Apparent Allyl Rotation in New Allylpalladium(II) Complexes with Pyrazolyl *N*-Donor Ligands

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The ligands 2,4,6-tris(pyrazol-1-yl)-1,3,5-triazine (TPzT), 2,4,6-tris(3,5-dimethyl-pyrazol-1-yl)-1,3,5-triazine (Me_2-TPzT), and 2,4,6-tris(3,4,5-trimethylpyrazol-1-yl)-1,3,5-triazine (Me_3-TPzT) have been synthesised and their reaction with $[Pd(\eta^3\text{-}C_4H_7)(THF)_2]X$ was explored. The reaction in a 1:3 molar ratio (ligand/solvate) leads to the new derivatives $[\{Pd(\eta^3\text{-}C_4H_7)\}_2(BPz'TO)]X$ (Pz′ = pyrazole, X = BF_4, **2a**; Pz′ = 3,5-dimethylpyrazole, X = PF_6, **2c**; Pz′ = 3,4,5-trimethylpyrazole, X = PF_6, **2d**) in which the N-donor ligand has been partially hydrolysed. The complexes exist in the form of two isomers, a *meso* form and a *d,l* pair. An apparent allyl rotation process leads to a *syn-syn/anti-anti* interconversion and also to an interchange between the two isomers. The values of $\Delta G_c^{\ddagger}$ at the coalescence temperature have been calculated. The results, which have also been compared with those previously obtained for the complex with the 4-methylpyrazole ligand, indicate that the activation barrier for the process is not affected by the change in the pyrazole group. Appreciable effects were not observed on changing the concentration or on the addition of water to the acetone solutions of **2c**. However, the influence of the solvent (acetone versus chloroform) is worth noting. A negative activation entropy has been found and a mechanistic proposal for the process is included. The molecular structure of **2c** has been determined by X-ray diffraction. The *meso* isomer, in which the two C–Me axes of the allylic groups are oriented in the same direction, is found in the solid state.

Introduction

The chemistry of (η^3-allyl)palladium complexes has been widely studied due to them acting as precursors or intermediates in different catalytic processes.[1] The fluxional behaviour of these systems, either directly related to the allyl group or to the ancillary ligands, has also attracted much attention.[2] Apart from the fundamental interest of these studies, the dynamics of the allylpalladium derivatives have important implications in a variety of catalytic processes, especially those involving nucleophilic attack on (η^3-allyl)palladium intermediates in enantioselective synthesis.[3] One process that the allyl group frequently undergoes is a mutual exchange of *syn* and *anti* groups, which can lead to isomer interconversions.[4−12] This interchange is normally believed to occur through an η^3-η^1-η^3 pathway that in some cases is selective[13−15] due to steric or electronic factors (a high *trans* influence of a group favours the opening of the allylic carbon atom situated in the *trans* position). Theoretical calculations concerning the mechanism of the η^3-η^1-η^3 isomerisation in (η^3-allyl)palladium complexes have led to the conclusion that the process involves tetracoordinate (η^1-allyl)palladium intermediates with coordination of a solvent molecule or an ancillary ligand.[16] A second dynamic process that is frequently observed in complexes with N-donor ligands is the apparent rotation of the allyl group.[17−27] In certain examples both of the aforementioned processes have been observed.[28−34] Depending on the molecular symmetry, the apparent rotation is observed as a *syn-syn*/*anti-anti* exchange and/or an isomerisation process. Different mechanisms have been proposed for the apparent allyl rotation and these may be classified into two groups: i) associative mechanisms[19,27,28,31,32] that involve pentacoordinate intermediates with coordination of the solvent, the anion or other molecules, ii) dissociative mechanisms[17,18,20−22,24,25,30,33] that involve formation of

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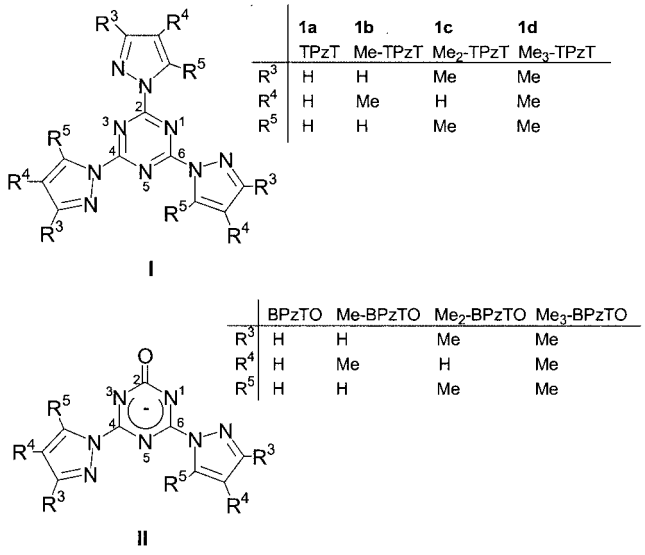
T-shaped three-coordinate intermediates after partial dissociation of a bidentate ligand, usually through Pd−N bond rupture. In some cases it has been reported that a ligand of higher basicity makes the apparent rotation more difficult,[20] while increased steric hindrance of the N-donor ligand facilitates the process.[19,28] In recent years we have been interested in the synthesis, structural characterisation and dynamic behaviour of (allyl)Pd^{II} complexes with N-donor ligands containing pyrazolyl substituents.[22−27,35] In most cases the process of apparent allyl rotation was observed and led to isomer interconversion. When the (allyl)-palladium fragment was treated with ligands of type **I** [2,4,6-tris(4-R-pyrazol-1-yl)-1,3,5-triazines; see Scheme 1; $R^3 = R^5 = H$, R^4 = Me, Br] it was found that during the course of the reaction one of the pyrazolyl residues was lost and, ultimately, the complexes formed were derived from the 4,6-bis(4-R-pyrazol-1-yl)-1,3,5-triazin-2-olate anion **II**[24] (see Scheme 1). The $\Delta G_c^{\ddagger}$ data led us to conclude that the main driving force of the hydrolysis process was the formation of a better coordinating ligand. In the work described here, we decided to explore the behaviour of similar ligands containing differently substituted pyrazolyl groups. In this way it was possible to analyse the influence (steric or electronic) of the pyrazolyl ring on the energy barrier of the apparent rotation process. We also decided to study the effect of concentration, the addition of water and a change in the solvent. Another aim was to determine whether the hydrolysis process was affected by differing basicity and consequently, the different leaving group character of the pyrazole moiety.



Scheme 1

The ligands used in this work were **1a**, **1c**, and **1d** (see Scheme 1). The ligand **1b**[24] is also included for the sake of comparison. The introduction of methyl substituents in positions 3 and 5 of the pyrazole rings increases the basicity and the steric hindrance, while the same substitution in position 4 would only be expected to cause an electronic change.

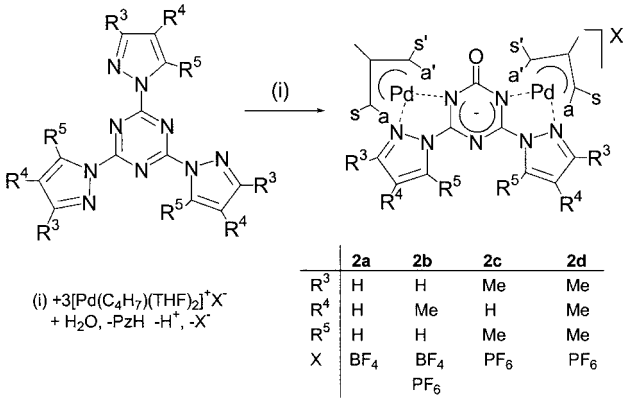
Results and Discussion

Synthesis of Ligands 1a−1d

Ligand **1a**,[36,37] ligand **1b** and its reaction with (allyl)palladium fragments,[24] and ligand **1c** and its X-ray molecular structure[38] have all been reported previously. The synthesis of **1d** is reported for the first time in this paper.

Synthesis of the Allyl Complexes

Reaction of the $[Pd(\eta^3\text{-}C_4H_7)(THF)_2]X$, X = BF_4^-, PF_6^- {obtained by mixing $[Pd(\eta^3\text{-}C_4H_7)(\mu\text{-}Cl)]_2$ and $AgBF_4$ or $AgPF_6$ in THF} with the ligands **1a**, **1c**, or **1d** gave complexes **2a**, **2c**, and **2d**, respectively, containing the hydrolysed ligand (see Scheme 2 and Exp. Sect.). Compounds **2b**·BF_4, **2b**·PF_6 and complexes with other anions have been described previously.[24]



Scheme 2

We tried unsuccessfully to isolate the intermediate $[Pd(\eta^3\text{-}C_4H_7)_2\cdot\mathbf{1}]X$ but, although the work was carried out under anhydrous N_2 and with freshly distilled (under N_2) solvents, hydrolysis to **2** always took place. Indeed, the hydrolysed products **2** were isolated even when the reaction was carried out at low temperature. The water necessary for the hydrolysis must arise from the silver salts and also perhaps from traces in the solvent. It was attempted to completely remove all water from $AgPF_6$ but this unfortunately proved impossible, even after drying the salt over P_2O_5 with a vacuum lower than 10^{-2} Torr for 5 d. Similar problems have been reported previously.[39] Given that the more basic the pyrazole the worse it is as a leaving group, ligand **1d** was selected (pK_a values: pyrazole 2.48, 4-methylpyrazole 3.04, 3,5-dimethylpyrazole 4.06, 3,4,5-trimethylpyrazole 4.56)[40] but, in this case, the same result was obtained. This observation is in accordance with our previous results[24] where it was found that the methoxy group, which is a poorer leaving group than pyrazole, also underwent the hydrolysis process. This result also supports our previously reported conclusion that the hydrolysis of the R-TPzT ligands, in the presence of the allylpalladium fragment, may have its origin in the bond reinforcement of the triazin-2-olate anion with the palladium centres. Complexes **2** are soluble in acetone, THF and dichloromethane but insoluble

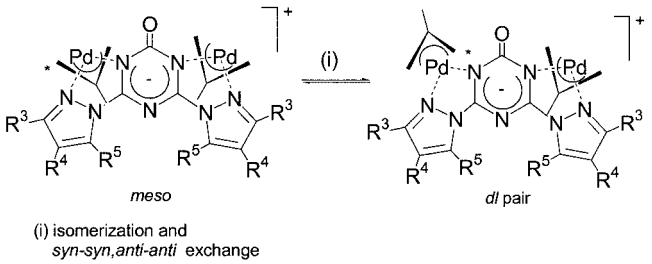
in diethyl ether, pentane and hexane. This solubility behaviour was used to obtain crystals of **2c**.

Structural Characterisation of Complexes 2a, 2c, and 2d

The IR spectra of the complexes contain a ν(C=O) band at 1696 (**2a**), [1685 (**2b**)],[24] 1691 (**2c**), or 1687 cm^{-1} (**2d**). The most characteristic peak in the FAB^+/MS corresponds to $[M - X]^+$ and this appears at 552 (**2a**), [580 (**2b**)],[24] 608 (**2c**), or 636 Da (**2d**). These peaks are due to the loss of the counterion from the molecular mass of the ionic complex. Secondary peaks that correspond to the loss of one or two allyl groups are also observed.

The data from the ^1H NMR spectra are compiled in Table 1. The signals of the complexes were assigned by comparison with the data for the corresponding ligands and considering the information obtained from NOE studies. For example, ligand **1d** and complex **2d** exhibit an NOE between Me^4 and Me^3/Me^5. The resonance for Me^3 also showed NOEs with H_{anti} and H_{syn} signals. A shift towards higher energies is observed in the resonances of the complexes with respect to the non-coordinated N-donor ligands.

At room temperature, **2a** showed only one broad signal for the H_{syn} or H_{anti} protons while the corresponding spectra for **2c** and **2d** contained two signals for each kind of protons. In all cases, signals corresponding to one type of pyrazole group were observed at this temperature. When the ^1H NMR spectra of the complexes were registered at low temperature, splitting of the signals was detected. Evidence was seen for two types of pyrazole groups in different ratios along with four H_{anti} and four H_{syn} (two types of intensities) protons. If we consider these data and the information deduced for the similar complex **2b**,[24] the situation observed must be due to the presence of two isomers − a *d*,*l* pair and a *meso* form − that differ in the relative orientation of the two allyl groups (see Scheme 3). Each isomer contains two equivalent pyrazole rings and two asymmetric and equivalent allylic groups. In the case of complex **2d**, where the allylic signals at low temperature are more differentiated than in the other complexes, we performed NOE studies at 213 K. It can be seen from the data in Table 1 that it was possible to identify, from the NOEs observed with the Me^3 signal, the resonances due to the allylic group *cis* to the pyrazole ring in each isomer. The H_{syn} and H_{anti} atoms of the same allylic carbon atom also showed a mutual NOE.



Scheme 3

The NOE studies at room temperature (and also in some cases at low temperature) showed a transfer of magnetisation within an allyl group between the two H_{syn} atoms on the one hand, and the two H_{anti} atoms on the other. This information, together with the observation of two isomers at low temperature that are seen as a single form at room temperature, is a clear indication of fluxional behaviour in the complexes. This possibility was further investigated by means of variable-temperature ^1H NMR spectroscopy studies and the results will be discussed in a separate section.

The $^{13}C\{^1H\}$ NMR spectroscopic data of the ligands and complexes at room temperature are reported in Table 2. The asymmetry of the 2-methylallyl group is apparent from the signals of the terminal carbon atoms at δ ≈ 60 ppm, one

Table 1. ^1H NMR spectroscopic data for ligands and complexes in [D_6]acetone (*M* = major isomer; *m* = minor isomer)

Compound	Temp. [K]	Pyrazole H^5/Me^5	Pyrazole H^3/Me^3	H^4/Me^4	Allyl H_{syn}	Allyl H_{anti}	Me
TpzT (**1a**)	293	8.80 (dd, J_{45} = 2.8 J_{35} = 0.7)	7.99 (dd, J_{34} = 1.5)	6.73 (dd)			
Me_2-TpzT (**1c**)	293	2.84 (s)	2.26 (s)	6.22 (s)			
Me_3-TpzT (**1d**)	293	2.69 (s)	2.28 (s)	1.96 (s)			
2a	293	9.0 (m)	8.4 (m)	6.99 (m)	4.5 (br. s)	3.33 (br. s)	2.20 (s)
2a *M* (56 %)	203	9.07 (dd, J_{45} = 2.9 J_{35} = 0.7)	8.45 (dd, J_{34} = 1.5)	6.99 (dd)	4.51 (s), 4.49 (s)	3.34 (s), 3.32 (s)	2.14 (s)
2a *m* (44 %)	203	9.12 (dd, J_{45} = 2.9 J_{35} = 0.5)	8.49 (dd, J_{34} = 1.5)	7.03 (dd)	4.57 (s), 4.49 (s)	3.35 (s), 3.29 (s)	2.18 (s)
2c	293	2.87 (s)	2.46 (s)	6.63 (s)	4.79 (br. s), 4.39 (br. s)	3.42 (s), 3.22 (s)	2.17 (s)
2c *M* (64 %)	213	2.87 (s)	2.45 (s)	6.83 (s)	4.67 (s), 4.41 (s)	3.40 (s), 3.17 (s)	2.19 (s)
2c *m* (34 %)	213	2.85 (s)	2.45 (s)	6.79 (s)	4.72 (s), 4.42 (s)	3.40 (s), 3.17 (s)	2.09 (s)
2d	293	2.81 (s)	2.44 (s)	2.11 (s)	4.79 (br. s), 4.39 (br. s)	3.41 (br. s), 3.21 (br. s)	2.17 (s)
2d *M* (56 %)	213	2.77 (s)	2.42 (s)	[a]	4.67 (br. s), 4.43[b] (br. s)	3.35 (s), 3.11[b] (s)	[a]
2d *m* (44 %)	213	2.74 (s)	2.42 (s)	[a]	4.72[b] (br. s), 4.48 (br. s)	3.37[b] (s), 3.17 (s)	2.16 (s)

[a] Overlapped with the solvent signal. [b] Resonances of the protons *cis* to the pyrazole ring.

Table 2. $^{13}C\{^1H\}$ NMR chemical shifts (ppm) for ligand and complexes at 293 K (unless specified, the signals are singlets; n.o.: not observed)

Compd.	Solvent	Triazine	Pyrazolyl substituents			Allyl		
			C^3 [Me^3]	C^4 [Me^4]	C^5 [Me^5]	−C=	CH_2	CH_3
TPzT (**1a**)	[D_6]acetone	165.0	146.6	111.3	131.9			
Me_2-TPzT (**1c**)	$CDCl_3$	164.3	153.3 [14.0]	111.9	144.4 [15.5]			
Me_3-TPzT (**1d**)	$CDCl_3$	164.1	153.5 [12.5]	118.0 [8.1]	139.6 [13.7]			
2a	[D_6]acetone	162.2	149.5	112.9	133.6	133.1	61.5 (br. s), 63.5 (br. s)	23.7
2c	[D_6]acetone	165.2	157.3 [15.5]	112.9	148.0 [16.2]	131.0	59.0 65.0	23.3
2d	$CDCl_3$	n.o.	155.8 [12.4]	119.4 [8.5]	142.9 [14.3]	130.2	57.7 65.1	23.5

close to the C=O and the other to the pyrazole. A number of the allyl signals are broad, indicating the existence of the afore-mentioned fluxional process. Complexation produces small effects on the signals of the ligands. HMQC experiments, relating ^1H and ^{13}C signals, proved particularly useful in assigning the methyl groups of the pyrazole rings.

X-ray Structure of 2c

The molecular structure of **2c** was determined by X-ray diffraction. The molecular structure consists of a dinuclear Pd monocation and a PF_6 counteranion. The ORTEP plot of the cation is shown in Figure 1, the crystallographic data are given in Table 6 and a selected list of bond lengths and angles is reported in Table 3. The N-donor ligand adopts a practically planar conformation with three coplanar heterocycles. The Pd centres are also practically coplanar with the azolylazine molecule. The bite angle of this ligand is ca. 76° in both coordination positions. The Pd−N bond lengths are also almost identical [2.076(6) and 2.102(5) Å], with the distance being slightly longer for the Pd−N(triazinolate) than for the Pd−N(pyrazole) bonds. The Pd−C bond lengths with the allyl groups are in the range expected for these types of complexes,[24] with the longer distance measured for the Pd−C(central) than for the Pd−C(terminal) bonds. The dihedral angle between the allylic plane and the palladium coordination plane is ca. 114°, with the C(central)-to-CH_3 vector pointing away from the metal centre. If we define a plane containing the Pd centre and the corresponding N-donor atoms (coordination plane), the terminal allylic carbon atoms are practically in the plane and the central carbon atom is clearly above it. The C(7)−O(1) bond length is 1.207(8) Å, which is indicative of a certain degree of double-bond character. The triazinolate ring C−N distances at C(7) are typical single-bond values (ca. 1.39 Å), and the remaining four C−N distances are narrowly spread in the double-bond range [between 1.319(8) and 1.334(9) Å]. If one also considers the planarity of the heterocycle, this situation points to a pentadienide delocalization bonding of the five atoms N(1)−C(5)−N(2)−C(6)−N(3).

Table 3. Bond lengths [Å] and angles [°] for **2c**

Pd(1)−N(4)	2.076(6)	N(4)−Pd(1)−N(1)	75.8(2)
Pd(1)−C(1)	2.094(7)	C(1)−Pd(1)−C(3)	68.0(3)
Pd(1)−N(1)	2.102(5)	N(6)−Pd(2)−N(3)	76.3(2)
Pd(1)−C(3)	2.117(8)	C(15)−Pd(2)−C(13)	68.3(4)
Pd(1)−C(2)	2.147(8)		
Pd(2)−N(6)	2.079(7)		
Pd(2)−N(3)	2.099(6)		
Pd(2)−C(15)	2.109(9)		
Pd(2)−C(13)	2.118(8)		
Pd(2)−C(14)	2.133(8)		
O(1)−C(7)	1.207(8)		
N(1)−C(5)	1.319(8)		
N(1)−C(7)	1.396(8)		
N(2)−C(6)	1.332(9)		
N(2)−C(5)	1.334(9)		
N(3)−C(6)	1.330(9)		
N(3)−C(7)	1.393(9)		

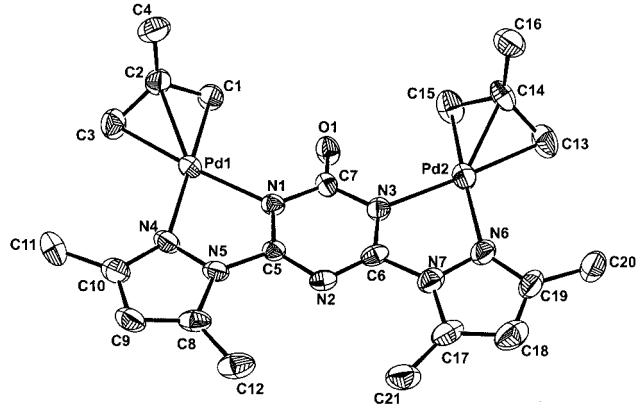


Figure 1. ORTEP view with atomic numbering of the cation of complex **2c**

Fluxional Behaviour of the Allyl Complexes

Variable-temperature ^1H NMR studies in [D_6]acetone were performed for **2a**, **2c**, and **2d** in the temperature range 183−323 K. As stated previously, low-temperature ^1H NMR spectra contain resonances corresponding to the presence of two isomers in a different ratio (a *d*,*l* pair, a *meso* form; see Scheme 3 and Table 1). Several coalescences were observed on increasing the temperature: the two signals due to each pyrazole proton and also the allylic methyl groups simplified to give one resonance and the four lines for the H_{syn} protons coalesced consecutively until finally only one resonance was observed (the same was seen for the H_{anti} signals). Consequently, a process was observed that involved an apparent allyl rotation that simultaneously

Table 4. Coalescence temperatures and free energies of activation for complexes **2a**−**d**

Compd.[a]	T_c [K]	$\Delta G_c^{\ddagger}$ [kJ/mol^{-1}]	Interchanging groups	Compd.	T_c [K]	$\Delta G_c^{\ddagger}$ [kJ/mol^{-1}]	Interchanging groups
2a	243	51.8	H^3	**2c**	253	56.0	H_{anti} (3+4)
	249	53.2	H^5		267	57.3	H_{syn} (1+2)
	251	53.5	H^4		268	58.0	H^4
	255	54.1	Me-allyl		285	60.3	Me-allyl
	258	55.1	H_{syn} (1+2)	**2d**	205	46.0	Me^3
	286	60.3	H_{anti} (1+2) + (3+4)		227	49.4	H_{anti} (1+2)
	300	60.9	H_{syn} (1+2) + (3+4)		235	49.2	H_{anti} (3+4)
2b[24]	243	53.6	H^3		243	53.9	Me-allyl
	253	54.4	H^5		259	55.4	H_{syn} (1+2)
	253	54.6	H_{syn} (1+2)		259	54.7	H_{syn} (3+4)
	258	56.0	H_{anti} (1+2)		259	55.4	Me^5
	263	58.0	H_{syn} (3+4)		283	58.2	Me^4
	288	60.5	H_{anti} (1+2) + (3+4)	**2d**; $CDCl_3$	307	70.5	Me-allyl
	302	60.9	H_{syn} (1+2) + (3+4)				

[a] Unless specified, [D_6]acetone solutions with a concentration of $7.94\cdot10^{-3}$ M. See Scheme 1 for the labelling scheme. For the allylic protons 1−4 refer to the signals in the order of decreasing frequency.

leads to an isomerisation and to a *syn-syn/anti-anti* interchange. Interconversion between H_{anti} and H_{syn} protons was not seen in these studies. It is possible that the absence of a ligand of high *trans* influence increases the energy of this process. Free energies of activation were calculated from the coalescence temperatures and the δν values between the coalescing signals. The corresponding data are shown in Table 4 and in each case the interchanging groups are indicated. The data for complex **2b**[24] have also been included for the sake of comparison. When the free energy of activation values are plotted against the coalescence temperatures for **2a**−**2d** (see Figure 2), it can be seen that the values do not differ significantly from one complex to another. Consequently, the process of apparent allyl rotation is not markedly affected by a change in the basicity or steric hindrance of the pyrazolyl fragment.

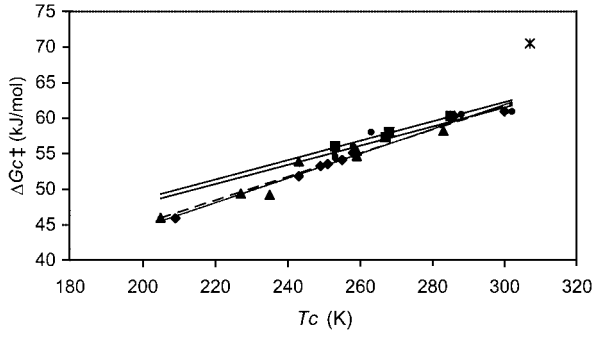


Figure 2. Linear plot of $\Delta G_c^{\ddagger}$ [kJ/mol] versus T_c [K] for complexes **2a**−**2d** in [D_6]acetone (see Table 4): **2a** (diamonds, -----), **2b** (dots, ——), **2c** (squares, ——), **2d** (triangles, ——), **2d** (star) in $CDCl_3$

In the case of complex **2d** a variable-temperature ^1H NMR spectroscopy study was also performed in $CDCl_3$. At low temperature (213 K) a splitting of the allylic methyl signal is observed. This enables the calculation of the corresponding free energy of activation (see Table 4). When the value obtained is compared with those calculated for complex **2d** in [D_6]acetone (see Figure 2), it is evident that in this poorly coordinating solvent the process of allyl rotation is clearly hindered. We must take into account that the anions in our complexes are also of low coordinating ability.

In the case of complex **2c**, variable-temperature studies were performed at different concentrations and also after the addition of water for one of the experiments. In this way, we tried to evaluate whether the presence of water in the deuterated solvent could influence the dynamic process. The $\Delta G_c^{\ddagger}$ values are collected in Table 5 and the appropriate plot is shown in Figure 3. The two lines corresponding to the studies with and without additional water are extremely similar. This means that in [D_6]acetone the addition of water does not affect the interconversion process. Moreover, the effect of the concentration, at least in the range studied, is also of minor importance.

It can be deduced unambiguously from Figures 2 and 3 that the value for the entropy of activation is negative. Con-

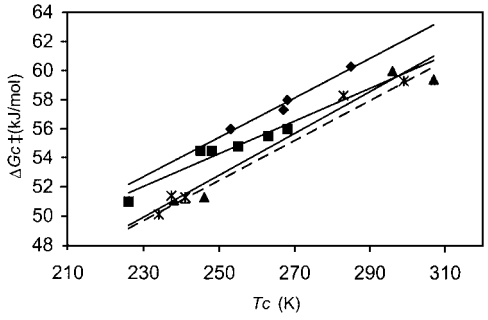


Figure 3. Linear plot of $\Delta G_c^{\ddagger}$ [kJ/mol] versus T_c [K] for complex **2c** in [D_6]acetone (see Tables 4 and 5): $7.94\cdot10^{-3}$ (diamonds, ——), $4.18\cdot10^{-3}$ (squares, ——); $2.10\cdot10^{-3}$ (triangles, -----); $2.10\cdot10^{-3}$ (stars, ——) with 15 μL of H_2O in 0.5 mL of solution

Table 5. Coalescence temperatures and free energies of activation for complex **2c** at different concentrations in [D_6]acetone (see also the data of **2c** in Table 4; see Scheme 1 for the labelling scheme; for the allylic protons 1−4 refer to the signals in the order of decreasing frequency)

Conc.	T_c [K]	$\Delta G_c^{\ddagger}$ [kJ/mol^{-1}]	Interchanging groups	Conc.	T_c [K]	$\Delta G_c^{\ddagger}$ [kJ/mol^{-1}]	Interchanging groups
$4.18\cdot10^{-3}$ M	226	51.0	Me^3	$2.1\cdot10^{-3}$ M	238	51.1	H_{syn} (1+2)
	245	54.5	Me^5		241	51.2	H^4
	248	54.5	H_{anti} (3+4)		246	51.3	Me-allyl
	255	54.8	H_{syn} (1+2)		296	60.0	H_{anti} (1+2) + (3+4)
	263	55.5	H^4		307	59.4	H_{syn} (1+2) + (3+4)
	268	56.0	Me-allyl	$2.1\cdot10^{-3}$ M[a]	234	50.1	H_{syn} (1+2)
					237.3	51.4	H^4
					241	51.3	Me-allyl
					283	58.3	H_{anti} (1+2) + (3+4)
					299	59.3	H_{syn} (1+2) + (3+4)

[a] With the addition of 15 μL of H_2O in 0.5 mL of solution.

sidering all these data, we propose an associative mechanism involving the coordination of acetone. Such a situation is in accordance with the negative sign of the entropy and the effect of the solvent. Even in the more concentrated solutions, it is assumed that acetone coordination takes place without difficulty and that the concentration does not significantly influence the process. After coordination of the acetone molecule, the system could evolve through pseudorotation of the allyl group.[2a,28] We cannot rule out the participation of the bond breaking of Pd−N(triazine) in this process. However, there is evidence that the Pd−N(pyrazole) bond rupture does not influence this process because ligands with pyrazole groups that differ substantially in their electronic (and steric) characteristics practically have the same energetic barrier.

Experimental Section

General Comments: All manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. The derivative [Pd(η^3-C_4H_7)(μ-Cl)]$_2$[41] and ligands **1a**,[36,37] **1b**,[24] and **1c**[38] were prepared according to literature procedures. Elemental analyses were performed with a Perkin−Elmer 240 B microanalyser. IR spectra where recorded as nujol mulls with a Perkin−Elmer PE 883 IR spectrometer. Mass spectra (position of the peaks in Da) were recorded with a VG Autospec spectrometer (University of Zaragoza) using the FAB$^+$ technique and *m*-nitrobenzylic alcohol as matrix, and HPLC1100-MSD (Quadrupole analyzer) for the electrospray technique. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with a Varian Unity 300 spectrometer using, unless specified, $(CD_3)_2CO$ as solvent and the chemical shifts are given in ppm. Standard experimental conditions were employed.[24,25] The ^{15}N NMR spectrum of compound **1d** was registered with a Bruker DRX 400 instrument with the chemical shifts in ppm, obtained by the heteronuclear-shift-correlation-spectra gs-HMQC and gs-HMBC with the standard pulse sequences[42] and referenced to an external sample of nitromethane. (^{1}H-^{1}H) COSY spectra: standard pulse sequence with an acquisition time of 0.214 s, pulse width 10 ms, relaxation delay 1 s, number of scans 16, number of increments 512. The NOE difference spectra were recorded with the following acquisition parameters: spectral width 5000 Hz, acquisition time 3.27 s, pulse width 18 ms, relaxation delay 4 s, irradiation power 5−10 dB, number of scans 240. For variable-temperature spectra the probe temperature (±1 K) was controlled by a standard unit calibrated with a methanol reference. Free energies of activation (kJ·mol^{-1}) were calculated[43] from the coalescence temperature (T_c) and the frequency difference between the coalescing signals (extrapolated at the coalescence temperature) with the formula $\Delta G_c^{\ddagger} = a\cdot T\cdot[9.972 + \log(T/\delta\nu)]$, $a = 1.914\cdot10^{-2}$. The estimated error in the calculated free energies of activation is ±1.1 kJ·mol^{-1}. *M* and *m* refer to the major or minor isomers, respectively.

Preparation of Compounds

(a) 2,4,6-Tris(3,4,5-trimethylpyrazol-1-yl)-1,3,5-triazine (1d): NaH (55.6 mg of 95 %, 2.2 mmol) was added to a solution of 3,4,5-trimethylpyrazole[44] (237 mg, 2.15 mmol) in freshly distilled dry THF (20 mL). After 1 h at 90 °C, the solution was cooled and 2,4,6-trichlorotriazine (cyanuric chloride) (99 % purity, Aldrich C9,550-1) (126.1 mg, 0.62 mmol) was added. The solution was heated at 90 °C for 10 h and at 70 °C for 18 h. The solvent was evaporated and the residue chromatographed on silica using $CHCl_3/CH_3OH$ (2:1) as eluent. Compound **1d** [R_f ($CHCl_3/CH_3OH$, 2:1) = 0.23], m.p. 295−297 °C, yield 49 % (135.7 mg). $C_{21}H_{27}N_9$ (405.24): calcd. C 62.20, H 6.71, N 31.09; found C 62.18, H 6.99, N 30.87. MS (FAB$^+$): *m*/*z* = 406.2 Da; (electrospray): *m*/*z* = 406.2 Da. ^{15}N NMR (40.56 MHz, $CDCl_3$, 25 °C): δ = −168.4 (N-1, pyrazole), −87.4 (N-2, pyrazole), −168.4 (N-triazine) ppm.

(b) [{Pd(η^3-C_4H_7)}$_2$(BPzTO)]BF_4 (2a): $AgBF_4$ (52.2 mg, 0.26 mmol) was added to a solution of [Pd(η^3-C_4H_7)(μ-Cl)]$_2$ (52.8 mg, 0.13 mmol) in THF (20 mL). The mixture was stirred for 2 h and protected from light. The solution was filtered through Celite to eliminate AgCl. The ligand TPzT (24.3 mg, 0.087 mol) was added and the mixture was stirred for 4 h. The solvent was evaporated to dryness and the pale yellow residue was washed with diethyl ether. The solid was crystallised in acetone/diethyl ether to obtain white crystals of **2a**. Yield: 36 % (20 mg). $C_{17}H_{20}BF_4N_7OPd_2$ (638.00): calcd. C 32.00, H 3.16, N 15.36; found C 31.75, H 3.28, N 15.24.

(c) [{Pd(η^3-C_4H_7)}$_2$(Me_2-BPzTO)]PF_6 (2c): A similar procedure to that used for **2a** was applied for **2c**. Amounts were as follows: $AgPF_6$ (145.6 mg, 0.58 mmol), [Pd(η^3-C_4H_7)(μ-Cl)]$_2$ (113.4 mg, 0.29 mmol), Me_2-TPzT (69.8 mg, 0.19 mmol). The solid was pale yellow in colour. Yield: 35 % (50 mg). $C_{21}H_{28}F_6N_7OPPd_2$ (752.27): calcd. C 33.53, H 3.75, N 13.03; found C 33.43, H 3.63, N 12.99.

(d) [{Pd(η^3-C_4H_7)}$_2$(Me_3-BPzTO)]PF_6 (2d): A similar procedure to that used for **2a** was applied for **2d**. Amounts were as follows: $AgPF_6$ (60.7 mg, 0.24 mmol), [Pd(η^3-C_4H_7)(μ-Cl)]$_2$ (48.0 mg, 0.12 mmol), Me_3-TPzT (32.4 mg, 0.08 mmol). The solid was pale yellow in colour. Yield: 30 % (19 mg). $C_{24}H_{32}F_6N_7OPPd_2$ (792.34): calcd. C 36.38, H 4.07, N 12.37; found C 36.02, H 4.33, N 12.59.

Preparation of NMR Spectroscopic Samples of 2: Samples for the studies found in Table 4. The corresponding amount of the complexes (**2a**: 2.53 mg; **2c**: 2.99 mg; **2d**: 3.14 mg) was dissolved in 0.5 mL of the deuterated solvent. Samples for the studies found in Table 5. Complex **2c** (3.14 mg) was dissolved in 1 mL of [D_6]acetone. After recording the NMR spectra, 0.25 mL of this solution was mixed with 0.25 mL of [D_6]acetone and the spectra were recorded. Finally, 15 μL of H_2O was added.

X-ray Data Collection, Structure Determination, and Refinement of Complex 2c: The crystallographic data and experimental details are given in Table 6. Crystals of complex **2c** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of the complex in acetone. Accurate unit cell parameters were determined by least-squares refinement of the setting angles of 25 randomly distributed and carefully centred reflections. The data collection was performed with a Nonius-Mach3 diffractometer equipped with a graphite monochromator [Mo-K_α radiation (λ = 0.71073 Å)] using an $\omega/2\theta$ scan technique to a maximum value of 56°. Data were corrected for Lorentz and polarisation effects. The structures were solved by direct methods (SIR92)[45] and refined first isotropically by full-matrix least squares using the SHELXL-97[46] program and then anisotropically by blocked full-matrix least squares for all the non-hydrogen atoms. The hydrogen atoms were included in calculated positions and refined "riding" on their parent carbon atoms. CCDC-212257 (**2c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 6. Crystal data and structure refinement for **2c**

Empirical formula	$C_{21}H_{28}N_7OPd_2{\cdot}PF_6$
Formula mass	752.27 Da
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	a = 8.815(5) Å, α = 106.560(5)°
	b = 12.936(5) Å, β = 102.890(5)°
	c = 13.074(5) Å, γ = 99.190(5)°
Volume	1352.6(11) Å^3
Z, calculated density	2, 1.847 g/cm^3
Absorption coefficient	14.59 cm^{-1}
F(000)	744
Crystal size	0.3 × 0.2 × 0.2 mm
Limiting indices	$-11 \le h \le 11$, $-17 \le k \le 16$,
	$0 \le l \le 17$
Reflections collected/unique	6808/6525 [R(int) = 0.0510]
Data/restraints/parameters	6525/37/398
Goodness-of-fit on F^2	0.951
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0559, $wR2$ = 0.1100
R indices (all data)	$R1$ = 0.1814, $wR2$ = 0.1444
Largest diff. peak and hole	0.502 and −0.652 e·Å^{-3}

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