$  appears as a sharp signal with no coupling (under the resolution limit of the instrument) with  $^{31}\text{P}$  nuclei of the  $\text{PPh}_3$  ligands on the palladium metal center, at variance with what observed for complexes II and  $\text{DAB}^{\text{II}}$ . Although the contribution of electronic factors cannot be assessed, a reduction in the  $^{31}\text{P}$  coupling constant would be expected on steric grounds, owing to the conformational change of the ligand upon chelation (the imino proton being forced into a "cis" position relative to palladium). The down-field shift of  $\delta(\text{N}=\text{C}-\text{H})$  signal is indicative of a  $\sigma$ -, *N*-bonding type of the 2-imino group on the basis of  $^1\text{H}$  NMR reports on coordinated  $\text{RN}=\text{CH}-\text{CH}=\text{NR}$  ligands [17].

The reaction 4 was shown to proceed via an ionic intermediate III ( $\text{M} = \text{Pd}$ ;  $\text{Y} = \text{Me}$ ):

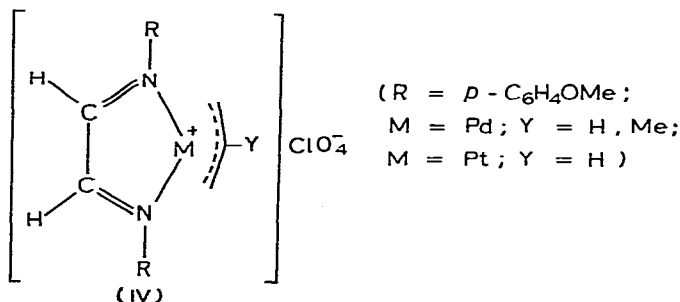


in which the exchange of  $\text{PPh}_3$  and  $\text{Cl}^-$  ligands between the cation and anion occurs essentially through a trinuclear transition state formed by opening of the 5-membered  $\alpha$ -diimino cycle of the cationic species upon interaction with the anion [16,18]:

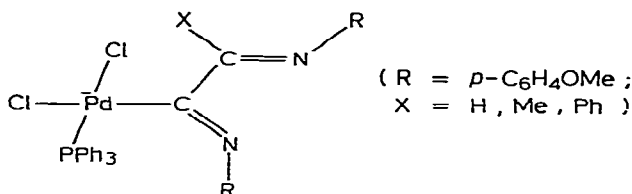


An intermediate of type III ( $\text{M} = \text{Pt}$ ;  $\text{Y} = \text{H}$ ) is likely to be involved also in

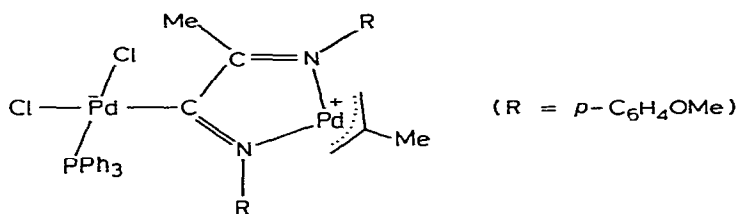
reaction 5, as suggested by conductivity measurements of  $\text{DAB}^{\text{I}}/1/2[\text{PtCl}(\text{C}_3\text{H}_5)_4]$  mixtures in 1,2-dichloroethane (see Experimental), and would explain the markedly reduced rate of reaction 5 compared to reaction 4, on the basis of different ease of  $\text{M}-\text{N}$  bond cleavage in the cationic species (the primary step involved in the formation of the trinuclear transition state). This may be related to the stability (towards dissociation of the  $\alpha$ -diimine ligand) of the mononuclear cationic complexes IV:



which increases considerably (ca. two order of magnitude) on going from Pd to Pt [13]. Both products of reaction 5 have been isolated and identified. The zwitterionic compound,  $[\text{Pt}(\eta^3\text{-C}_3\text{H}_5)(\text{DAB}^{\text{IV}})]$ , is non-conducting and monomeric in 1,2-dichloroethane solution. Its structural formulation rests mainly on spectroscopic evidence. Two  $\nu(\text{Pd}-\text{Cl})$  bands at 304 and 280  $\text{cm}^{-1}$  are observed in the far-infrared spectrum, which are characteristic of coordinated anionic ligands of the type [7,16,19]:



The coordination of the  $\alpha$ -diimino moiety is indicated by the occurrence of  $\nu(\text{C}=\text{N})$  at 1551  $\text{cm}^{-1}$  (i.e., very close to the  $\nu(\text{C}=\text{N})$  values of the  $\text{DAB}^{\text{I}}$  and  $\text{DAB}^{\text{III}}$  binuclear adducts) and by the low-field signal of the imino proton (9.15 ppm), which appears as a triplet because of coupling with  $^{195}\text{Pt}$  isotope. The chemical shift and the coupling constant values (74.0 Hz) agree well with those reported for the mononuclear cationic complex IV ( $\text{M} = \text{Pt}; \text{Y} = \text{H}; \delta(\text{N}=\text{C}-\text{H})$  9.10 ppm,  $^3J(\text{Pt}-\text{H})$  74.4 Hz), in which the  $\alpha$ -diimine ligand is  $\sigma, \sigma$ - $\text{N}, \text{N}$  chelated to the platinum center [13]. The  $^1\text{H}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  at  $-40^\circ\text{C}$  shows also the presence of an  $\eta^3$ -bound allyl group (at room temperature, the allyl resonances are somewhat broader as the result of dynamic processes discussed elsewhere for  $[\text{Pd}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{DAB}^{\text{IV}})]$  and closely related complexes [16]). Further support to the formulation of  $[\text{Pt}(\eta^3\text{-C}_3\text{H}_5)(\text{DAB}^{\text{IV}})]$  is given by the X-ray structural analysis of the zwitterionic complex [16]. The electronic spectra of the binuclear products of reactions 3–5 are characterized by intense bands in the range 330–550 nm, which are typical of the



5-membered metallocycle chromophore and have essentially a metal-to-ligand charge-transfer character, indicated by their dependence on the nature of the metal M and of the C- and N-imino substituents, as well as by solvatochromic effects. The MLCT bands of complex [ZnCl<sub>2</sub>(DAB<sup>I</sup>)] are shown in Fig. 3 along with those of the analogue [ZnCl<sub>2</sub>(DAB)].

As can be seen, substitution of the proton by a methyl group at the 2-imino carbon atom brings about a marked decrease in intensity and a shift of the band maximum to higher frequency. Such a shift appears to be quite general for  $\alpha$ -diimine complexes, and is ascribed to inductive destabilization of the lowest energy antibonding orbital of these ligands by C-imino methyl substituents [20].

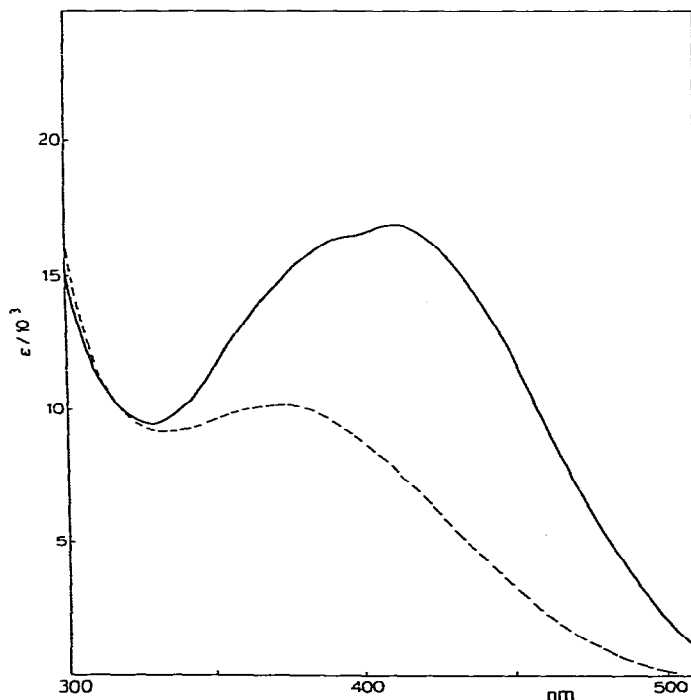


Fig. 3. Electronic spectra in 1,2-dichloroethane of [ZnCl<sub>2</sub>(DAB<sup>I</sup>)] (—) and [ZnCl<sub>2</sub>(DAB)] (-----).

## Experimental

The isocyanide  $\text{CNC}_6\text{H}_4\text{OMe-}p$  [21] and the complexes  $[\text{Pd}(\text{PPh}_3)_4]$  [22],  $[\text{PdCl}(\eta^3\text{-2-MeC}_3\text{H}_4)]_2$  [23],  $[\text{PtCl}(\text{C}_3\text{H}_5)]_4$  [24] were prepared by published methods. All the other chemicals were reagent grade, and used without further purification. Infrared spectra were recorded with a Perkin-Elmer 597 instrument, using hexachlorobutadiene mulls and NaCl plates in the range  $4000\text{--}1300\text{ cm}^{-1}$ , Nujol mulls and CsI plates in the range  $1700\text{--}250\text{ cm}^{-1}$ . Electronic spectra in solution were recorded with a Cary model 14 recording spectrophotometer in the range  $2000\text{--}500\text{ nm}$ , and with a Bausch-Lomb Spectronic 210-UV spectrophotometer in the range  $600\text{--}250\text{ nm}$  at  $20^\circ\text{C}$ , using quartz cells of  $1\text{ cm}$  path length.  $^1\text{H}$  NMR spectra were recorded with a Varian EM-390 90-MHz spectrometer at room temperature. Magnetic moments were determined in the solid state with a Bruker Magnet BM6 instrument at  $20^\circ\text{C}$ . Molecular weights were measured with a Knauer osmometer in 1,2-dichloroethane at  $37^\circ\text{C}$ . The conductivity measurements were carried out with a Philips PR9500 bridge at  $20^\circ\text{C}$ .

### *Preparation of trans-[PdCl{C(=NR)CH=NR}(PPh<sub>3</sub>)<sub>2</sub>] (R = p-C<sub>6</sub>H<sub>4</sub>OMe, DAB<sup>I</sup>)*

A solution of the isocyanide  $\text{CNC}_6\text{H}_4\text{OMe-}p$  (0.80 g, 6 mmol) in 20 ml of toluene was added dropwise to a stirred suspension of  $[\text{Pd}(\text{PPh}_3)_4]$  (3.46 g, 3 mmol) in 80 ml of toluene under dinitrogen. The mixture was stirred for ca. 1 h until complete dissolution of the reactants, and then cooled to  $-70^\circ\text{C}$  with a solid  $\text{CO}_2$ /acetone bath. An 0.22 M ethanolic solution of HCl (13.6 ml, 3 mmol), diluted with 55 ml of toluene, was slowly added dropwise during ca. 2 h. After the addition the mixture was stirred at  $-70^\circ\text{C}$  for 90 min and then allowed to warm to room temperature (ca. 3 h). The resulting dark-red solution contained a yellow precipitate, which was filtered off and identified as  $[\text{PdCl}_2(\text{PPh}_3)_2]$  (0.30 g). The clear solution was concentrated to small volume (ca. 15 ml) until incipient precipitation of the product was observed. The precipitation was completed by dilution with diethyl ether. The yellow-brown crude product was redissolved in a 1,2-dichloroethane (80 ml)/diethyl ether (8 ml) mixture in order to separate the insoluble  $[\text{PdCl}_2(\text{PPh}_3)_2]$  (0.15 g) still present. After treatment with activated charcoal, filtration and concentration, the analytically pure product was precipitated by slow addition of diethyl ether (yield 1.54 g, 55% of the theoretical amount based on the initial quantity of  $[\text{Pd}(\text{PPh}_3)_4]$ ).

The yield is even lower if HCl is quickly added to the  $[\text{Pd}(\text{PPh}_3)_4]/2\text{CNC}_6\text{H}_4\text{OMe-}p$  mixture and if the reaction sequence is changed, i.e., when the isocyanide is added to a  $[\text{Pd}(\text{PPh}_3)_4]/\text{HCl}$  reaction mixture. In a typical experiment, an 0.26 M ethanolic solution of HCl (3.9 ml, 1 mmol) was slowly added dropwise (30 min) to a stirred suspension of  $[\text{Pd}(\text{PPh}_3)_4]$  (1.15 g, 1 mmol) in ca. 50 ml of toluene, at  $-70^\circ\text{C}$  under dinitrogen. A solution of the isocyanide (0.27 g, 2 mmol) in 5 ml of toluene was then added dropwise during ca. 10 min. The resulting yellow solution was allowed to warm to room temperature (ca. 2 h), during which the colour changed from yellow to deep-red. Concentration and addition of diethyl ether gave a crude product (0.55 g) which was separated into  $[\text{PdCl}_2(\text{PPh}_3)_2]$  (0.35 g) and DAB<sup>I</sup> (0.15 g, 16% yield) by fractional precipitation from 1,2-dichloroethane/diethyl ether.

### Protonation and acid hydrolysis of $DAB^I$

(a) A solution of  $DAB^I$  (0.47 g, 0.5 mmol) in 30 ml of 1,2-dichloroethane was treated with an 0.5 M methanolic solution of  $HClO_4$  (1.2 ml, 0.6 mmol). An immediate change of colour (from yellow to orange) occurred. After 5 min stirring, the mixture was concentrated to small volume at reduced pressure and the yellow-orange product I was precipitated by adding diethyl ether. It was purified by reprecipitation from 1,2-dichloroethane/diethyl ether (yield 0.42 g, 81%).

(b) The complex  $DAB^I$  (0.47 g, 0.5 mmol) dissolved in 50 ml of  $CH_2Cl_2$  was treated with 5 M  $HCl$  (1 ml). The mixture was stirred for 6 h and then taken to dryness. The solid residue was washed several times with water and dried in vacuo for 3–4 h. The crude product, which consists of protonated *trans*- $[PdCl\{\overline{C(=NR)CH=O}\}(PPh_3)_2]$ , was dissolved in  $CH_2Cl_2$  (10 ml) and treated with  $NEt_3$  (1 ml). The mixture was taken to dryness at reduced pressure and the solid residue was washed several times with water and dried. The pure final product II was obtained after two successive precipitation from benzene solution diluted with diethyl ether/*n*-hexane (1/4 v/v) mixture (yield 0.32 g, 79%).

### Preparation of complexes $DAB^{II}$ and $DAB^{III}$

(a) The condensation reaction between *trans*- $[PdCl\{\overline{C(=NR)CH=O}\}(PPh_3)_2]$  and  $NH_2Me$  was carried out as previously described for the analogous *trans*- $[PdCl\{\overline{C(=NR)C(Me)=O}\}(PPh_3)_2]$  [2b]. The progress of the reaction was monitored by IR spectroscopy in solution, following the disappearance of the  $\nu(C=O)$  band at  $1695\text{ cm}^{-1}$ . The reaction was complete in ca. 4 h (yield 52%).

(b) The preparation of  $DAB^{III}$  from the reaction of  $DAB^I$  with  $Na[dmtc] \cdot 2H_2O$  was carried out as previously reported for the corresponding reaction of *trans*- $[PdCl\{\overline{C(=NR)C(Me)=NR}\}(PPh_3)_2]$ ,  $DAB$ , [7] (yield 74%).

### Reaction of $DAB^I$ with anhydrous $MCl_2$ ( $M = Co, Ni, Cu, Zn$ )

The ligand  $DAB^I$  (0.47 g, 0.5 mmol) dissolved in 40 ml of 1,2-dichloroethane was added to a solution of  $MCl_2$  (0.5 mmol) in 10–15 ml of anhydrous MeOH. The reaction was very fast and accompanied by a rapid change of colour. After 10 min stirring, the mixture was treated with charcoal, then filtered, and the clear filtrate was concentrated to small volume at reduced pressure. Addition of diethyl ether gave the 1/1 binuclear adducts as microcrystalline solids. The products were purified by reprecipitation from 1,2-dichloroethane/diethyl ether (yield of  $[CoCl_2(DAB^I)]$  84%,  $[NiCl_2(DAB^I)]$  72%,  $[CuCl_2(DAB^I)]$  86%,  $[ZnCl_2(DAB^I)]$  65%).

### Reaction of $ZnCl_2$ with $DAB^{II}$ and $DAB^{III}$

These reactions were carried out as described above for  $DAB^I$  ligand (yield of  $[ZnCl_2(DAB^{II})]$  96%,  $[ZnCl_2(DAB^{III})]$ , 90%).

### Reaction of $DAB^I$ with $[PdCl(\eta^3\text{-}2\text{-MeC}_3\text{H}_4)]_2$ and $[PtCl(C_3H_5)]_4$

(a) A solution of  $DAB^I$  (0.467 g, 0.5 mmol) in 50 ml of 1,2-dichloroethane was treated with  $[PdCl(\eta^3\text{-}2\text{-MeC}_3\text{H}_4)]_2$  (0.20 g, 0.5 mmol). The reaction, the progress of which was followed by conductivity measurements, was complete in ca. 20 min. The volume of the clear orange solution was reduced to ca. 5 ml

at reduced pressure. Addition of diethyl ether gave a solid product which, after reprecipitation from the same solvents, was identified as  $[\text{Pd}(\eta^3\text{-2-MeC}_3\text{H}_4)\text{(DAB}^{\text{IV}})]$  (yield 0.33 g, 76%). The mother liquor from the first precipitation was concentrated and a diethyl ether/n-hexane (1/1 vv) mixture was added to give a pale-yellow precipitate (0.20 g), identified as  $[\text{PdCl}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{PPh}_3)]$  by comparing its IR and  $^1\text{H NMR}$  spectra with those of an independently prepared authentic sample.

(b) The complex  $[\text{PtCl}(\text{C}_3\text{H}_5)]_4$  (0.18 g, 1/6 mmol) was added to a solution of  $\text{DAB}^{\text{I}}$  (0.31 g, 1/3 mmol) in 30 ml of 1,2-dichloroethane. The mixture was stirred for 15 min until complete dissolution of the allyl platinum tetramer. The resulting dark-red solution was set aside for 12 h and then worked up as described above for the methallyl palladium dimer, to give  $[\text{Pt}(\eta^3\text{-C}_3\text{H}_5)(\text{DAB}^{\text{IV}})]$  (0.27 g, 86%) and  $[\text{PtCl}(\eta^3\text{-C}_3\text{H}_5)(\text{PPh}_3)]$  (0.12 g), the latter product being identified from its IR and  $^1\text{H NMR}$  spectra [25]. Again it was possible to monitor the course of the reaction by conductivity measurements. Starting from a  $10^{-3}$  M solution of  $\text{DAB}^{\text{I}}$  in 1,2-dichloroethane, to which the appropriate amount of  $[\text{PtCl}(\text{C}_3\text{H}_5)]_4$  was added in order to give a  $\text{DAB}^{\text{I}}/\text{Pt}$  ratio of 1/2, and using a cell with a constant of  $0.813\text{ cm}^{-1}$ , it was found that the conductivity decreased slowly from an initial value of  $10^{-5}\text{ ohm}^{-1}$  to a constant value of  $1.1 \times 10^{-6}\text{ ohm}^{-1}$  in ca. 12 h.

## References

- 1 Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, **13** (1974) 438.
- 2 a) B. Crociani, M. Nicolini and R.L. Richards, *J. Organometal. Chem.*, **104** (1976) 259; b) B. Crociani and R.L. Richards, *ibid.*, **154** (1978) 65; c) B. Crociani, M. Nicolini and R.L. Richards, *J. Chem. Soc. Dalton*, (1978) 1478.
- 3 P.L. Sandrini, A. Mantovani and B. Crociani, *J. Organometal. Chem.*, **185** (1980) C13.
- 4 a) G.R. Clark, J.M. Waters and K.R. Whittle, *J. Chem. Soc. Dalton*, (1975) 2556; b) D.F. Christian, H.C. Clark and R.F. Stepaniak, *J. Organometal. Chem.*, **112** (1976) 209; c) M. Ciriano, M. Green, D. Gregson, J.A.K. Howard, J.L. Spencer, F.G.A. Stone and P. Woodward, *J. Chem. Soc. Dalton*, (1979) 1294; d) M.I. Bruce and R.C. Wallis, *J. Organometal. Chem.*, **164** (1979) C6; e) R.D. Adams and N.M. Golembeski, *J. Amer. Chem. Soc.*, **101** (1979) 2579.
- 5 L. Malatesta and F. Bonati, *Isocyanide Complexes of Metals*, Wiley, New York (1969) p. 164.
- 6 B. Crociani, *Inorg. Chim. Acta*, **23** (1977) L1.
- 7 B. Crociani, M. Nicolini and A. Mantovani, *J. Organometal. Chem.*, **177** (1979) 365.
- 8 a) D.A. Brown, W.K. Glass and M.A. Burke, *Spectrochim. Acta*, **32A** (1976) 137; b) K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd Edition, Wiley, New York (1970) p. 256.
- 9 L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen, London (1966) p. 132.
- 10 B. Crociani, G. Bandoli and D.A. Clemente, *J. Organometal. Chem.*, **184** (1980) 269.
- 11 O. Exner and J.M. Kliegmann, *J. Org. Chem.*, **36** (1971) 2014.
- 12 J.M. Kliegmann and R.K. Barnes, *Tetrahedron*, **26** (1970) 2555.
- 13 B. Crociani, T. Boschi and P. Uguagliati, *Inorg. Chim. Acta*, **48** (1981) 9.
- 14 B. Crociani, G. Bandoli and D.A. Clemente, *J. Organometal. Chem.*, **190** (1980) C97.
- 15 R.J.H. Clark and C.S. Williams, *Inorg. Chem.*, **4** (1965) 350.
- 16 B. Crociani, R. Bertani, T. Boschi and G. Bandoli, *J. Chem. Soc. Dalton*, in press.
- 17 a) H. tom Dieck and A. Orlopp, *Angew. Chem. Internat. Ed.*, **14** (1975) 251; b) H. van der Poel, G. van Koten and K. Vrieze, *J. Organometal. Chem.*, **135** (1977) C63; c) L.H. Staal, A. Oskam and K. Vrieze, *J. Organometal. Chem.*, **145** (1978) C7; d) H. van der Poel, G. van Koten and K. Vrieze, *Inorg. Chem.*, **19** (1980) 1145.
- 18 B. Crociani, P. Uguagliati, R. Bertani and L. Calligaro, *Inorg. Chim. Acta*, **45** (1980) L75.
- 19 B. Crociani, U. Belluco and P.L. Sandrini, *J. Organometal. Chem.*, **177** (1979) 385.
- 20 H. tom Dieck and I.W. Renk, *Chem. Ber.*, **104** (1971) 110.
- 21 I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer and K. Offermann, *Angew. Chem. Internat. Ed.*, **4** (1965) 472.

- 22 D.R. Coulson, *Inorg. Synt.*, 13 (1972) 121.  
23 F.R. Hartley and S.R. Jones, *J. Organometal. Chem.*, 66 (1974) 465.  
24 J. Lukas, B.E. Morris and R.A. Clement, *Inorg. Synt.*, 15 (1974) 79.  
25 a) B.E. Mann, B.L. Shaw and G. Shaw, *J. Chem. Soc., A*, (1971) 3536; b) G. Carturan, A. Scrivanti, B. Longato and F. Morandini, *J. Organometal. Chem.*, 172 (1979) 91.