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Synthesis and fluxional behaviour of allylpalladium complexes with poly(pyrazol-1-yl)methane ligands

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Abstract

The reaction of the solvento-complex $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(S)_2]X$ (S = Me_2CO) with the stoichiometric amounts of the following poly(pyrazol-1-yl)methanes: bis(pyrazol-1-yl)methane (bpzm), bis(3,5-dimethylpyrazol-1-yl)methane(3,5-Me_2bpzm), tris(pyrazol-1-yl)methane (tpzm) and tris(3,5dimethylpyrazol-1-yl) methane (3,5-Me_2-tpzm) leads to the cationic complexes $[(\eta^3\text{-}C_4H_7)Pd(bpzm)]BF_4$, (**1**), $[(\eta^3\text{-}C_4H_7)Pd(bpzm)]PF_6$, (**2**), $[(\eta^3\text{-}C_4H_7)Pd(tpzm)]BF_4$, (**3**), $[(\eta^3\text{-}C_4H_7)Pd(3,5\text{-}Me_2bpzm)]PF_6$, (**4**), and $[(\eta^3\text{-}C_4H_7)Pd(3,5Me_2tpzm)]PF_6$, (**5**). Resonances in the ^1H NMR spectra have been assigned by considering the NOE effects between the methylene or methyne protons and the H(**5**) or Me(5) groups. NOE effects have also been observed between the H(3) or Me(3) and the H(syn) allylic protons. The ^{13}C NMR resonances have been assigned using $^1H\text{–}^{13}C$ HETCOR experiments. The fluxional behaviour of **4** and **5** has been studied by ^1H NMR spectroscopy. Two conformers of **4** are discernible at low temperature, and they interchange when the temperature is increased. The AB systems corresponding to methylene groups of both conformers coalesce to a single A_2 system. A mechanism is proposed on the basis of this observation and the activation free energies at the coalescence temperature calculated. The ^1H NMR spectrum of **5** shows the equivalence of the coordinated and uncoordinated pyrazole rings. The energy barrier of this phenomenon is too low to be determined by NMR spectroscopy. A tumbling motion, as proposed for similar observations, seems a likely pathway of exchange.

Keywords: Palladium; Poly(pyrazolyl)methane; NMR spectroscopy Fluxionality; Allyl

1. Introduction

π-Allyl palladium complexes have received considerable attention during the last few decades [1]. They are precursors or intermediates in some catalytic reactions [2], and interest in chiral π-allyl complexes has increased because they may be intermediates in synthetic processes leading to optically active derivatives [3]. The polydentate *N*-donors poly(pyrazol-1-yl)alkanes [4] are interesting because they are easily modified so as to modulate electronic and steric effects, and they also exhibit interesting conformational and fluxional behaviour which is not possible for planar ligands. π-Allyl palladium complexes with this type of ligand were first reported by Trofimenko [5] in 1970, who synthesized $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CRR'\}]PF_6$ (pz = pyrazol-1-yl, R = R′ = H; R = R′ = pz; R = H, R′ = pz, R = R′ = Me and $[Pd(\eta^3\text{-}C_3H_5)\{(3,5\text{-}Me_2pz)_3CH\}]PF_6$. Similar complexes with the isoelectronic poly(pyrazol-1-yl)borates are more unstable thermally [6]. Recently, Brown et al. [7] isolated $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_3CH\}]$-$[PdBr_2(\eta^3\text{-}C_3H_5)]$ as a result of a reductive-elimination process from an unstable palladium (IV) intermediate. The same salt was also obtained from the direct reaction of $[\{PdBr(\eta^3\text{-}C_3H_5)\}_2]$ with $(pz)_3CH$ in acetone. The synthesis of $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}][PdBr_2(\eta^3\text{-}C_3H_5)]$ followed by reaction with $AgBF_4$, allowed the isolation of $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}]BF_4$.

Non-allylic palladium poly(pyrazol-1-yl)alkane (L) complexes of formula [PdXR(L)] [7–13] (X = Cl, Br, or I and R = Me; X = Br, R = CH_2Ph; X = R = Me; X = R = Cl; [Pd(C-N)L] [14]. (C–N = cyclometallated group) $[L_2Pd]^{2+}$ [8,12] and palladium(IV) derivatives [7,15–17] such as $[PdMe_2(CH_2Ph)\{(pz)_3CH\}]Br$ [7] and $[PdMe_3\{(pz)_3CH\}]X$ (X = BF_4 or I) [17] are also known.

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$$[\{Pd(\eta^3\text{-}C_4H_7)Cl\}_2] + 2\ AgX \xrightarrow{\text{acetone}} 2\ [Pd(\eta^3\text{-}C_4H_7)(S)_2]X + 2\ AgCl$$

$$\downarrow L\text{–}L$$

$$2\ [Pd(\eta^3\text{-}C_4H_7)(L\text{–}L)]X$$

L–L = bpzm, X = PF_6 (**1**), BF_4 (**2**)
tpzm, X = BF_4 (**3**)
3,5-Me_2bpzm, X = PF_6 (**4**)
3,5-Me_2tpzm, X = PF_6 (**5**)

Scheme 1.

When the L are bidentate, a facile ring fluxional boat-to-boat inversion process is usually found by NMR spectroscopy, though an increase of the bulk of L seems to hinder this process. Room temperature ^{1}H NMR spectra of complexes containing one or two uncoordinated pyrazole groups indicate a rapid exchange of coordinated and uncoordinated groups, which has been ascribed to a "tumbling motion" or to an associative-dissociative mechanism, presumably via five-coordinate intermediates [12,14,18]. Fluxional motions in metal π-allyl compounds [19] may be a result of motions of the allyl group relative to the other part of the complex, or of the fluxional behaviour of the whole complex, such as pseudorotations.

Here, we describe the synthesis and characterization of new allylpalladium complexes with bis(pyrazol-1-yl)methane (bpzm), tris(pyrazol-1-yl) methane (tpzm) and their related 3,5-dimethyl derivatives and a study of their fluxional behaviour. The bis(pyrazolyl) ligands were chosen in order to observe the inversion of the $Pd(N\text{–}N)_2C$ metallocycle, whereas the tris(pyrazolyl) ligands would allow the study of the interchange of the pyrazolyl groups. The behaviour of the complexes with the methylated ligands reflect steric influences. Finally we were also interested in the fluxional behaviour associated with the allyl groups.

2. Results and discussion

2.1. Synthesis of the allylpalladium poly(pyrazol-1-yl)methane complexes

The new complexes were obtained in quite high yield (63–87%) by addition of the pyrazolyl methane to an acetone solution $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(S)_2]X$ (S = Me_2CO), which is formed by reaction of the dimer $[\{Pd(\eta^3\text{-}2Me\text{-}C_3H_4)Cl\}_2]$ and a silver salt in acetone (Scheme 1).

The complexes are air-stable, both in the solid state and in solution, and they are white to pale yellow or

Table 1
^{1}H NMR chemical shifts (δ) and coupling constants (Hz) for complexes **1–5** and free bases

Compound	H(5) (J_{45})	H(3) (J_{34})	Me(5)	Me(3)	H(4)	CH_2 or CH	Allyl		
							H(*syn*)	H(*anti*)	Me
bpzm [a]	7.61(d) (2.4)	7.50(d) (1.8)			6.23(pt)	6.23(s)			
1 [a]	8.40(d) (2.7)	7.63(d) (2.2)			6.35(pt)	6.79(bs)	3.97(s)	3.10(s)	2.19(s)
2 [a]	8.22(d) (2.7)	7.64(d) (2.2)			6.44(pt)	6.46(bs)	4.08(s)	3.23(s)	2.29(s)
2 [b]	8.26(d) (2.7)	8.08(d) (2.2)			6.61(pt)	6.82(bs)	4.32(s)	3.40(s)	2.28(s)
tpzm [a]	7.61(d) (2.2)	7.55(d) (2.1)			6.26(pt)	8.62(s)			
3 [a]	8.29(d) (2.7)	7.65(d) (1.9)			6.40(pt)	9.30(s)	3.95(s)	3.43(s)	2.22(s)
3 [b]	8.28(d) (2.7)	8.02(d) (1.9)			6.62(pt)	9.31(s)	4.20(s)	3.26(s)	2.15(s)
3,5Me_2bpzm			2.45(s)	2.08(s)	5.76(s)	6.03(s)			
4 [b]			2.55(s)	2.32(s)	6.21(s)	6.60(bs)	4.36(s)	3.67(s)	2.25(s)
3,5Me_2tpzm			2.09(s)	2.03(s)	5.92(s)	8.20(s)			
5 [b]			2.35(s)	2.26(s)	6.26(s)	8.47(s)	4.09(s)	3.01(s)	1.80(s)

[a] In $CDCl_3$. [b] In $(CD_3)_2CO$.

orange. They are soluble in common polar organic solvents and insoluble in diethyl ether and hexane. The complexes with methylated ligands show higher solubility. Complexes **1–5** should be monomeric according to our data and to that of refs. [8] and [12], where poly(pyrazol-1-yl)methanes are described as behaving as *N*-donor chelate ligands. The new complexes have been characterized by elemental analysis, IR, mass, and ^{1}H and ^{13}C NMR spectroscopy, and also by NOE and $^{1}H-^{13}C$ heteronuclear correlation (HETCOR) experiments. Mass spectral analysis of **1**, **3** and **4** provided molecular ion peaks at m/z 309, 375 and 365 respectively, corresponding to monomeric cations. The abundances of the signals around the parent ion are consistent with the natural isotopic abundances. Additional signals corresponding to the dimer fragments $\{[Pd(\eta^3-C_4H_7)(L)]_2X\}^+$ are also observed. The very low intensity of these signals, and the lack of fragments intermediate between the monomer and dimer implies that some association occurs during the analysis.

2.2. Characterization of the complexes by NMR spectroscopy

Table 1 shows the values for the ^{1}H resonances and H–H coupling constants for complexes **1–5** and also for the free pyrazolylmethanes at room temperature. In all cases, the allyl resonances appear as three singlets corresponding to H(*syn*), *H*(*anti*) and the methyl group. Upon coordination, all the pyrazolyl signals shift to lower field, as previously observed for other derivatives (see, for example, refs. [8] and [10]. This effect is higher for the H(5) and CH_2 than for H(3) protons, in the complexes **1**, **2** and **3**. These resonances are also the most affected by a change of the anion (see resonances for complexes **1** and **2**) suggesting that some interaction between the anion and this region of the pyrazolyl moiety of the cation takes place. This effect has also been observed for the complexes $[PdMe_3\{(pz)_3CH\}]X$ (X = I or BF_4) [4].

In complexes **1–3**, signals corresponding to only one type of pyrazole ring are observed, the H(3) and H(5) resonances appearing as doublets because of coupling with H(4), while the H(4) signal appears as a pseudotriplet. An increase in the values of coupling constants ($^{3}J_{H-H}$) was observed upon coordination. The assignment of the H(5) and H(3) proton resonances was made by NOE experiments. There is a clear NOE effect between the CH_2 (or CH) resonances and the signals which were consequently assigned to H(5). In this way it has been verified that the general rule for non-coordinated pyrazole groups [20], $J_{45} > J_{34}$ is fulfilled in our complexes. This has also been established in some ruthenium complexes [21]. In addition, a NOE effect between H(3) and the H(*syn*) of the allyl group was observed for complexes **1–3**.

Complexes **4** and **5** show three singlets in their ^{1}H NMR spectra corresponding to H(4), Me(3) and Me(5). There was a NOE effect between the CH resonances and the signals assigned to the Me(5) groups. An effect between the Me(3) resonances and the H(*syn*) of the allyl groups was also observed for **4** and **5**.

For complexes **1** and **2**, the CH_2 resonances are broad, while those for **4** appear as a complex signal indicating the existence of a fluxional process. The equivalence of the three pyrazole rings for **3** and **5** is also indicative of stereochemical non-rigidity in these complexes. (see below).

The values for the ^{13}C resonances and $^{1}J_{C-H}$ for complexes **1–5** and the free pyrazolylmethanes are col-

Table 2
^{13}C NMR chemical shifts (δ) and coupling constants (Hz) for complexes **1–5** and free bases

Compound	C(5) ($^{1}J_{CH}$)	C(3) ($^{1}J_{CH}$)	Me(5)	Me(3)	C(4) ($^{1}J_{CH}$)	CH_2 or CH ($^{1}J_{CH}$)	Allyl		
							C(2)	$CH_2/(^{1}J_{CH})$	$Me/(^{1}J_{CH})$
bpzm [a]	129.5	140.64			106.95	65.00			
	(186.7)	(184.8)			(176.8)	(152.8)			
2 [a]	133.52	145.55			107.30	62.90	[c]	60.48	22.12
	(195.8)	(192.9)			(183.8)	(159.7)		(155.5)	(135.0)
tpzm [b]	129.40	141.70			107.20	83.20			
	(191.7)	(188.4)			(183.8)	(168.9)			
3 [b]	133.67	144.44			107.78	77.90	[c]	58.74	23.23
	(194.3)	(190.8)			(181.3)	(167.3)		(158.0)	(128.2)
$3,5Me_2$bpzm	140.00 and 148.20		11.1	13.42	106.20	60.40			
			(128.1)	(126.3)	(171.2)	(151.0)			
4	142.60 and 152.1		9.82	13.34	107.15	60.1	132.3	57.39	21.97
			(117.1)	(129.2)	(177.3)	(c)		(c)	(127.0)
$3,5Me_2$tpzm	140.3 and 147.2		9.67	12.55	106.70	80.2			
			(128.3)	(126.5)	(172.0)	(162.0)			
5	143.5 and 151.8		9.85	12.43	108.1	74.21	131.10	58.70	22.48
			(123.0)	(123.0)	(178.0)	(165.0)		(163.3)	(123.0)

[a] In $(CD_3)_2CO$. [b] In CD_3Cl. [c] Not detected.

lected in Table 2. A downfield coordination shift for the resonances corresponding to the carbons of the pyrazole ring is observed, while an increase in the $^1J_{C-H}$ values upon coordination was noted. The assignment of the resonances has been made by $^1H-^{13}C$ heteronuclear correlations (HETCOR), except for the quaternary carbon atoms. Because the proton resonances were unambiguously assigned by NOE experiments, the ^{13}C resonances are consequently assigned with certainty. Hence we showed that in our complexes, J_{C-H5} is always higher than J_{C-H3}, consistent with the rule established for free pyrazole or its derivatives [20]. The quaternary allyl carbon resonance was assigned using ref. [22] but, with our data, we were unable to distinguish between the C_3 and C_5 pyrazole carbons.

2.3. Fluxional behaviour of the complexes

In order to better understand the fluxional behaviour of our complexes, we carried out variable temperature ^1H NMR studies on complexes **3–5**.

For complex **4** (see Fig. 1), a splitting of the methyl, the H(*syn*) and H(*anti*) allyl resonances as well as of the pyrazole methyls and H(4) proton into two signals (9:1 ratio) is observed at low temperature. When the temperature is raised, the signals coalesce to a single resonance, permitting the free energies of activation ($\Delta G_T^{\#}$) for the different coalescence temperatures to be calculated as follows: H(*syn*), $T_c = 283$ K, 64.01; H(*anti*), $T_c = 285$ K, 64.48; Me(5), $T_c = 256$ K, 57.68; Me(3), $T_c = 268$ K, 60.49 kJ mol^{-1}. $\Delta G_T^{\neq}$ for the pyrazole H(4) was not calculated because slow interchange takes place below the freezing temperature of the deuterated solvent.

The different free energies of activation are linearly related to the coalescence temperatures ($r = 1.000$). The two AB-systems of the methylene protons are in a 9:1 ratio at low temperature. An increase in the temperature initially transforms the minor AB system to an A_2 signal ($T_c = 256$ K). This A_2 signal coalesces with the major AB system at 278 K and finally, up to 328 K a clear broadening of this signal is observed, which is a clear indication of the development of an A_2 system. We have also calculated $\Delta G_T^{\#}$ for the transformation $AB \rightarrow A_2$ for the minor system (52.72 kJ mol^{-1}). Although this figure is not very accurate because the signal is simultaneously coalescing with the major AB signal, it fits reasonably also the plot obtained with the other $\Delta G_T^{\#}$ data though is ca. 5 KJ mol^{-1} smaller than expected. This suggests a common interconversion process.

The addition of pyrazolymethane to a solution of **4** speeds up the whole process and the AB system is a single broad signal (A_2) at room temperature. Other signals, appearing as narrow singlets before the addition of the pyrazolylmethane, are broadened, indicating interchange between free and coordinated donor.

To rationalize these results we propose the presence of two isomers, I and II (Fig. 2). Disregarding the methylene signals, the low- and high-temperature limiting spectra indicate slow and rapid interconversions respectively of these isomers on the NMR time scale.

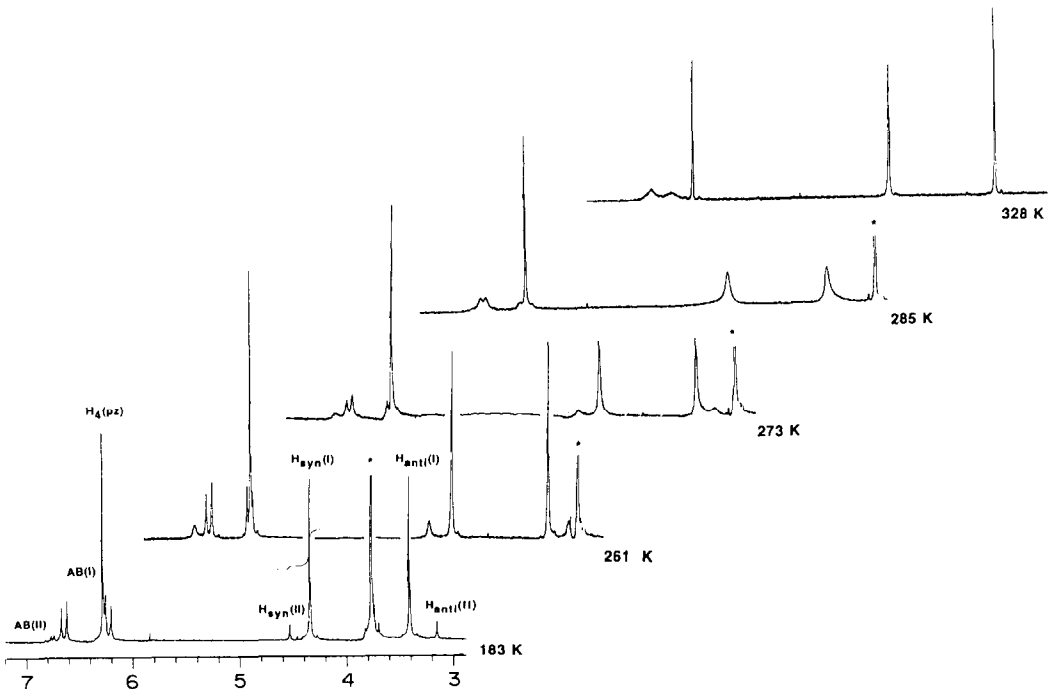

Fig. 1. Selected spectra from the variable-temperature ^1H NMR study for complex **4** in $(CD_3)_2CO$. Only the aromatic and allylic regions are shown. Peaks marked with * correspond to residual water.

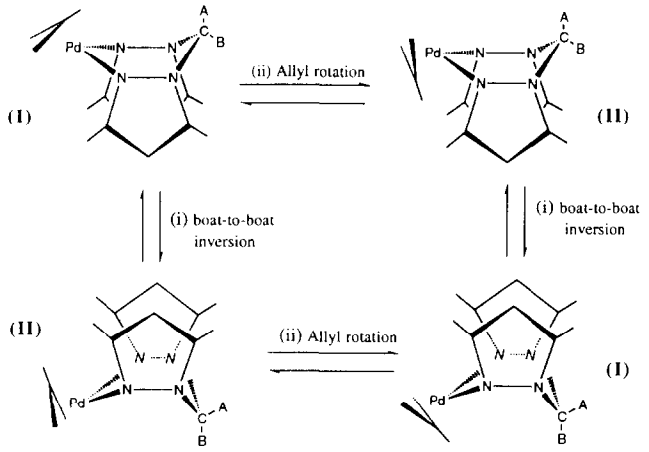

Fig. 2. Conformers I and II for complex **4** and possible pathways of interconversion.

Because steric effects play the main role in the stability of the conformers, we tentatively propose I as the major isomer although molecular models indicate that II should have stronger allyl....Mepz(3) interactions.

A σ-π-σ movement for the isomerization of these two species, which is frequently observed in allyl-containing halophosphine and arsine complexes or other derivatives [3e,23], is excluded because the average chemical shifts H(*syn*) and H(*anti*) are unchanged over the whole range of temperatures.

The interconversion between isomers I and II by boat-to-boat inversion (Fig. 2, path i) is possible. Rotation of the allyl group in a plane about an axis containing the palladium or else a flip motion would also interconvert the conformers [19] (path ii). However, the transformation of AB to A_2 needs two simultaneous processes. If the two pathways are available, the $\Delta G_T^{\#}$ obtained for the AB-A_2 transformation should correspond to the higher energy process whereas conformer interconversion should take place via the less energetically demanding route. However, the free energy of activation at the coalescence temperature for the AB-A_2 transformation is lower than the estimated value for the isomerization at this temperature.

Although the simple rotation of the allyl ligand is a mechanism often proposed to account for some isomerizations in complexes of metals such as Mo, W, and Fe [24], it is not widely accepted for square-planar palladium complexes and orbital considerations suggest a high activation barrier in square-planar geometries. This rotation is apparently more facile via a possible pentacoordinate intermediate [19]. Two consecutive Berry pseudorotations in a pentacoordinate activation state may also explain allyl inversions [19,25]. Dissociative pathways with monodentate ligands such as amines [26], $SnCl_3$, CO [27], macrocycles [28], polyenes [29], and also *N*-donor chelate ligands [30] have been proposed. Gogoll et al. [30b] have explained the dynamic behaviour in asymmetric allyl palladium complexes with *N*-donor chelate ligands by cleavage of a Pd–N bond to give a tricoordinate palladium intermediate. We also support a dissociative pathway on the basis of the above considerations and the observed accelerating effect of the addition of donor. We have also found [31] dissociative mechanisms in other allypalladium complexes with *N*-donor chelate ligands which show similar values of $\Delta G_T^{\#}$. The proposed mechanism (see Fig. 3) involves cleavage of a Pd–N bond followed by rotation around the remaining Pd–N bond and isomerization of the T-shaped intermediate [32] and finally by re-formation of the Pd–N bond. All the interconversions that are seen in our spectra can be explained by this mechanism. According to our proposals, the boat-to-boat inversion must have a higher activation barrier, though it has been proposed [7] by Brown et al. for example, in $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}]BF_4$ to account for the existence of two conformers in 5 : 3 ratio at 203 K which exchange at higher temperatures. We think that in our complex the methyl(3) of the pyrazole ring creates steric hindrance high enough to render the boat-to-boat inversion difficult and to facilitate the Pd–N bond dissociation. In fact, other frozen boat-to-boat inversions with methylated bis(pyrazolyl) ligands have been found. For example, in the spectrum of $[PdCl_2\{CH_2(pz)_2\}]$ at room temperature [8] the CH_2 protons of the methylene chain give rise to a singlet. In contrast, when CH_3 substituents

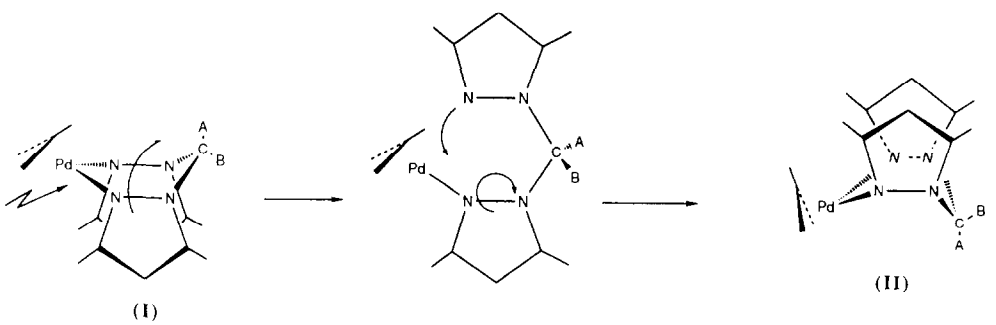

Fig. 3. Proposed mechanism for the conformer interconversion and the simultaneous transformation of AB to A_2.

are present on the pyrazole rings, as in $[PdCl_2\{3,5\text{-}Me_2pz)_2CH_2\}]$ the CH_2 protons display a well-resolved AB system at room temperature.

With regard to the tris(pyrazolyl)derivatives temperature decrease to 183 K of an acetone solution of complex **3** produces a slight broadening of the ^1H NMR resonances, but coalescence is not achieved. This indicates that even at low temperature in the NMR time scale, fluxional motions in the molecule are fast. We therefore undertook a variable-temperature ^1H NMR study of complex **5**, which because of higher steric hindrance, should show slower motions. A splitting of the Me(5) resonance is observed when the temperature of an acetone solution is decreased but unfortunately one part of this signal is obscured by the Me(3) resonance and the coalescence temperature was not determined accurately. It must be between 198 K and 188 K. Below 188 K, the visible part of the signal narrows. Lowering the temperature also produces a broadening of the Me(3), H(4), H(*anti*) and Me allyl signals. At 180 K (minimum temperature achieved) only the H(4) resonance begins to split although obviously the low-temperature limiting spectrum was not reached and therefore it was not possible to calculate the free activation energy.

We think the dissociative mechanism proposed for complex **4** must also operate for **5**, but it seems that another pathway of interconversion with a lower activation barrier may be present. We propose that the ability of the uncoordinated pyrazole ring to interact with the metal allows access to a pentacoordinate intermediate and consequently to a different mechanism from that proposed for **4**. The associative-dissociative mechanism or "tumbling motion" [12,14,18] proposed in the literature may also operate in our tris(pyrazol-1-yl) complex.

3. Experimental details

3.1. General

All manipulations and reactions were carried out using standard Schlenk-line techniques under dinitrogen. All solvents were freshly distilled from appropriate drying agents and degassed before use.

The compound $[\{Pd(\eta^3\text{-}C_4H_7)(\mu\text{-}Cl)\}_2]$[33] and bpzm [34], tpzm [35], 3,5-Me_2-bpzm [36] and 3,5-Me_2tpzm [37] were prepared as described. $AgBF_4$ and $AgPF_6$ were purchased from Aldrich.

Elemental analysis were performed with a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded as KBr pellets or Nujol mulls in the region 4000–200 cm^{-1} with a Perkin-Elmer PE 883 IR spectrometer. Mass spectra were recorded on a VG autospec instrument using the FAB technique and nitrobenzyl alcohol as matrix.

NMR spectra were recorded (292 K) on a Varian Unity FT-300 spectrometer. ^1H (300 MHz) and ^{13}C (75 MHz) are reported as δ values with respect to $SiMe_4$. NOE difference spectra were recorded with the following acquisition parameters: spectral width 5000 Hz, acquisition time 3.27 s, pulse width μs (90°), relaxation delay 4 s, irradiation power 5–10 L, number of scans 120. Two-dimensional NMR spectra were acquired using standard VARIAN FT software, and processed using an IPC-Sun computer. NMR probe temperatures were varied using an Oxford Intruments VTC 4 unit, measured by a thermocouple and calibrated with CD_3OD.

The rate constants at the coalescence temperature (K_c) for the exchanging systems with unequal populations were calculated by the conventional approximate method of Shanan-Atidi and Bar-Eli [38] and, the free energies of activation from the $\Delta G_T^{\#} = 1.914 \times 10^{-2} \times Tc[10.319 + \log(T_c/K_c)]$. For equally populated AB systems the following expression was employed [39]: $\Delta G_T^{\#} = 1.914 \times 10^{-2} \times T_c\{9.972 + \log[T_c/(\Delta\nu^2 + 6J_{AB}^2)^{1/2}]\}$.

3.2. Synthesis of complexes $[Pd(\eta^3\text{-}C_4H_7)(L\text{–}L)]X$ ($X = BF_4$ or PF_6) complexes

To a solution of $[\{Pd(\eta^3\text{-}C_4H_7)(\mu\text{-}Cl)\}_2]$ (0.200 g, 0.5 mmol) in 25 ml of acetone was added $AgBF_4$(0.198 g, 1 mmol) or $AgPF_6$(0.260 g, 1 mmol). The solution was stirred at room temperature for ca. 4 h protected from light. The white AgCl was then filtered off. To the yellow solution then obtained, bpzm (0.198 g, 1 mmol), tpzm (0.217 g, 1 mmol), 3,5-Me_2bpzm (0.260 g, 1 mmol) or 3,5-Me_2tpzm (0.299 g, 1 mmol) were added. The solution was allowed to stir for 1 h and the solvent was removed in vacuo. The solid obtained was washed with diethyl ether (2 × 20 ml) and dried. Data for the complexes are as follows.

$[Pd(\eta^3\text{-}C_4H_7)(bpzm)]BF_4$, **1**: White solid. Yield: 0.168 g, 85%. Anal. Found: C, 33.53; H, 3.87; N, 14.02. $C_{11}H_{15}BF_4N_4Pd$ Calc.: C, 33.32; H, 3.78; N, 14.12%. Mass spectrum: m/z 309, $(M^+ - BF_4)$.

$[Pd(\eta^3\text{-}C_4H_7)(bpzm)]PF_6$, **2**: White solid. Yield: 0.198 g, 87%. Anal. Found: C, 29.28; H, 3.30; N, 12.31. $C_{11}H_{15}F_6N_4$ PPd Calc.: C, 29.06; H, 3.30; N, 12.32%.

$[Pd(\eta^3\text{-}C_4H_7)(tpzm)]BF_4$ 0.25 $[(CH_3)_2CO]$, **3**: Pale-orange solid. Yield: 0.150 g, 63%. Anal. Found: C, 37.13; H, 3.75; N, 17.64 $C_{14.75}H_{17.5}BF_4N_6O_{0.25}Pd$ Calc.: C, 37.13; H, 3.88; N, 17.61%. Mass spectrum: m/z 375, $(M^+ - BF_4)$.

$[Pd(\eta^3\text{-}C_4H_7)(3\text{-}5\text{-}Me_2bpzm)]PF_6$. **4**: White solid. Yield: 0.189 g, 74%. Anal. Found: C, 35.87; H, 4.57; N, 10.79. $C_{15}H_{23}F_6N_4$ PPd Calc.: C, 35.27; H, 4.50; N, 10.96%. Mass spectrum: m/z 365, $(M^+ - PF_6)$.

$[Pd(\eta^3\text{-}C_4H_7)(3,5\text{-}Me_2tpzm)]PF_6$, **5**: Pale-yellow solid. Yield: 0.233 g, 77%. Anal. Found: C, 40.10; H,

4.92; N, 13.53. $C_{20}H_{29}F_6N_6PPd$ Calc.: C, 39.72; H, 4.79, N, 13.89%.

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