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**AN NMR STUDY OF THE INTERACTION OF α -DIIMINES
(RN=CHCH=NR) WITH CYCLOMETALLATED PALLADIUM(II)
COMPOUNDS [{2-Me₂NCH(Z)C₆H₄PdX}]₂ (Z = H or (S)-Me; X = Cl, Br)**

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Summary

When [{2-Me₂NCH(Z)C₆H₄PdX}]₂ is treated with an α -diimine (RN=CHCH=NR; R-dim) an equilibrium mixture of starting material and [{2-Me₂NCH(Z)C₆H₄PdX}]_n(R-dim) (*n* = 1 or 2) is obtained, the composition depending on the metal complex/ligand ratio. Intermolecular exchange in these mixtures is slow on the NMR time scale.

The mononuclear complexes [2-Me₂NCH(Z)C₆H₄PdX(R-dim)] show an intramolecular dynamic behaviour which is slow on the NMR time scale at -50°C (¹³C NMR) and -80°C (¹H NMR). In the slow exchange limit the complex is a four-coordinate Pd^{II} complex having the halogen atom *trans* to the C atom and *cis* to a monodentate (σ -N)-bonded R-dim ligand. In the fast exchange a rapid head-to-tail rearrangement occurs in which the R-dim ligand changes its point of attachment to the Pd^{II} centre (σ -N \rightleftharpoons σ -N' rearrangement).

In solution the dinuclear complex has a structure consisting of two 2-Me₂NCH(Z)C₆H₄PdX units containing *trans*-positioned C and X ligands; these units are bridged by a R-dim ligand in the *s-trans* conformation. The NMR data for these complexes are compared with those of stable palladium and platinum analogues [{MCl₂(ER'₃) }]_n(R-dim) (*n* = 1 or 2; R = *t*-Bu, EtMe₂C-; E = As, P; R' = *n*-Bu, Ph).

Introduction

In previous papers we showed that the bonding mode of the α -diimine ligand (R-dim is RN=CHCH=NR) in *trans*-[MX₂L(R-dim)] complexes (M = Pd and Pt) is strongly dependent on the natures of both R (electronic and branching

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effects) and the coligand L. The influence of L is demonstrated by the following examples in which R is a tertiary-butyl group.

In five-coordinate $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{t-Bu-dim})]$ the α -diimine is σ, σ - N, N' chelate-bonded [1] while in four-coordinate $[\{\text{PtCl}_2(\text{PBu}_3)_n(\text{t-Bu-dim})\}]$ complexes σ - N monodentate ($n = 1$) [2] and σ - N, σ - N' bridging ($n = 2$) [1a, 3] bonding modes have been observed. These last two modes have also been found in the analogous square planar palladium complexes $[\{\text{PdCl}_2(\text{PEt}_3)_2(\text{t-Bu-dim})\}]$ [3] and $[\text{PdCl}_2(\text{PPh}_3)(\text{t-Bu-dim})]$ [2]. However, while the palladium analogue of the five-coordinate $[\text{PtCl}_2(\eta^2\text{-olefin})(\text{t-Bu-dim})]$ could not be prepared, *trans*- $[\text{PdCl}_2(\text{t-Bu-dim})_2]$ which contains two σ - N monodentate-bonded t-Bu-dim ligands seems to have no analogue in Pt^{II} chemistry [2].

In order to study further the influence of X and of L on the coordination mode of the R-dim ligand in $[\text{MX}_2\text{L}(\text{R-dim})]$ complexes, the halogen bridge-splitting reactions of $[\{2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdCl}\}_2]$ were investigated. The 2-Me₂NCH(Z)C₆H₄ ligand was chosen for this study for two reasons: (i) this ligand is bonded via one carbon (X) and one nitrogen (L) atom to the palladium centre which allows study of *trans* influences in such complexes, and (ii) the prochiral CH₂ and NMe₂ (if coordinated) or chiral benzylic-C (if Z = Me) centres of the 2-Me₂NCH(Z)C₆H₄ ligand are useful probes for ¹H and ¹³C NMR detection of the bonding modes in the complexes [4].

Experimental

Reactions were carried out under dry oxygen-free nitrogen. Solvents were purified and distilled before use.

IR spectra were recorded on a Perkin-Elmer M 283 on solutions in CHCl₃ and benzene. ¹H NMR spectra were recorded on A-60 (Varian), T-60 (Varian), and WH 90 (Bruker) spectrometers and the ¹³C NMR spectra on a CFT 20 (Varian) spectrometer. The ¹H NMR spectra on the WH 90 spectrometer were obtained by Dr. J.W. Marsman.

Elemental analysis were carried out in the Analytical Department of the Inst. for Org. Chem., T.N.O., The Netherlands.

Synthesis of the compounds

1-(*S*)-(Dimethylamino)ethylbenzene was prepared by treating 1-(*S*)-aminoethylbenzene with a formaldehyde/formic acid mixture [4a].

The α -diimine derivatives t-Bu-dim and EtMe₂C-dim (R-dim is RN=CHCH=NR) [2] as well as the starting palladium dimers $[\{2\text{-Me}_2\text{NCH}_2\text{-C}_6\text{H}_4\text{PdX}\}_2]$ (I) [5] and $[\{(S)\text{-}2\text{-Me}_2\text{NCH}(\text{Me})\text{C}_6\text{H}_4\text{PdX}\}_2]$ (II) [5] (X = Cl or Br) were synthesized by previously described procedures.

$[\{2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{PdCl}\}_2(\text{t-Bu-dim})]$ (III). t-Bu-dim (1.1 mmol) was added to a stirred suspension of I (1.0 mmol) in methanol (5 ml). The mixture was stirred for 30 min, during which a bright yellow precipitate formed in the orange-coloured solution. The precipitate was filtered off, washed with hexane (5 × 5 ml), and dried in vacuo. Elemental analysis was consistent with the stoichiometry $[\{2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{PdCl}\}_2(\text{t-Bu-dim})]$ (see also Discussion). Found: C, 45.42; H, 6.12; N, 7.52; Cl, 10.11. C₂₈H₄₄N₄Cl₂Pd₂ calcd.: C, 46.68; H, 6.16; N, 7.78; Cl, 9.84%. cf.: Calcd. for I: C, 39.16; H, 4.38; Cl, 12.84% and for $[2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{PdCl}(\text{t-Bu-dim})]$: C, 54.77; H, 7.22; N, 9.78; Cl, 11.55%.

Solutions for ^1H and ^{13}C NMR studies

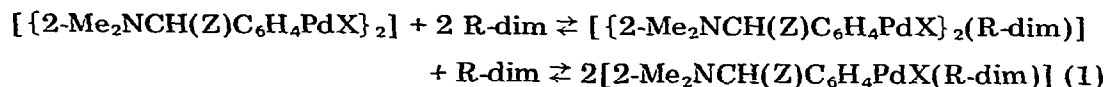
Solutions of $[\{2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}\}_2(\text{R-dim})]$ ($\text{Z} = \text{H}$: $\text{R} = \text{t-Bu}$ (IIIa) $\text{R} = \text{EtMe}_2\text{C-}$ (IIIb); $\text{Z} = \text{Me}$: $\text{R} = \text{t-Bu}$ (IVa), $\text{EtMe}_2\text{C-}$ (IVb)) and $[2\text{-Me}_2\text{NCH}(\text{Z})\text{-C}_6\text{H}_4\text{PdX}(\text{R-dim})]$ ($\text{Z} = \text{H}$: $\text{R} = \text{t-Bu}$ (Va) $\text{R} = \text{EtMe}_2\text{C-}$ (Vb); $\text{Z} = \text{Me}$: $\text{R} = \text{t-Bu}$ (VIa) $\text{R} = \text{EtMe}_2\text{C-}$ (VIb)) were produced in situ by mixing I or II and the appropriate R-dim ligand in molar ratios ranging from 1/0.5 to 1/4 in either CDCl_3 or CD_2Cl_2 . The spectra were recorded at various temperatures between -80°C and 34°C .

Results and discussion

Reactions of $[\{2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}\}_2]$ ($\text{Z} = \text{H}$ or Me (*S*) enantiomer; $\text{X} = \text{Cl}$ or Br) with *t*-Bu-dim and *EtMe*₂C-dim

Addition of 1 equivalent of R-dim ($\text{R} = \text{t-Bu}$, $\text{EtMe}_2\text{C-}$) to a suspension of the yellow palladium dimers $[\{2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}\}_2]$ ($\text{Z} = \text{H}$ (I), Me (II)) in methanol resulted in a colour change of the solid to pale yellow. Addition of a second equivalent of R-dim caused dissolution of the precipitate and formation of a clear yellow-orange solution. These observations pointed to the occurrence of a stepwise reaction, a view which was supported by distinctly different ^1H and ^{13}C NMR spectra for solutions of the Pd dimers with R-dim ligands in 1/1 and 1/2 molar ratios (vide infra and Tables 1 and 2). Attempts to isolate these $[\{2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}\}_n(\text{R-dim})]$ ($n = 1, 2$) failed. When the solid material obtained by evaporation of freshly prepared solutions of the Pd-dimers I or II with *t*-Bu-dim were washed with hexane, *t*-Bu-dim was released from the complexes present. Slow crystallization of a mixture of I and R-dim (1/4 molar ratio) gave yellow crystalline material. Only in the case of $\text{R} = \text{t-Bu}$ did elemental analytical data indicate that a fairly pure complex (stoichiometry $[\{2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{PdCl}\}_2(\text{t-Bu-dim})]$) had been isolated (see Experimental section). Dissolution of this material in CDCl_3 resulted in partial dissociation of R-dim ligands from the complex.

These observations point to weak bonding of the R-dim ligand in $[\{2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}\}_n(\text{R-dim})]$ ($n = 1, 2$) complexes, and the equilibria shown in eq. 1 are postulated.



Addition of NaI to solutions of $[\{2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdCl}\}_n(\text{R-dim})]$ ($n = 1, 2$) in acetone resulted in halide exchange and formation of the corresponding iodide complexes, which were identified from their ^1H and ^{13}C NMR spectra.

Structure of $[2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}(\text{R-dim})]$ in solution

The ^1H and ^{13}C NMR spectra of solutions of R-dim ($\text{R} = \text{t-Bu}$, $\text{EtMe}_2\text{C-}$) and I or II in an exact 1/1 molar ratio showed the resonance patterns of the free R-dim ligand and two further resonance patterns which were assigned to: (i) a dinuclear complex of the type $[\{2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}\}_2(\text{R-dim})]$ ($\text{Z} = \text{H}$: $\text{R} = \text{t-Bu}$ (IIIa), $\text{EtMe}_2\text{C-}$ (IIIb); $\text{Z} = \text{Me}$: $\text{R} = \text{t-Bu}$ (IVa), $\text{EtMe}_2\text{C-}$ (IVb) with $\sigma\text{-N}$, $\sigma\text{-N}'$ bridge-bonded R-dim and (ii) a mononuclear complex $[2\text{-Me}_2\text{NCH}(\text{Z})\text{-}$

TABLE 1

 $^1\text{H}^\alpha$ NMR DATA FOR $[(2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4)_2\text{PdX}]_n$ ($n = 1, 2$) COMPLEXES

	CH_3	CH_2	$\text{CH}=\text{N}$	$\text{N}(\text{CH}_3)_2$	NCH_2	$\text{N}-\text{CH}$
$\sigma\text{-N}, \sigma\text{-N}'$ bridge <i>R</i> -dim						
$[(\text{PdCl}(\text{dMBA}))_2(\text{t-Bu-dim})]$	1.62s		9.80s	2.82s, 2.97s	3.51d, 4.34d ^b	
$[(\text{PdBr}(\text{dMBA}))_2(\text{t-Bu-dim})]$	1.63s		9.83s	2.82s, 3.07s	3.48d, 4.43d ^c	
$[(\text{PdI}(\text{dMBA}))_2(\text{t-Bu-dim})]$	1.63s		9.82s	2.88s, 3.23s	3.43d, 4.52d ^d	
$[(\text{PdCl}(\text{dMBA}))_2(\text{EtMe}_2\text{C-dim})]$	0.83t, 1.60s	1.80q	9.82s	2.78s, 2.95s	3.50d, 4.42d ^e	
$[(\text{PdBr}(\text{dMBA}))_2(\text{EtMe}_2\text{C-dim})]$	0.83t, 1.61s	1.80q	9.78s	2.80s, 3.07s	3.43d, 4.47d ^f	
$\sigma\text{-N}, \sigma\text{-N}'$ fluxionally <i>R</i> -dim						
$[(\text{PdCl}(\text{dMBA}))_2(\text{t-Bu-dim})]$	1.43s		8.77s	2.84s	3.91s	
	[1.23s, 1.62s]		[7.88d, 9.40d ^h]	[2.63s, 2.74s]	[3.39d, 4.19d ^h]	
$[(\text{PdBr}(\text{dMBA}))_2(\text{t-Bu-dim})]$	1.49s		8.77s	2.92s	3.94s	
	[1.32s, 1.75s]		[8.08d, 9.62d ⁱ]	[3.0 Br]	[3.64d, 4.53d ^j]	
$[(\text{PdI}(\text{dMBA}))_2(\text{t-Bu-dim})]$	1.41s		8.75s	3.01s	3.98s	
$[(\text{PdCl}(\text{dMBA}))_2(\text{Et-Me}_2\text{C-dim})]$	0.85t, 1.37s, 1.42s	1.80q	8.80s	2.88s	3.93s	
$[(\text{PdBr}(\text{dMBA}))_2(\text{Et-Me}_2\text{C-dim})]$	0.85t, 1.40s, 1.45s	1.80q	8.80s	2.95s	3.98s	
$\sigma\text{-N}, \sigma\text{-N}'$ bridge <i>R</i> -dim						
$[(\text{PdBr}(\text{dMEPA}))_2(\text{t-Bu-dim})]$	1.63s		9.85s, 9.87s	2.70s, 2.92s		3.83q
$[(\text{PdBr}(\text{dMEPA}))_2(\text{Et-Me}_2\text{C-dim})]$	0.85m, 1.57s, 1.60s	1.80m	9.82s, 9.84s	2.77s, 2.90s		4.01q
$\sigma\text{-N}, \sigma\text{-N}'$ fluxionally <i>R</i> -dim						
$[(\text{PdCl}(\text{dMEPA}))_2(\text{t-Bu-dim})]$	1.40s, 1.47s		8.56d, 9.05d ^k	2.70s, 2.88s		3.72q
			[8.05d, 9.60d ^l]			
$[(\text{PdBr}(\text{dMEPA}))_2(\text{t-Bu-dim})]$	1.38s, 1.50s		8.45d, 9.11d ^m	2.80s, 2.29s		3.68q
$[(\text{PdCl}(\text{dMEPA}))_2(\text{EtMe}_2\text{C-dim})]$	0.96m, 1.30s, 1.34s, 1.47s, 1.50s	1.80m	8.48d, 9.12d ⁿ	2.77s, 2.90s		3.70q
$[(\text{PdBr}(\text{dMcPA}))_2(\text{EtMe}_2\text{C-dim})]$	0.90m, 1.38s, 1.40s, 1.51s, 1.54s	1.80m	8.57d, 9.14d ^o	2.85s, 2.97s		3.78q
			[8.07d, 9.70d ^p]			

^a Chemical shifts (δ , ppm) in CDCl_3 relative to TMS, 2-Me₂NCH(Z)C₆H₄ abbreviated as dMBA if Z = H, as dMEPA if Z = S-CH₃, low temperature -55°C data in brackets. *b-f*, *h, j* AB pattern NCH₂ ²*J*(¹H-¹H) = 13 Hz, $\Delta\delta$ AB = 51 Hz (*b*); 13 Hz, 58 Hz (*c*); 13 Hz, 65 Hz (*d*); 14 Hz, 66 Hz (*e*); 14 Hz, 62 Hz (*f*); 14 Hz, 74 Hz; -80°C CD₂Cl₂ 90 MHz (*h*); 13 Hz, 53 Hz; -55°C 60 MHz (*j*). *g, i, k-p* AB pattern (HC=N)₂ ³*J*(¹H-¹H) = 7 Hz, $\Delta\delta$ AB = 134 Hz; -80°C CD₂Cl₂ 90 MHz (*g*); 8 Hz, 92 Hz (*i*); 8 Hz, 36 Hz (*k*); 7 Hz, 31 Hz (*l*); 7 Hz, 38 Hz (*m*); 7 Hz, 141 Hz; -55°C 90 MHz (*p*).

TABLE 2

 ^{13}C NMR DATA FOR $[\{2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}\}_n(\text{R-dim})]$ ($n = 1, 2$) COMPLEXES

	CH_3	CH_2	C-N	C=N	N(CH_3) $_2$	C-N(Me) $_2$
$[\{\text{PdCl}(\text{dMBA})_2(\text{t-Bu-dim})\}]$	31.51		65.71	165.03	50.91, 53.06	72.50
$[\{\text{PdBr}(\text{dMBA})_2(\text{t-Bu-dim})\}]$	31.63		65.76	165.54	51.04, 54.43	72.45
$[\{\text{PdCl}(\text{dMBA})_2(\text{EtMe}_2\text{C-dim})\}]$	8.58, 28.19, 29.42	35.40	68.71	165.37	50.75, 53.09	73.03
$[\{\text{PdBr}(\text{dMBA})_2(\text{EtMe}_2\text{C-dim})\}]$	8.60, 28.36, 29.39	35.40	68.79	165.72	50.90, 54.40	73.85
$[\text{PdCl}(\text{dMBA})(\text{t-bu-dim})]$	30.26		61.71	161.38	51.78	73.83
	[28.51], 31.29]		[64.27, 59.33]	[158.02, 163.43]	[50.27, 52.54]	[73.15]
$[\text{PdBr}(\text{dMBA})(\text{t-Bu-dim})]$	30.34		61.81	161.61	52.63	73.79
$[\text{PdI}(\text{dMBA})(\text{t-Bu-dim})]$	30.44		61.95	161.84	54.19	73.53
$[\text{PdCl}(\text{dMBA})(\text{EtMe}_2\text{C-dim})]$	8.06, 26.41, 27.23	34.85	64.03	161.30	51.29	73.61
	[7.80, 27.73, 28.67]	[34.93]	[61.55, 66.41]	[158.33, 162.87]	[50.28, 52.47]	[73.30]
$[\text{PdBr}(\text{dMBA})(\text{EtMe}_2\text{C-dim})]$	8.22, 26.66, 27.33	35.03	64.21	161.54	52.19	73.47
	[8.93, 27.73, 28.20]	[34.93]	[61.62, 66.88]	[158.02, 162.40]	[50.43, 53.72]	[72.76]
$[\text{PdCl}(\text{dMEPA})(\text{S})(\text{t-Bu-dim})]$	29.77, 30.48		60.87, 62.39	160.66, 161.96	47.03, 51.56	75.30, 20.35
$[\text{PdBr}(\text{dMEPA})(\text{S})(\text{t-Bu-dim})]$	29.77, 30.75		60.73, 62.66	160.61, 162.41	48.61, 52.14	75.92, 20.75
	[28.47, 31.35]		[59.30, 64.20]	[158.04, 163.71]	[50.20, 52.13]	[76.04], 24.52
$[\text{PdBr}(\text{dMEPA})(\text{S})(\text{EtMe}_2\text{C-dim})]$	8.46, 26.51, 27.12	35.55	63.58, 65.73	161.09, 162.71	48.55, 52.15	75.98, 20.81
	8.66, 27.45, 28.14					
	[8.93, 24.92, 25.25	[35.1]	[61.82, 67.32]	[159.06, 163.53]	[49.95, 52.20]	[76.03]
	27.66, 28.65]					

^a Chemical shifts (δ , ppm) in CDCl_3 relative to TMS, 2-Me $_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4$ abbreviated as dMBA if Z = H, as dMEPA if Z = S-CH $_3$, low temperature -56°C data in brackets.

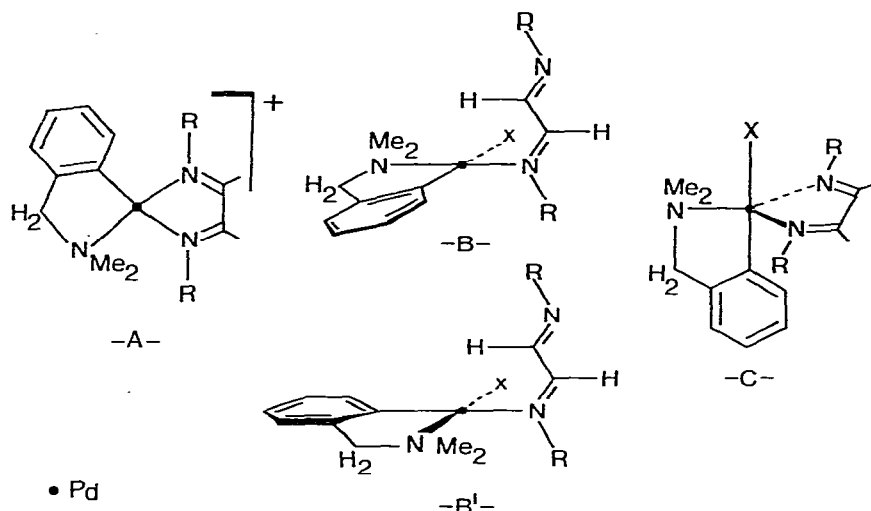


Fig. 1. Possible structures for complexes with stoichiometry $[2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}(\text{R-dim})]$ ($\text{R} = \text{t-Bu}$ or $\text{EtMe}_2\text{C-}$, $\text{X} = \text{Cl}$ or Br , $\text{Z} = \text{H}$ or Me).

$\text{C}_6\text{H}_4\text{PdX}(\text{R-dim})]$ ($\text{Z} = \text{H}$: $\text{R} = \text{t-Bu}$ (Va), $\text{EtMe}_2\text{C-}$ (Vb); $\text{Z} = \text{Me}$: $\text{R} = \text{t-Bu}$ (VIa), $\text{EtMe}_2\text{C-}$ (VIb)). On stepwise increase in the molar ratio of Pd-dimer to R-dim from 1/1 to 1/4 the peak area ratio between the two patterns changed until signals only from free R-dim and the mononuclear species Va, b or VIa, b were present.

Intermolecular exchange between the species present in these equilibrium mixtures is slow on the NMR time scale in the temperature range -80°C to 34°C . However, the resonance pattern of the mononuclear palladium complexes Va,b and VIa,b appeared to be temperature dependent (*vide infra*), which points to a fluxional behaviour of either one or both of the two different bidentate ligand systems bonded to the Pd^{II} centre.

The $2\text{-Me}_2\text{NC}^*\text{H}(\text{CH}_3)_3$ -substituent has a stable centre of chirality and in the case of $\text{Pd-N}(\text{Me})_2$ coordination, the methyl groups at the N atoms become diastereotopic, whereas in the non-coordinated situation rapid pyramidal inversion would render these methyl groupings homotopic [4]. In the ^1H and ^{13}C NMR spectra of Va,b and VIa,b anisochronous signals for the NMe_2 groups are observed which points to diastereotopic Me groups i.e. to $\sigma, \sigma\text{-N, C}$ chelating behaviour of the $2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4$ -ligand. Accordingly the observed NMR behaviour must arise from fluxional bonding of the R-dim ligand to the Pd centre. In Fig. 1 four possible structures for Va, b, of which two are stereoisomers (B and B'), are depicted.

From the IR and NMR results the ionic structure A, which is the structure found for cyclopalladated halogen complexes containing bidentate ethylenediamine or 1,2-bis(diphenylphosphino)ethane [6], can be excluded. Firstly, the IR spectra of V and VI in CHCl_3 and C_6H_6 solutions shows a $\nu(\text{PdCl})^*$ at $275\text{--}282\text{ cm}^{-1}$. Secondly, the chemical shifts of the hydrogen and carbon atoms of the coordinated $\text{CH}(\text{Z})\text{NMe}_2$ group, in particular, are clearly dependent on the halogen atom present (see Tables 1 and 2) and shifts to low field occur on going from the chlorine to the iodine complexes.

* $\nu(\text{PdBr})$ of V 162 cm^{-1} (in CHCl_3).

The combined ^1H and ^{13}C NMR data at low temperature are in complete agreement with a $\sigma\text{-N}$ monodentate-bonded R-dim ligand, i.e. structure B or B', vide infra, and so the five-coordinate structure C is excluded for the molecule in the groundstate. Comparison of the $\nu(\text{PdCl})$ in our complexes with those reported for the four-coordinate $[\text{2-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{PdCl}(\text{L})]$ (L = pyridines, phosphines) complexes [6,7] points to structure B, in which the N-donor ligands are *trans* to each other. This configuration is also in line with the dependence of $\delta(\text{NMe}_2)$ and $\delta(\text{CH})$ on the halogen X because they are mutually *cis* positioned in the B isomer.

The features observed in the ^1H and ^{13}C NMR spectra of Va,b and VIa,b and of previously reported $[\text{MCl}_2(\text{PR}_3)(\text{R-dim})]$ (M = Pd, Pt) [2,3] at low temperature are very similar. The two t-Bu-N=CH halves of the t-Bu-dim ligand of Va and VIa are non-equivalent, as shown by anisochronous t-Bu resonances and the AX pattern for the imine hydrogen atoms. Compared to the free ligand, one of the imine hydrogen atoms has undergone a characteristic downfield shift ($\Delta\delta$ 1.5 ppm) which in the case of $[\text{PdX}_2(\text{t-Bu-dim})_2]$ [2] and $[\text{PdCl}_2(\text{PPh}_3)(\text{t-Bu-dim})]$ [2] was interpreted in terms of a *s-trans* conformation of the coordinated t-Bu-dim ligand. In this conformation the β -imine hydrogen resides above the coordination plane close to the palladium centre and thus experiences the magnetic anisotropy of this metal centre. With such a conformation of the R-dim ligand, in the slow exchange limit isomer B may be expected to exist on the NMR time scale in two enantiomeric forms which in the case of $[\text{2-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{PdX}(\text{R-dim})]$ have isochronous resonance patterns. However, $[(S)\text{-2-Me}_2\text{NC}^*\text{H}(\text{Me})\text{C}_6\text{H}_4\text{PdX}(\text{R-dim})]$ has a second chiral centre with a stable ((S), see Experimental section) configuration and thus B should exist in two diastereoisomeric forms, (S)(α) and (S)(β), which would have anisochronous resonance patterns. In the room temperature ^{13}C NMR spectrum of VIa,b (containing this (S) ligand) only one resonance is observed for the $\alpha\text{-CH}_3$ groups, but at -80°C this peak is noticeably broadened relative to other resonances of the complex, and this indicates that decoalescence may be occurring. However, the chemical shift differences between diastereomers can be expected to be small, especially since the $\text{CH}(\text{Me})\text{NMe}_2$ group is opposite to the R-dim ligand (see Fig. 1B).

At room temperature each of the compounds Va,b or VIa,b is undergoing fast exchange, in a process which relates exclusively to the R-dim ligand because the $\text{2-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4$ ligand remains coordinated via C and N (vide supra). At this temperature the hydrogen and carbon resonances of the t-Bu, $\text{EtMe}_2\text{C-}$ and N=CH groupings are coalesced at the averaged positions of the respective slow exchange chemical shifts. This can be interpreted in terms of a rapid interconversion (on the NMR time scale) between the two enantiomeric (monodentate bonded α -diimine) forms of isomer B which leads to the coordination plane appearing as a molecular symmetry plane. For complex Vb (R = $\text{EtMe}_2\text{C-}$) further evidence that this process is not dissociative in nature comes from the fact that within the two, non-equivalent $\text{EtMe}_2\text{C-}$ groupings the $\alpha\text{-Me}$ groups remain diastereotopic and two singlet NMR resonances are observed for both the methyl hydrogen and methyl carbon atoms.

By contrast, the fluxional process (room temperature, fast exchange limit) in VIa,b does not render the R-N= groups of the coordinated R-dim ligand

enantiotopic because of the presence of the stable chiral centre in the (*S*)-2-Me₂NC*H(Me)C₆H₄ ligand. The hydrogen and carbon atoms of t-Bu-N=CH- remain diastereotopic and for the EtMe₂C groups four singlets are observed for both the α -methyl hydrogen and the carbon atoms.

The fluxional process we propose for these complexes is similar to that postulated for [MCl₂(PR₃)(R-dim)] (M = Pd, Pt) complexes which were studied in detail by ¹H, ¹³C, ¹⁵N, ³¹P and ¹⁹⁵Pt NMR spectroscopy, including the use of ¹⁵N-labelled compounds [2,8] (see Fig. 7 in ref. 2). In the present complexes the process also proceeds via a five-coordinate intermediate or transition state for which a trigonal bipyramidal structure seems likely (as depicted in Fig. 1C). This trigonal bipyramidal array is strongly destabilized because for the bidentate 2-Me₂NCH(Z)C₆H₄ ligand the metallated C atom occupies an axial position (with the N donor atom in the equatorial plane), and a more stable situation would be provided if the N donor atom were in the axial position [4a,9].

The occurrence of an alternative process involving Pd-X bond dissociation with concomitant σ, σ -N,N' chelate bonding of the R-dim ligand can be excluded. This process would be equivalent to rotation of the σ -N-bonded R-dim ligand around the Pd-N axis, because the halogen atom always has to return *trans* to the C ligand. In such a process the same N side of the molecule would coordinate and dissociate and this is not in agreement with the observed coalescence behaviour of the anisochronous NMR resonance patterns discussed above.

Structure of [$\{2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}\}_2(\text{R-dim})$] in solution

The ¹H and ¹³C NMR spectra of solutions of 1/1 mixtures of I or II with R-dim revealed the presence of the dinuclear species [$\{2\text{-Me}_2\text{NCH}(\text{Z})\text{-C}_6\text{H}_4\text{PdX}\}_2(\text{R-dim})$] (Z = H: R = t-Bu (IIIa), R = EtMe₂C- (IIIb); Z = Me: R = t-Bu (IVa), EtMe₂C- (IVb)), the mononuclear species [$2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}(\text{R-dim})$] (Va,b and VIa,b), and unreacted I or II. Intermolecular exchange in this equilibrium mixture is slow on the NMR time scale. The ¹H and ¹³C resonance patterns of the dinuclear species are temperature independent and show striking similarities to the [$\{M\text{Cl}_2(\text{PR}'_3)\}_2(\text{R-dim})$] (M = Pd, Pt) complexes for one member of which a σ -N, σ -N'-bridged structure was established by X-ray analysis [3].

In particular the benzylic hydrogen atoms in [$\{2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{PdX}\}_2(\text{R-dim})$] as well as the N(Me)₂ groups are diastereotopic. The imine-hydrogen atoms are isochronous and lie ~1.5 ppm downfield (vide supra) from the position for the free ligand, an observation consistent with an *s-trans* Pd-N-C-C-N-Pd skeleton. The influence of X on the ¹H and ¹³C NMR chemical shifts of NMe₂ and CH₂ groups seems indicative of a *cis* arrangement of the N and X ligands in each of the [$2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}$] units. For IIIa, b and IVa, b the values of $\nu(\text{PdX})$ was in line with halide coordinated *trans* to a C atom.

Accordingly the dimeric structure, lacking a symmetry plane (shown in Fig. 2) is proposed for these dinuclear complexes IIIa, b and IVa, b.

Puckering of the five-membered $2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{Pd}$ ring

On the basis of the *sp*² and *sp*³ hybridization of the C and N atoms in the five-membered chelate ring ($2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{Pd}$) in complexes IIIa,b-VIa,b

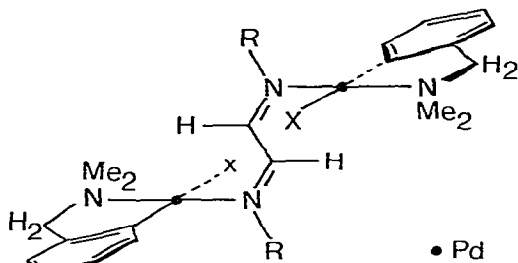


Fig. 2. Proposed structure for $[\{(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{PdX})_2(\text{R-dim})\}]$ ($\sigma\text{-N}, \sigma\text{-N}'$ -bridging R-dim) complexes (R = *t*-Bu or EtMe₂C-, X = Cl, Br, Z = H or Me).

a puckered conformation is expected for this ring. In view of the stereochemistry of these Pd complexes, both for the dinuclear and mononuclear species, this puckering represents an additional element of dissymmetry, though in compounds such as $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{SnBrMePh}$ the process of ring puckering inversion is fast on the NMR time scale [4]. However, in the $\sigma\text{-N}, \sigma\text{-N}'$ -bridged R-dim complex and for the $\sigma\text{-N}$ situation (low temperature) of the mononuclear Pd-R-dim complexes the ring puckering seems to be rigid on the NMR time scale. Support for this comes from the observation that only one of the N—Me resonances is shifted to increasing lower field on going from X = Cl, Br to I in $[\{2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{PdX}\}_n(\text{R-dim})]$ ($n = 1, 2$). This can be explained by a rigid ring puckering where one N—Me group is closer to the coordination plane, i.e. closer to the *cis* halogen atom, than the other, which points away from this plane. The in-plane Me group of the NMe₂ unit therefore experiences the anisotropy of the halogen atom more than the other. In the $[\{(S)\text{-}2\text{-Me}_2\text{NCH}(\text{Me})\text{C}_6\text{H}_4\text{PdX}\}_n(\text{R-dim})]$ ($n = 1, 2$; X = Cl, Br) complexes this relation between the nature of the halogen and the NMe₂CH(Me) chemical shift is not so apparent, probably because the Me group at the benzylic C atom has an appreciable influence on the actual ring conformation adopted (see also ref. 4).

Conclusions

The present work shows that the interaction of R-dim ligands with cyclo-metallated palladium complexes is weaker than with the *trans*- $[\{\text{PdCl}_2(\text{ER}'_3)\}_2]$ (E = P, As) dimers and gives rise to equilibrium mixtures. The replacement of one Cl and one phosphine ligand in the $[\{\text{PdCl}_2(\text{ER}'_3)\}_n(\text{R-dim})]$ (E = P, As) complexes by a carbon-nitrogen donor ligand thus destabilizes the Pd—N(imine) interaction, since such a C,N-bonded ligand causes enhanced electron density on the Pd centre, thereby reducing the possibility of σ donation from the imine N atom to the metal.

In contrast to the slow intermolecular exchange in these equilibrium mixtures, the intramolecular dynamic behaviour in each of the species is fast enough to be observable by NMR techniques. The structures proposed for the dinuclear $\sigma\text{-N}, \sigma\text{-N}'$ -bridged R-dim species and for the mononuclear species $[2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{PdX}(\text{R-dim})]$ are analogous in respect of the conformation of the Pd-R-dim entity to those found for *trans*- $[\{\text{MCl}_2(\text{ER}'_3)\}_n(\text{R-dim})]$ (E = P, As; M = Pd, Pt; $n = 1, 2$) complexes.

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