Apparent Allyl Rotation and Pd−N Bond Rupture in Allylpalladium Complexes with N-Donor Ligands − Evidence of an Associative Mechanism

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The new didentate N-donor ligands 2-(4-methyl-1*H*-pyrazol-1-yl)pyrimidine (4Me-pzpm, **1**) and 2-(4-bromo-1*H*-pyrazol-1-yl)pyrimidine (4Br-pzpm, **2**) have been synthesised and used to obtain the allylpalladium derivatives [Pd(η^3-2Me-C_3H_4)(NN′)]X [X = BAr'_4^-, NN′ = **1** (**3**), NN′ = **2** (**4**); X = $CF_3SO_3^-$, NN′ = **1** (**5**), NN′ = **2** (**6**)]. In complexes **3**–**6** two types of fluxional process have been found: apparent allyl rotation that is observed as H_{syn}–H_{syn}, H_{anti}–H_{anti} interconversions and H^4–H^6 interchange of the pyrimidine protons that must involve Pd–N(pm) bond rupture. The influence of different factors on both processes — such as the nature of the N-donor ligand, counterion, solvent, complex concentration and addition of water — has been studied. It has been concluded that the apparent allyl rotation has a lower free energy of activation and in both cases the presence of a species with coordinating ability favours the process. Negative entropies of activation have been found. Associative mechanisms involving participation of five-coordinate intermediates have been proposed.

Introduction

The chemistry of (η^3-allyl)palladium complexes has received a great deal of attention because these derivatives can act 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 been widely studied.[2] Besides the fundamental interest in these studies, the fluxional behaviour of allylpalladium derivatives has 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 frequently encountered in allylpalladium complexes is a mutual exchange of *syn* and *anti* groups.[4−12] This process is believed to occur through an η^3-η^1-η^3 pathway that in some cases is selective[6a,9a,10,13−16] due to steric or electronic factors. On the basis of theoretical calculations concerning the mechanism of the η^3-η^1-η^3 isomerisation in (η^3-allyl)palladium complexes, it has been proposed that the process involves tetracoordinate (η^1-allyl)palladium intermediates with coordination of a solvent molecule or an ancillary ligand.[17] A second dynamic process that is frequently observed in complexes with N-donor ligands is the apparent rotation of the allyl group.[18−28] In certain examples both of the aforementioned processes have been observed.[16,29−35] The apparent rotation is observed as a *syn-syn*, *anti-anti* exchange and/or an isomerisation process, depending on the molecular symmetry. Two main mechanisms have been proposed for the apparent allyl rotation: (i) associative mechanisms[20,28,29,32,35] that involve five-coordinate intermediates (coordination of the solvent, the anion or other molecules) that can undergo allyl pseudorotation, and (ii) dissociative mechanisms[18,19,21−23,25,26,31,33] with formation of T-shaped three-coordinate intermediates after dissociation of monodentate or didentate (partial dissociation) ligands. Consequently, one question that is open to debate is whether the apparent allyl rotation in derivatives with N-donor ligands involves Pd−N bond breaking or not. In the case of didentate ligands this question is interesting because it would involve the dissociation of one arm of a chelate, a subject of potential interest, especially in relation to catalytic processes. In some examples it has been reported that a ligand of higher basicity makes the apparent rotation more difficult,[21] while increased steric hindrance of the N-donor ligand can facilitate[20,29] or slow down[21] the process. Negative entropies of activation have been found in some cases[29,32] and it has been reported that the process takes place more easily with coordinating anions[19,29,31] or solvents such as DMSO.[20b] It has also been reported that the addition of ligand or water has a negligible effect on the process in a number of examples;[18,21] other examples have been described where the effect of adding ligand or chlorides is accelerative.[19,28,29] The effect of the anion has also been analysed.[29,31a] As far as the effect of the complex concentration is concerned, positive effects,[28,20b] at least to a limiting value, have been described but in some cases it has been found that this factor has no influence.[31a,35] In recent years we have been interested in the synthesis, structural characterisation and dynamic behaviour of allylpal-

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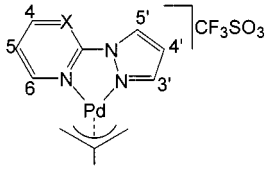
ladium(II) complexes with N-donor ligands containing pyrazolyl groups.[23−28,35] We have described the synthesis and fluxional behaviour of the complexes $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)(NN')]CF_3SO_3$ [NN′ = 2-(1*H*-pyrazol-1-yl)pyrimidine = pzpm (**I**); NN′ = 2-(1*H*-pyrazol-1-yl)pyridine = pzpy (**II**)][23] (see Scheme 1) where the *syn-syn*, *anti-anti* interconversion was detected along with an interchange process between the H^4 and H^6 protons of the pyrimidine ring in complex **I**. This last interchange is only possible through Pd−N(pm) bond rupture. Moreover, an NOE between the allylic H_{syn} and H_{anti} protons and $H^{5'}$ of the pyrazole ring was also detected in the case of complex **II** and this can only be explained through Pd−N(pz) bond rupture (see Scheme 1). Considering these facts, and given the similarities between our work and other results reported previously,[19] we proposed that it was possible that the apparent allyl rotation could also take place through an initial Pd−N bond rupture. In the work described here we have attempted to gain a further insight into these processes by looking for more data concerning the free energies of activation. More precisely, we were interested in determining whether or not the apparent allyl rotation processes and the H^4-H^6 pyrimidine proton interconversion have the same energy barrier and a common mechanism. Given that the H^4-H^6 interconversion must involve a Pd−N bond-breaking step, comparison of the free energies of activation for the two processes could provide information about the participation of Pd−N bond rupture in the apparent allyl rotation. As stated above, this aspect is now a matter of debate. We also decided to explore the influence on the processes of several factors such as the type of ligand, counterion, solvent, complex concentration and addition of water. These studies may prove useful in elucidating the type of mechanism (associative or dissociative) operating in the apparent allyl rotation process.

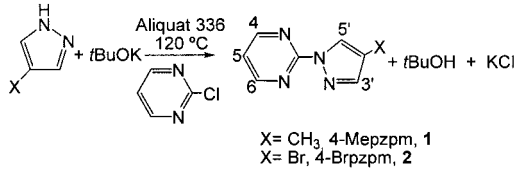


Scheme 1

Results and Discussion

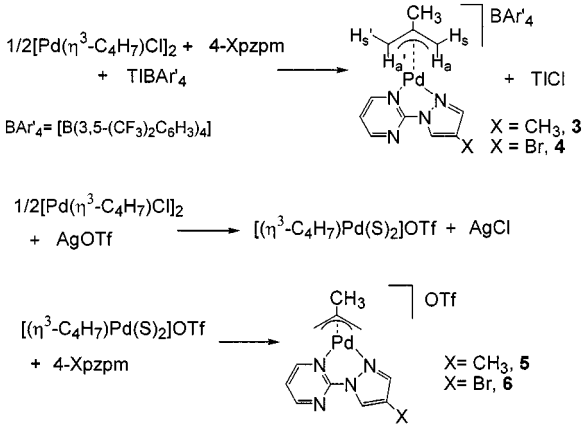
Synthesis of the New Ligands and Complexes

We decided to prepare allylpalladium complexes with two different ligands containing a pyrimidine ring (in order to study the H^4-H^6 interconversion process) and different 4-substituted pyrazole groups: 2-(4-methyl-1*H*-pyrazol-1-yl)-pyrimidine (4Me-pzpm, **1**) and 2-(4-bromo-1*H*-pyrazol-1-yl)pyrimidine (4Br-pzpm, **2**; Scheme 2). The results obtained on these complexes could be compared with those obtained with pzpm. The differences in the three ligands are limited to the substituent in the 4-position of the pyrazole, and so it is foreseeable that, if any influence exists, it will be only electronic in nature. The pK_a values for the three pyrazole heterocycles are as follows: 4-methylpyrazole 3.04; pyrazole 2.48; 4-bromopyrazole 0.63.[36] The new ligands were prepared by reaction of the deprotonated pyrazole rings with 2-chloropyrimidine (see Scheme 2 and Exp. Sect.).



Scheme 2

We synthesised allyl derivatives with two types of counterion: triflate (OTf), which has coordinative ability, and the voluminous tetrakis(3,5-trifluoromethylphenyl)-borate ($BAr'_4{}^-$), which is non-coordinating. In both cases the starting material was $[Pd(\eta^3\text{-}2Me\text{-}C_3H_4)Cl]_2$ and this was allowed to react in one step with a stoichiometric amount of the nitrogen ligands and $TlBAr'_4$ or, alternatively, in two steps with prior elimination of the chlorides with $AgCF_3SO_3$ and addition of the nitrogen ligands after the AgCl had been filtered off (see Scheme 3).



Scheme 3

The products are soluble in polar solvents such as acetone, dichloromethane and THF but are insoluble in hexane, pentane and diethyl ether.

Structural Characterisation

The new ligands and products were characterised by elemental analysis, and IR, ^1H and ^{13}C NMR spectroscopy. For the majority of the derivatives, HSQC experiments were also performed and, in some cases, NOE experiments were carried out.

The IR spectra of the ligands and complexes exhibit the stretching vibration bands for ν(C=N) (see Exp. Sect.). The

Table 1. ^{1}H NMR spectroscopic data for ligands **1** and **2** and complexes **3**−**6**[a]

	Pyrazole			Pyrimidine		Allyl		
	$H^{5'}$	CH_3	$H^{3'}$	H^5	H^4/H^6	H_{syn}	H_{anti}	CH_3
1	8.38 (s)	2.14 (s)	7.62 (s)	7.36 (t), $J_{5,4/5,6}$ = 4.8	8.78 (d) $J_{4,5/6,5}$ = 4.8	–	–	–
2	8.73 (s)	–	7.84 (s)	7.48 (t), $J_{5,4/5,6}$ = 4.8	8.85 (d) $J_{4,5/6,5}$ = 4.8	–	–	–
3	8.72 (s)	2.27 (s)	8.28 (s)	[b]	9.20 (bs)	4.49 (s)	3.44 (s)	2.25 (s)
3[c]	8.90 (s)	2.22 (s)	8.33 (s)	[b]	9.25 (bs)	4.49 (s)	3.46 (s)	2.18 (s)
							3.32 (s)	
4	9.12 (s)	–	8.53 (s)	7.91 (bs)	9.51 (bs)	4.57 (s)	3.49 (s)	2.27 (s)
4[c]	9.41(s)	–	8.69 (s)	7.93 (t), $J_{5,4/5,6}$ = 4.9	9.32 (d)	4.54 (s)	3.49 (s)	2.17 (s)
					9.27 (d)	4.51 (s)	3.34 (s)	
4[d]	8.57 (s)	–	7.93 (s)	7.14 (t), $J_{5,4/5,6}$ = 5.1	8.56 (d)	3.93 (s)	2.91 (s)	2.05 (s)
					8.70 (d)	4.16 (s)	3.05 (s)	
5	8.67 (s)	2.27 (s)	8.22 (s)	7.75 (bs)	9.19 (bs)	4.49 (s)	3.43 (s)	2.25 (s)
5[c]	8.88 (s)	2.23 (s)	8.33 (s)	7.85 (t), $J_{5,4/5,6}$ = 5.1	9.31 (d)	4.50 (s)	3.48 (s)	2.20 (s)
					9.25 (d)		3.34 (s)	
6	9.14 (s)	–	8.56 (s)	7.86 (t), $J_{5,4/5,6}$ = 5.3	9.32 (bs)	4.58 (s)	3.49 (s)	2.27 (s)
					9.25 (bs)			
6[c]	9.45 (s)	–	8.73 (s)	7.95 (t), $J_{5,4/5,6}$ = 5.1	9.36 (d)	4.59 (s)	3.55 (s)	2.22 (s)
					9.31 (d)	4.57 (s)	3.40 (s)	
6[e]	8.71 (s)	–	8.04 (s)	7.72 (bs)	9.15 (bs)	4.35 (s)	3.39 (s)	2.17 (s)
					8.99 (bs)	4.29 (s)	3.20 (s)	

[a] Unless otherwise specified, room temperature and [D_6]acetone as solvent; s: singlet; d: doublet; bs: broad singlet; t: triplet. See Scheme 2 for the atom numbering. [b] Resonance under $BAr'_4{}^-$ signals. [c] −90 °C. [d] −60 °C, $CDCl_3$. [e] −80 °C, CD_2Cl_2. The resonances for the $BAr'_4{}^-$ anion are for **3**: δ = 7.79 (s, H*o*) and 7.68 (H*p*) ppm; for **4**: δ = 7.78 (s, H*o*) and 7.66 (H*p*) ppm.

allyl ligand gives rise to a band at 838 cm^{-1} in all the complexes due to the $\nu(C-CH_3)$ vibration. The presence of the corresponding counterions was confirmed by the presence of the expected bands (see Exp. Sect.).

The ^{1}H NMR spectroscopic data for the ligands and complexes are collected in Table 1. In the cases of derivatives **3** and **4**, due to some overlap with the resonances of the counterion, the spectra were recorded both in $CDCl_3$ and [D_6]acetone. The assignment for the nitrogen-ligand resonances was made on the basis of previous studies with similar ligands.[23,37] The $H^{3'}$ and $H^{5'}$ protons of the pyrazolyl rings appear as singlets both in the ligands and complexes as a result of the presence of the substituent in the 4-position. In the free ligands the H^5 proton of the pyrimidine ring appears as a triplet coupled to H^4 and H^6, which are equivalent. In the complexes the protons H^4 and H^6 are inequivalent due to coordination. However, signals for the two protons are only observed separately at room temperature in complex **6**. In the other cases these protons give rise to a single broad signal at this temperature. This phenomenon clearly indicates that the H^4-H^6 interconversion process previously detected in [Pd(η^3-2Me-C_3H_4)(pzpm)]CF_3SO_3 (**I**)[23] is also operating (see section on fluxional behaviour). In general, a shift towards higher frequency is observed for the corresponding resonances of the complexes with respect to the free ligands due to the ligand-to-metal σ-donation. As far as the allylic signals are concerned, a single resonance is observed at room temperature for the H_{syn} and also for the H_{anti} protons. This observation is not in accordance with a static situation of the complexes, where two different terminal allylic carbons would be expected due to the asymmetry of the nitrogen ligands. This constitutes a clear indication of a dynamic situation that involves a *syn-syn*, *anti-anti* interconversion, such as an apparent allyl rotation process, which will be analysed in the section on fluxional behaviour. The differentiation between the two methyl resonances of complex **3** [D_6]acetone was achieved with the help of NOE experiments. When $H^{5'}$ of the pyrazole ring was irradiated an NOE was found for the resonance at δ = 2.27 ppm. An NOE for the resonance at δ = 2.25 ppm and for the H_{anti} signal was also found when the H_{syn} resonance was irradiated.

The corresponding $^{13}C\{^1H\}$ NMR spectroscopic data are gathered in Table 2. The assignment for the nitrogen ligands was made on the basis of literature data[23,26,37−39] and HSQC experiments. In a similar way to the ^{1}H NMR spectra, a single signal was observed for the C^4 and C^6 pyrimidine carbons (in complex **4** this signal was not observed). A signal shift towards higher frequency with respect to the

Table 2. $^{13}C\{^1H\}$ NMR spectroscopic data for ligands **1** and **2** and complexes **3**−**6**[a]

	Pyrazole				Pyrimidine			η^3-Allyl		
	$C^{3'}$	$C^{4'}$	$C^{5'}$	CH_3	C^2	C^5	C^4/C^6	CH_2	C_{quat}	CH_3
1[b]	145.1	119.5	127.5	9.2	156.1	118.3	158.9			
1[c]	145.2	119.8	128.2	9.3	157.0	119.7	159.8			
2[b]	144.3	97.6	129.4	–	155.3	119.4	159.2			
2[c]	143.9	97.0	129.9	–	156.0	120.4	159.7			
3[b]	148.4	[d]	[e]	9.0	154.1	120.4	161.3	61.2 (bs)	136.3	23.4
4[b]	147.9	[d]	131.3	–	[d]	121.3	[e]	61.9 (bs)	137.1	23.4
5[c]	148.1	122.5	129.4	8.3	154.8	121.0	162.2	61.2 (bs)	135.5	22.7
6[c]	147.8	99.4	131.7	–	153.9	121.9	162.3	61.9 (bs)	136.0	22.7

[a] Unless specified, the signals are singlets; bs = broad singlet. See Scheme 2 for the atom numbering. [b] In $CDCl_3$. [c] In [D_6]acetone. [d] Not observed. [e] Resonances under $BAr'_4{}^-$ signals. The resonances of the anions are given in the Exp. Sect.

free ligands is also seen. The allylic carbon resonances also reflect the apparent allyl rotation process as a single broad signal appears for the terminal carbons. The expected coupling with boron or fluorine is observed for the C_{ipso} and CF_3 carbons, respectively, of the BAr'_4 anion.[40]

Fluxional Behaviour

As stated previously, with these new allyl complexes we tried to obtain sufficient information concerning their fluxional behaviour to draw a conclusion as to whether the apparent allyl rotation process and the H^4-H^6 interconversion have the same energy barrier and follow a common mechanism. This information and the study of the influence of different factors could also shed light on the controversy surrounding mechanisms (associative or dissociative). In the case of derivative **I**,[23] the corresponding representation of free energy of activation versus coalescence temperature did not allow a conclusion to be drawn as to whether the two points for the apparent allyl rotation and the one for the H^4-H^6 interconversion were in a straight line — the information was insufficient to conclude, with certainty, whether the two process have the same energy barrier.

In order to analyse the dynamic behaviour of complexes **3**−**6** we performed variable temperature ^1H NMR studies under different conditions in order to obtain the coalescence temperatures (T_c) of the interconversion processes $H_{syn}-H_{syn}$, $H_{anti}-H_{anti}$ and H^4-H^6. For the majority of the complexes, two H_{syn} signals, two H_{anti} signals and separate signals for H^4 and H^6 were observed at low temperature, as one would expect for a static situation (see Table 1). An increase in the temperature allowed the corresponding coalescence temperatures to be determined. These values are given in Table 3 along with the δν values and the calculated free energies of activation.[41] However, in some cases it was not possible to determine the $\Delta G_c^{\ddagger}$ values. The reasons for this are that either the signals were not split at the minimum experimental temperature or the coalescence was not reached at the maximum temperature allowed by the solvent (in this case it is indicated that the T_c values are higher than the maximum temperature registered and the $\Delta G_c^{\ddagger}$ values

Table 3. δν, T_c and $\Delta G_c^{\ddagger}$ data for complexes **3**−**6** and **I**[a]

Entry	Complex	Anion	Solvent	Interchanging groups	ν_c (Hz)	T_c (K)	$\Delta G_c^{\ddagger}$ (kJ/mol)
1	**3**	BAr'_4	[D$_6$]acetone	$H_{anti}-H_{anti}$	39.8	213	43.6
2[b]	**4**	BAr'_4	[D$_6$]acetone	$H_{anti}-H_{anti}$	74.7	244	48.9
3[b]	**4**	BAr'_4	[D$_6$]acetone	$H_{syn}-H_{syn}$	2.0	204	46.7
4[b]	**4**	BAr'_4	[D$_6$]acetone	H^4-H^6	45.3	303	62.6
5	**5**	OTf	[D$_6$]acetone	$H_{anti}-H_{anti}$	41.5	237	48.6
6	**5**	OTf	[D$_6$]acetone	H^4-H^6	14.7	217	46.3
7	**6**	OTf	[D$_6$]acetone	$H_{anti}-H_{anti}$	48.1	246	50.4
8	**6**	OTf	[D$_6$]acetone	$H_{syn}-H_{syn}$	1.8	208	47.8
9	**6**	OTf	[D$_6$]acetone	H^4-H^6	28.5	300	63.2
10[b]	**6**	OTf	[D$_6$]acetone	$H_{anti}-H_{anti}$	73.2	250	50.3
11[b]	**6**	OTf	[D$_6$]acetone	$H_{syn}-H_{syn}$	1.9	205	47.1
12[b]	**6**	OTf	[D$_6$]acetone	H^4-H^6	51.2	304	62.5
13	**I**	OTf	[D$_6$]acetone	$H_{anti}-H_{anti}$	40.9	230	47.3
14	**I**	OTf	[D$_6$]acetone	$H_{syn}-H_{syn}$	10.3	216	47.8
15	**I**	OTf	[D$_6$]acetone	H^4-H^6	26.6	268	55.4
16	**4**	BAr'_4	$CDCl_3$	$H_{anti}-H_{anti}$	13.8	252	54.2
17	**4**	BAr'_4	$CDCl_3$	$H_{syn}-H_{syn}$	60.3	284	57.9
18	**4**	BAr'_4	$CDCl_3$	H^4-H^6	74.1	>331	>67.1
19	**6**	OTf	CD_2Cl_2	$H_{anti}-H_{anti}$	51.1	245	49.9
20	**6**	OTf	CD_2Cl_2	$H_{syn}-H_{syn}$	18.5	221	48.9
21	**6**	OTf	CD_2Cl_2	H^4-H^6	29.7	311	65.4
22[c]	**6**	OTf	CD_2Cl_2	$H_{anti}-H_{anti}$	71.3	251	50.5
23[c]	**6**	OTf	CD_2Cl_2	$H_{syn}-H_{syn}$	29.0	229	47.6
24[c]	**6**	OTf	CD_2Cl_2	H^4-H^6	54.8	>311	>63.8
25[c]	**6**	OTf	[D$_6$]acetone	$H_{anti}-H_{anti}$	56.3	246	49.9
26[c]	**6**	OTf	[D$_6$]acetone	$H_{syn}-H_{syn}$	1.7	209	48.2
27[c]	**6**	OTf	[D$_6$]acetone	H^4-H^6	28.5	303	63.8
28[c]	**4**	BAr'_4	$CDCl_3$	$H_{anti}-H_{anti}$	20.3	233	49.2
29[c]	**4**	BAr'_4	$CDCl_3$	$H_{syn}-H_{syn}$	63.7	263	53.3
30[c]	**4**	BAr'_4	$CDCl_3$	H^4-H^6	79.1	>330	>66.9
31[d]	**4**	BAr'_4	$CDCl_3$	$H_{syn}-H_{syn}$	62.3	226	45.6
32[d]	**4**	BAr'_4	$CDCl_3$	H^4-H^6	46.0	290	59.8
33[e]	**6**	OTf	[D$_6$]acetone	$H_{anti}-H_{anti}$	45.7	244	49.9
34[e]	**6**	OTf	[D$_6$]acetone	$H_{syn}-H_{syn}$	5.9	205	45.2
35[e]	**6**	OTf	[D$_6$]acetone	H^4-H^6	16.3	298	64.1

[a] Unless specified the complex concentration is 1.41×10^{-2} M and a 300 MHz spectrometer is used. [b] At 500 MHz. [c] Complex concentration of 7.05×10^{-3} M. [d] With addition of water (5.60×10^{-2} M in water; H_2O:complex = 4:1). [e] With addition of water (3.52×10^{-2} M in water; H_2O:complex = 2.5:1).

are higher than those calculated for these temperatures). In the following discussion we will detail our conclusions concerning the influence of different factors on the fluxional behaviour of our allyl complexes.

Effect of the Ligand

Comparison of the data for complexes **3** and **4** (Entries 1−4) on the one hand and for **5** and **6** on the other, as well as those for complex **I**[23] (Entries 5−9 and 13−15), gives an indication of the influence of the ligand. Unfortunately, in the case of complexes with the 4-Mepzpm ligand it was not possible to determine all the coalescence temperatures and obtain the corresponding data. In the case of complex **3** it was only possible to detect the $H_{anti}-H_{anti}$ interconversion process while for **5** the splitting of the H_{syn} signals was not achieved. As far as the allylic interconversions are concerned, and although it would be desirable to have more data, it seems that the type of ligand does not have a clear influence, especially concerning the type of pyrazole ring. With respect to the H^4-H^6 interchange, three sets of data are available in the case of compounds containing the triflate anion. In these compounds there is an increase in the coalescence temperature and in the free energy of activation on changing from 4Me-pzpm to pzpm to 4Br-pzpm, but the three points fit reasonably well ($R^2 = 0.9924$) to a straight line (with positive slope), which might again indicate the lack of influence of the type of pyrazole in the ligand on the process. It is possible that the electronic differences between the three ligands are not sufficient to clearly influence the processes under investigation. In any case, it is necessary to bear in mind that for the H^4-H^6 interchange process the bond that must be broken is between the palladium and the pyrimidine ring, not the pyrazole heterocycle.

Type of Interchange

Before analyzing the influence of other factors, it is important to consider carefully the data for complex **6**. Although the δν value for the $H_{anti}-H_{anti}$ interconversion (48.1 Hz, Entry 7) is clearly higher than that for the H^4-H^6 interchange (28.5 Hz, Entry 9), the T_c and $\Delta G_c^{\ddagger}$ values are markedly higher in the latter case. This clearly indicates that the H^4-H^6 interchange has a higher energy barrier and will also have a different mechanism than the apparent allyl rotation. In order to obtain more data for this complex, we decided to perform the same study with an NMR spectrometer of different magnetic field (500 MHz as opposed to 300 MHz). In this way, we could obtain four data points for the allylic interconversions (Entries 7, 8, 10 and 11) and two for the H^4-H^6 interchange (Entries 9 and 12). The corresponding data are represented in Figure 1. The points for the allylic interconversions fit very well to a straight line ($R^2 = 0.9985$) while the other two values have free energies of activation that are clearly higher (7.9−8.9 kJ·mol^{-1}). This trend is consistent with our previous conclusion that the H^4-H^6 interchange has a higher energy barrier than the apparent allyl rotation. The difference in free energy of activation between the two processes will also be clear in other plots presented in this paper aimed at evaluating the influence of other factors (see below).

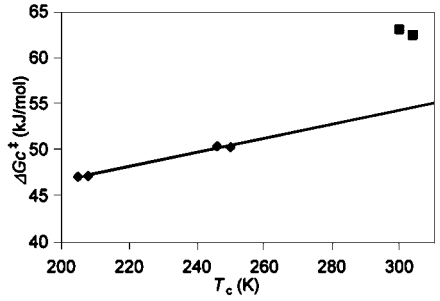


Figure 1. Linear plot of $\Delta G_c^{\ddagger}$ (kJ/mol) versus T_c (K) for complex **6** in [D$_6$]acetone (1.41×10^{-2} M) using data from 300 and 500 MHz NMR spectrometers (see Table 3): allylic interchange (diamonds, −−); ($R^2 = 0.9985$); H^4-H^6 interchange (squares)

Effect of the Counteranion

A comparison of Entries 1, 5 and 6 for the complexes with the 4-Mepzpm ligand and Entries 2−4 and 7−12 for those with the 4-Brpzpm ligand should give an indication of the influence of the counteranion on the processes in question. However, the lack of data for the 4-Mepzpm complexes precludes a clear conclusion from being drawn. However, with the 4-Brpzpm complexes (see Figure 2) it is possible to conclude that, at least in [D$_6$]acetone solution, there is a negligible influence of the anion on both the apparent allyl rotation and the H^4-H^6 interconversion. The data represented in Figure 2 also confirm the previous conclusion that the apparent allyl rotation has a lower free energy of activation than the H^4-H^6 interconversion.

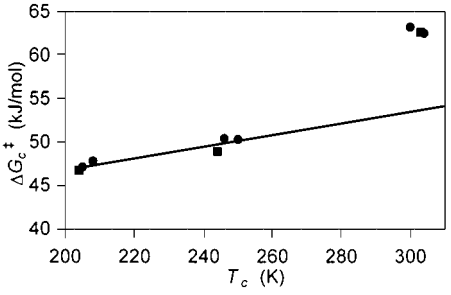


Figure 2. Linear plot of $\Delta G_c^{\ddagger}$ (kJ/mol) versus T_c (K) for complexes **4** and **6** in [D$_6$]acetone (1.41×10^{-2} M; see Table 3): **4** (squares); **6** (circles); allylic interchange (−−); $R^2 = 0.9706$

Effect of the Solvent

The studies described below are centred on complexes **4** and **6**, which contain the ligand 4-Brpzpm, because more coalescence points can usually be measured than for the 4-Mepzpm derivatives. For complex **4**, the data previously obtained in [D$_6$]acetone solution (Entries 2−4) were compared with those obtained in $CDCl_3$ at the same concentration (Entries 16−18). These data are represented in Fig-

ure 3. The coalescence temperature for the H^4-H^6 interchange in $CDCl_3$ was not reached and this is indicated by an arrow in the figure to reflect the fact that the actual value is higher than the one indicated. As far as the apparent allyl rotation process is concerned, higher $\Delta G_c^{\ddagger}$ values are obtained when the solvent is $CDCl_3$ and the same seems to apply to the H^4-H^6 interchange. Consequently, for this complex, which contains a counteranion (BAr'_4^-) that does not have coordinating ability, the presence of a solvent that it is able to coordinate has a positive effect on the processes.

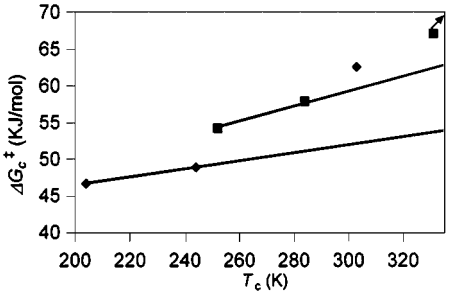


Figure 3. Linear plot of $\Delta G_c^{\ddagger}$ (kJ/mol) versus T_c (K) for complex **4** (1.41×10^{-2} M; see Table 3): $CDCl_3$ (squares); [D_6]acetone (diamonds); allylic interchange (−−)

A similar solvent effect is not observed in complex **6** where the anion (OTf^-) has coordinating ability. In this case the comparison is made between the [D_6]acetone (Entries 7−12) and CD_2Cl_2 (Entries 19−21) data. It can clearly be seen from Figure 4 that the solvent does not have any influence on the apparent allyl rotation, while for the H^4-H^6 interchange the conclusion is not as straightforward. Once again, this figure demonstrates the difference in free energy of activation between the apparent allyl rotation and the H^4-H^6 interchange.

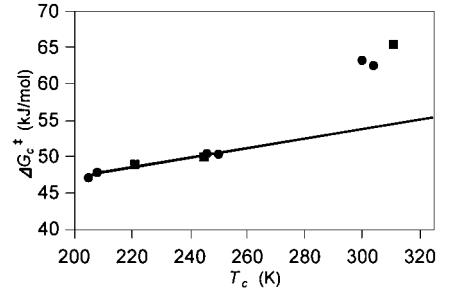


Figure 4. Linear plot of $\Delta Gc^{\ddagger}$ (kJ/mol) versus T_c (K) for complex **6** (1.41×10^{-2} M; see Table 3): CD_2Cl_2 (squares); [D_6]acetone (circles); allylic interchange (−−); $R^2 = 0.9914$

Effect of the Complex Concentration

In order to obtain information about the possible participation of bimolecular species in these processes, we carried out several variable temperature ^1H NMR studies with two different concentrations (1.41×10^{-2} and 7.05×10^{-3} M). For complex **6**, we performed the studies both in [D_6]acetone (Entries 7−12 and 25−27) and in CD_2Cl_2 solutions (Entries 19−24) and for complex **4** in $CDCl_3$ solutions (Entries 16−18 and 28−30). The coalescence of the H^4 and H^6 resonances was not reached up to the maximum temperature allowed by the solvent for complex **6** in CD_2Cl_2 or complex **4** in $CDCl_3$. When the results at the two concentrations are compared, it is possible to conclude that in the case of **6** in [D_6]acetone the three pairs of data are practically identical — the concentration does not influence either of the two processes. In the other two studies, there is insufficient information about the H^4-H^6 interchange and for the apparent allyl rotation the influence, if it exists, is very small (at least in the range of concentrations used).

Effect of the Addition of Water

The study of the influence of the addition of water was performed with complex **4** in $CDCl_3$ (Entries 16−18 and 31−32) in order to have a counterion and a solvent without coordinating ability. The data were obtained for a water-free $CDCl_3$ solution and after the addition of four mol of water per mol of product in this solution. The addition of water induces a general lowering of the coalescence temperatures, and the splitting of the H_{anti} resonances is not observed even down to −60 °C. However, the coalescence of the H^4-H^6 resonances, which was not achieved in the water-free solution, was observed at 17 °C after the addition of water. When the data for the allylic interconversions are taken into amount, it is concluded that the value obtained after the addition of water is 4.9 kJ·mol^{-1} below the straight line obtained with the data for the water-free solution. Consequently, at least in the situation where the counteranion and solvent are non-coordinating, the addition of water favours the apparent allyl rotation. We also studied the effect of the addition of water when there are species of coordinating ability in the reaction medium, for example for complex **6** in [D_6]acetone solution (comparison of Entries 7−9 with 33−35). In this case, there is no appreciable effect observed in the values of free energy of activation after the addition of water.

When the different plots for the apparent allyl rotation process are considered, a positive slope in the straight line obtained is observed. Although we do not believe that it is possible to give accurate data for the entropy of activation, it is clear that this parameter is negative.

It must be emphasised that our results indicate that care must be taken when studying these types of process in solvents that do not have coordinating ability. In solvents such as acetone, as observed previously,[35] the presence of small amounts of water does not influence the energy barrier of the process.

Conclusions of the ^1H NMR Variable Temperature Studies

We deduced that there is a lower energy barrier for the apparent allyl rotation process than for the H^4-H^6 interconversion and, consequently, the two processes follow different mechanisms. In the case of the apparent allyl rotation process, and concerning the effect of different factors

on this phenomenon, we can state the following: (i) a clear influence of the type of pyrazole present in the nitrogen-containing ligand is not found; (ii) the results are the same when, in [D_6]acetone solutions, the counterion is changed (cf. $BAr'_4{}^-$ versus OTf^-) or when, for the complexes with the OTf^- anion, two different solvents are used ([D_6]acetone and CD_2Cl_2); (iii) in the complex with the $BAr'_4{}^-$ anion, the free energy of activation values are higher in a non-coordinating solvent such as $CDCl_3$ than in [D_6]acetone; (iv) the complex concentration does not affect the process in the range studied; (v) when the complex contains a non-coordinating anion and the study is carried out in $CDCl_3$, the addition of water decreases the free energy of activation. However, the addition of water does not affect the dynamic behaviour in [D_6]acetone when the counterion present is OTf^-; (vi) the entropy of activation is negative.

In the case of the H^4-H^6 interconversion process it is more difficult to draw conclusions because only one $\Delta G_c^{\ddagger}$ data point could be obtained for each study. Despite this, we believe that the following general points can be made: (i) the type of anion, ligand or complex concentration does not have any influence when the solvent is [D_6]acetone; (ii) when both the solvent ($CDCl_3$) and anion ($BAr'_4{}^-$) are non-coordinating, the addition of water reduces the free energy of activation but this addition does not affect the values of $\Delta G_c^{\ddagger}$ in [D_6]acetone when the counterion is OTf^-; (iii) the entropy of activation is negative.

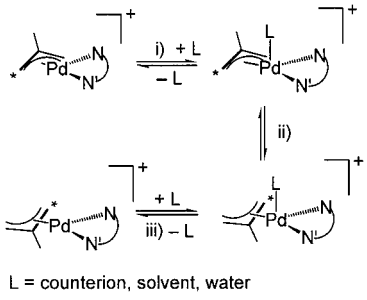
During the studies described here, broadening of the H_{syn} or H_{anti} resonances was not observed in any case after coalescence was achieved. This fact indicates that if the $H_{syn}-H_{anti}$ interconversion process (usually proposed to occur through an η^3-η^1-η^3 mechanism) exists, it must be of higher energy and is therefore not observed under the conditions used here.

Mechanistic Proposal

Apparent Allyl Rotation

The negative sign of the entropy of activation points to an associative process with the formation of five-coordinate intermediates. On the basis of some of the conclusions outlined above (ii, iii and v), it is possible to state that a species with coordinating ability (counteranion, solvent or water) clearly favours the process. We must consider that when the counterion is $BAr'_4{}^-$, the solvents are CD_2Cl_2 or $CDCl_3$ and water is not added, the two processes, although with higher energies of activation, do take place. It is possible that in these cases traces of water or Cl^- in the solvents (decomposition of CD_2Cl_2 or $CDCl_3$), or the low coordinating ability of the solvents, allows the process to occur. Conclusion iv indicates that bimolecular species are not formed and that the free nitrogen of the pyrimidine ring does not participate in the formation of the five-coordinate intermediates. It is necessary to consider that the formation of an "ion pair" between the cation and the anion should be favoured in concentrated solutions. This would be particularly true in the case of a non-coordinating solvent, such as complex **6** in CD_2Cl_2. This phenomenon has been found by other authors[20b] but, depending on the temperature and the concentration range, the effect can be rather small because of the existence of a limiting constant value.

It is also important to consider that the energy barrier for the apparent allyl rotation is lower than for the H^4-H^6 interconversion process. This latter process necessarily involves a Pd−N(pm) bond rupture, probably as the limiting step. Consequently, the apparent allyl rotation process should occur through a path that does not involve Pd−N(pm) bond rupture and has a lower energy of activation. The breaking of the Pd−N(pyrazole) bond is less likely because of the higher basicity of this heterocycle (except for the case of 4-Br-pyrazole) with respect to the pyrimidine ring [pK_a(pyrimidine) = 1.1]. This again makes a dissociative mechanism less likely and points to an associative pathway. The partial dissociation of the didentate N-donor ligand in the five-coordinate intermediate has sometimes been considered.[20b] In our case, however, this possibility can be excluded. Consequently, the associative mechanism[20,28,29,32,35] we propose would have the following steps (see Scheme 4): (i) formation of a five-coordinate intermediate through coordination of the anion, solvent or water (L); (ii) pseudorotation of the allyl group in the intermediate formed, which interchanges the two allylic terminals; and (iii) decoordination of the L group, leading to the final product in which the observed $H_{syn}-H_{syn}$, $H_{anti}-H_{anti}$ interchange has taken place.

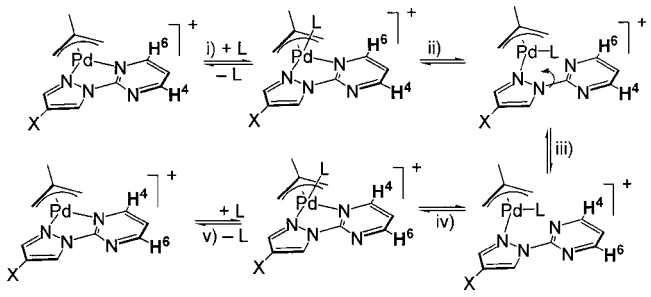


Scheme 4

H^4-H^6 Interconversion

The negative entropy of activation, the positive effect of the addition of water when both the solvent and the anion are non-coordinating, and the absence of other effects when the solvent is [D_6]acetone all indicate that, in this case, an associative mechanism is in operation. The mechanism should involve the following steps (see Scheme 5): (i) formation of the five-coordinate intermediate through coordination of the solvent, anion or water (L); (ii) Pd−N(pm) bond rupture; (iii) internal rotation of the ligand[19] through the C−N bond that links the two heterocycles in the tetracoordinate intermediate formed; (iv) recoordination of the pyrimidine ring through the other nitrogen atom; and (v) decoordination of the L group, leading to the final species

in which the interchange between the positions of the H^4 and H^6 pyrimidine protons has taken place.



Scheme 5

Conclusions

New allylpalladium derivatives with N-donor ligands have been obtained and their fluxional behaviour studied. Two processes of apparent allyl rotation (observed as $H_{syn}-H_{syn}$, $H_{anti}-H_{anti}$ interconversions) and also H^4-H^6 interconversion of the pyrimidine protons have been observed. This last process must involve, probably as the limiting step, Pd−N(pyrimidine) bond rupture. It has been concluded that the apparent allyl rotation process has a lower free energy of activation. Consequently, this allyl rotation must not involve Pd−N bond rupture. The influence of factors such as counterion, solvent and addition of water has been studied and it is possible to conclude that the presence of a species with coordinating ability clearly favours both processes. A bimolecular mechanism can be excluded in both cases because the complex concentration does not affect the free energy of activation. Negative entropies of activation were obtained. Associative mechanisms with participation of five-coordinate intermediates have been proposed for both processes, with a step involving Pd−N(pyrimidine) bond rupture in the case of the H^4-H^6 interconversion.

On the basis of our studies it is possible to conclude that, for these types of process, the presence of traces of water in coordinating solvents like acetone does not affect the free energy of activation. However, this is not the case for non-coordinating solvents and great care must be taken in studies involving such solvents.

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 $[Pd(\eta^3\text{-}C_4H_7)(\mu\text{-}Cl)]_2$ was synthesised according to a literature procedure.[42] Elemental analyses were performed with a Carlo Erba Instruments EA 1108 CHNS/O microanalyser (University of La Coruña). IR spectra were recorded as nujol mulls with a Perkin−Elmer PE 883 IR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Varian Unity 300 and an Innova 500 spectrometer using $CDCl_3$, CD_2Cl_2 and $(CD_3)_2CO$ as solvents; the chemical shifts are given in ppm. Standard experimental conditions were employed.[25,26] 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 ^1H-^{13}C g-HSQC spectra the standard Varian pulse sequences were used (V NMR 6.1 C software). The spectra were acquired using 7996 Hz (^1H) and 30154 Hz (^{13}C) spectral widths; 16 transients of 2048 data points were collected for each 256 increments. 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[41] from the coalescence temperature (T_c) and the frequency difference between the coalescing signals (extrapolated at the coalescence temperature) with the formula $\Delta G_c^{\ddagger} = a \cdot T \cdot [9.972 + \log(T/\delta\nu)]$, where $a = 1.914 \times 10^{-2}$. The estimated error in the calculated free energies of activation is ±1.1 kJ·mol^{-1}. *o* = *ortho*, *m* = *meta*, *p* = *para*.

2-(4-Methyl-1*H*-pyrazol-1-yl)pyrimidine (1): A mixture of 4-methylpyrazole (0.248 mL, 3 mmol), potassium *tert*-butoxide (600 mg, 6 mmol) and aliquat 336 (80 mg, 10%) was stirred at 120 °C for 30 min. 2-Chloropyrimidine (515 mg, 4.5 mmol) was then added at 120 °C and the reaction mixture was stirred at this temperature for 1 h. Extraction with dichloromethane (50 mL), removal of the solvent from the extract and flash chromatography of the residue on silica gel using ethyl acetate as the eluent allowed the isolation of **1**. Yield: 62% (298 mg). IR: $\tilde{\nu}$ = 1573 cm^{-1} [ν(C−N)]. $C_8H_8N_4$ (160.18): calcd. C 59.99, H 5.03, N 34.98; found C 59.70, H 5.29, N 34.62.

2-(4-Bromo-1*H*-pyrazol-1-yl)pyrimidine (2): A similar procedure to that used for **1** was applied for **2**. Amounts were as follows: 4-bromopyrazole (440.8 mg, 3 mmol), potassium *tert*-butoxide (600 mg, 6 mmol), aliquat 336 (80 mg, 10%) and 2-chloropyrimidine (515 mg, 4.5 mmol). Yield 60% (405.1 mg). IR: $\tilde{\nu}$ = 1570 cm^{-1} [ν(C−N)]. $C_7H_5BrN_4$ (225.05): calcd. C 37.36, H 24.89, N 2.24; found C 37.25, H 24.99, N 2.18.

$[Pd(\eta^3\text{-}C_4H_7)(4\text{-Mepzpm})]BAr'_4$ (3): 4-Mepzpm (24.3 mg, 0.152 mmol) and $TlBAr'_4$ (162.3 mg, 0.152 mmol) were added to a solution of $[Pd(\eta^3\text{-}C_4H_7)(\mu\text{-}Cl)]_2$ (30 mg, 0.076 mmol) in 10 mL of toluene. The mixture was stirred at room temperature for 1 h. The resulting suspension was filtered off. The solid was then extracted with dichloromethane (40 mL) and the solution was evaporated to dryness. The light-brown solid was washed with hexane and dried. Yield: 66% (119.1 mg). IR: $\tilde{\nu}$ = 1598 and 1566 [ν(C−N)], 1275, 890 (BAr'_4), 839 cm^{-1} ν[(C−CH_3), allyl]. $C_{44}H_{27}BF_{24}N_4Pd$ (1184.9): calcd. C 44.60, H 2.30, N 4.73; found C 44.52, H 2.44, N 4.69. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K; BAr'_4 resonances): δ = 161.9 (q, $^1J_{B,C}$ = 50.0 Hz, 4 C, C_{ipso}), 135.0 (s, 8 C, C_o), 129.2 (m, 8 C, C_m), 124.7 (q, $^1J_{C,F}$ = 272.6 Hz, 8 C, CF_3), 117.7 (s, 4 C, C_p) ppm.

$[Pd(\eta^3\text{-}C_4H_7)(4\text{-Brpzpm})]BAr'_4$ (4): A similar procedure to that used for **3** was applied for **4**. Amounts were as follows: $[Pd(\eta^3\text{-}C_4H_7)(\mu\text{-}Cl)]_2$ (20 mg, 0.051 mmol), 4-Brpzpm (22.9 mg, 0.102 mmol) and $TlBAr'_4$ (108.9 mg, 0.102 mmol). The solid was pale brown in colour. Yield: 66% (83.7 mg). IR: $\tilde{\nu}$ = 1599 and 1568 [ν(C−N)], 1279, 890 (BAr'_4), 838 cm^{-1} ν[(C−CH_3), allyl]. $C_{43}H_{24}BBrF_{24}N_4Pd$ (1249.8): calcd. C 41.32, H 1.94, N 4.48; found C 41.67, H 2.19, N 4.49. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K; BAr'_4 resonances): δ = 161.9 (q, $^1J_{B,C}$ = 49.3 Hz, 4 C, C_{ipso}), 134.9 (s, 8 C, C_o), 129.8 (m, 8 C, C_m), 124.7 (q, $^1J_{C,F}$ = 272.2 Hz, 8 C, CF_3), 117.7 (s, 4 C, C_p) ppm.

[Pd(η^3-C_4H_7)(4-Mepzpm)]OTf (5): $AgCF_3SO_3$ (104.3 mg, 0.406 mmol) was added to a solution of [Pd(η^3-C_4H_7)(μ-Cl)]$_2$ (80 mg, 0.203 mmol) in THF (20 mL). The mixture was stirred for 1 h and protected from light. The solution was filtered through Celite to eliminate AgCl. The ligand 4-Mepzpm (65 mg, 0.406 mmol) was then added and the mixture was stirred for 1 h. The solvent was evaporated to dryness and the pale-yellow residue was washed with diethyl ether. Yield 70% (133.7 mg). IR: $\tilde{\nu}$ = 1596 and 1565 [ν(C−N)], 1266, 1154, 1032, 784 and 639 (OTf^-), 839 cm^{-1} ν[(C−CH_3), allyl]. $C_{13}H_{15}F_3N_4O_3PdS$ (470.75): calcd. C 33.17, H 3.21, N 11.90; found C 33.46, H 3.11, N 12.23. $^{13}C\{^1H\}$ NMR (125 MHz, [D_6]acetone, 298 K): δ = 121.7 (q, $^1J_{C,F}$ = 322.2 Hz, 1 C, CF_3) ppm.

[Pd(η^3-C_4H_7)(4-Brpzpm)]OTf (6): A similar procedure to that used for **5** was applied for **6**. Amounts were as follows: Ag CF_3SO_3 (78.1 mg, 0.304 mmol), [Pd(η^3-C_4H_7)(μ-Cl)]$_2$ (60 mg, 0.152 mmol), 4-Brpzpm (68.4 mg, 0.304 mmol). The solid was white in colour. Yield: 80% (126.6 mg). IR: $\tilde{\nu}$ = 1597 and 1566 [ν(C−N)], 1269, 1147, 1034, 785 and 639 (OTf^-), 838 cm^{-1} ν[(C−CH_3), allyl]. $C_{12}H_{12}BrF_3N_4O_3PdS$ (535.62): calcd. C 26.91, H 2.26, N 10.46; found C 27.01, H 2.11, N 10.27. $^{13}C\{^1H\}$ NMR (125 MHz, [D_6]-acetone, 298 K): δ = 121.8 (q, $^1J_{C,F}$ = 322.2 Hz, 1 C, CF_3) ppm.

Preparation of NMR Spectroscopic Samples: Samples with a concentration of 1.41 × 10^{-2} M were prepared by dissolving the corresponding amount of the complex in 0.5 mL of the deuterated solvent. Samples with a concentration of 7.05 × 10^{-3} M were prepared by adding 0.5 mL of the corresponding deuterated solvent to the previous sample. Samples for the studies of Entries 31 and 32 (Table 3) were prepared by adding 0.510 μL (2.8 × 10^{-2} mmol) of water to the original solution. Samples for the studies of Entries 33−35 were prepared by adding 0.320 μL (1.76 × 10^{-2} mmol) of water to the original sample.

Acknowledgments

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[1] [1a] J. Tsuji, *Palladium Reagents and Catalysts, Innovation in Organic Synthesis*, J. Wiley & Sons, Chichester, **1996**. [1b] S. A. Godleski, in *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon Press: New York, **1991**, vol. 4, chapter 3.3. [1c] P. J. Harrington, in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson, R. J. Puddephatt), Elsevier, New York, **1995**, vol. 12, p.797. [1d] J.-E. Bäckvall, *Metal-Catalysed Cross Coupling Reactions*, VCH, Weinheim, Germany, **1998**, p. 339. [1e] B. M. Trost, C. Lee, in *Catalytic Asymmetric Synthesis*, 2nd ed. (Ed.: I. Ojima), Wiley-VCH, New York, **2000**, p. 593−649. [1f] A. Pfaltz, M. Lautens, in *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Heidelberg, **1999**, p.833−886.

[2] [2a] K. Vrieze, *Dynamic Nuclear Magnetic Resonance Spectroscopy* (Eds.: L. M. Jackman, F. A. Cotton), Academic Press, New York, **1975**, chapter 11, p. 441. [2b] P. S. Pregosin, R. Salzmann, *Coord. Chem. Rev.* **1996**, *155*, 35−68. [2c] J. W. Faller, in *Encyclopedia of Inorganic Chemistry* (Ed.: R. B. King), John Wiley and Sons, Chichester, **1994**, vol. 7, p. 3925−3926. [2d] F. A. Jalón, B. R. Manzano, F. Gómez-de la Torre, A. M. Guerrero, A. M. Rodríguez, *Targets in Heterocyclic Systems, Chemistry and Properties* (Eds.: O. A. Attanasi, D. Spinelli), Roma, **1999**, vol. 3, p. 399−438.

[3] [3a] B. M. Trost, D. L. Van Vranken, *Chem. Rev.* **1996**, *96*, 395−422. [3b] B. M. Trost, *Pure Appl. Chem.* **1996**, *68*, 779−784. [3c] J. D. Oslob, B. Åkermark, P. Helquist, P. O. Norrby, *Organometallics* **1997**, *16*, 3015−3021. [3d] C. Larksarp, H. Alper, *J. Am. Chem. Soc.* **1997**, *119*, 3709−3715. [3e] H. Hagelin, B. Åkermark, P.-O. Norrby, *Organometallics* **1999**, *18*, 2884−2895. [3f] J. C. Anderson, R. J. Cubbon, J. D. Harling, *Tetrahedron: Asymmetry* **2001**, *12*, 923−935. [3g] P. J. Harrington, in *Comprehensive Organometallic Chemistry* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson, L. S. Hegedus), Pergamon, Oxford, **1995**, vol. 12, p. 882−894 and references cited therein.

[4] [4a] P. W. N. M. van Leeuwen, P. W. Praat, *J. Chem. Soc., Chem. Commun.* **1970**, 365−366. [4b] F. G. A. Stone, N. M. Boag, M. Green, J. L. Spencer, *J. Organomet. Chem.* **1977**, *127*, C51−C54. [4c] R. E. Rülke, V. E. Raasjager, P. Wehman, C. J. Elsevier, P. W. N. M. van Leeuwen, K. Vrieze, J. Fraanje, K. Boubitz, A. L. Spek, *Organometallics* **1996**, *15*, 3022−3031.

[5] [5a] J. M. Brown, D. I. Hulmes, P. J. Guiry, *Tetrahedron* **1994**, *50*, 4493−4506. [5b] T. D. W. Claridge, J. M. Long, J. M. Brown, D. Hibbs, M. B. Hursthouse, *Tetrahedron* **1997**, *53*, 4035−4050.

[6] [6a] P. Barbaro, P. S. Pregosin, R. Salzmann, A. Albinati, R. W. Kunz, *Organometallics* **1995**, *14*, 5160−5170. [6b] T. Hosokawa, Y. Wakabayashi, K. Hosokawa, T. Tsuji, S. I. Murahashi, *Chem. Commun.* **1996**, 859−860. [6c] S. Ramdeehul, L. Barloy, J. A. Osborn, A. De Cian, J. Fischer, *Organometallics* **1996**, *15*, 5442−5444. [6d] H. A. Ankersmit, N. Veldman, A. L. Spek, K. Vrieze, G. Van Koten, *Inorg. Chim. Acta* **1996**, *252*, 339−354. [6e] L. Barloy, S. Ramdeehul, J. A. Osborn, C. Carlotti, F. Taulelle, A. De Cian, J. Fisher, *Eur. J. Inorg. Chem.* **2000**, *12*, 2523−2532.

[7] L. Canovese, F. Visentin, P. Uguagliati, V. Lucchini, G. Bandoli, *Inorg. Chim. Acta* **1998**, *277*, 247−252.

[8] [8a] I. Schwarz, J. Rust, C. W. Lehmann, M. Braun, *J. Organomet. Chem.* **2000**, *605*, 109−116. [8b] F. Gómez-de la Torre, Y. Gutiérrez, F. A. Jalón, B. R. Manzano, A. Rodríguez, *Monatsh. Chem.* **2000**, *131*, 1267−1280.

[9] [9a] J. Krause, R. Goddard, R. Mynott, K.-R. Pörschke, *Organometallics* **2001**, *20*, 1992−1999. [9b] P. Braunstein, F. Naud, A. Dedieu, M. M. Rohmer, A. De Cian, S. J. Rettig, *Organometallics* **2001**, *20*, 2966−2981.

[10] M. Kollmar, B. Goldfuss, M. Reggelin, F. Rominger, G. Helmchen, *Chem. Eur. J.* **2001**, *7*, 4913−4927.

[11] L. Canovese, G. Chessa, C. Santo, F. Visentin, P. Uguagliati, *Organometallics* **2002**, *21*, 4342−4349.

[12] M. Ogasawara, K. Takizawa, T. Hayashi, *Organometallics* **2002**, *21*, 4853−4861.

[13] [13a] C. Breutel, P. S. Pregosin, R. Salzmann, A. Togni, *J. Am. Chem. Soc.* **1994**, *116*, 4067−4068. [13b] P. S. Pregosin, R. Salzmann, A. Togni, *Organometallics* **1995**, *14*, 842−847. [13c] J. Herrmann, P. S. Pregosin, R. Salzmann, A. Albinati, *Organometallics* **1995**, *14*, 3311−3318.

[14] R. Fernández-Galán, F. Jalón, B. R. Manzano, J. Rodríguez de la Fuente, M. Vrahami, B. Jedlicka, W. Weissensteiner, *Organometallics* **1997**, *16*, 3758−3768.

[15] P. Dotta, P. G. A. Kumar, P. S. Pregosin, *Magn. Reson. Chem.* **2002**, *40*, 653−658.

[16] B. Crociani, S. Antonaroli, G. Bandoli, L. Canovese, F. Visentin, P. Uguagliati, *Organometallics* **1999**, *18*, 1137−1147.

[17] N. Solin, K. J. Szabó, *Organometallics* **2001**, *20*, 5464−5471.

[18] A. Albinati, R. W. Kunz, C. J. Ammann, P. S. Pregosin, *Organometallics* **1991**, *10*, 1800−1806.

[19] A. Gogoll, J. Örnebro, H. Grennberg, J.-E. Bäckvall, *J. Am. Chem. Soc.* **1994**, *116*, 3631−3632.

[20] [20a] B. Crociani, F. Di Bianca, A. Giovenco, T. Boschi, *Inorg. Chim. Acta* **1987**, *127*, 169−182. [20b] B. Crociani, S. Antonaroli, M. Paci, F. Di Bianca, L. Canovese, *Organometallics* **1997**, *16*, 384−391.

[21] A. Gogoll, H. Grennberg, A. Axén, *Organometallics* **1997**, *16*, 1167−1178.

[22] Y. Takao, T. Takeda, J. Watanabe, J. Setsune, *Organometallics* **1999**, *18*, 2936−2938.
[23] J. Elguero, A. Fruchier, A. de la Hoz, F. A. Jalón, B. R. Manzano, A. Otero, F. Gómez-de la Torre, *Chem. Ber.* **1996**, *129*, 589−594.
[24] F. A. Jalón, B. R. Manzano, A. Otero, M. C. Rodríguez, *J. Organomet. Chem.* **1995**, *494*, 179−185.
[25] F. Gómez-de la Torre, A. de la Hoz, F. A. Jalón, B. R. Manzano, A. Otero, A. M. Rodríguez, M. C. Rodríguez-Pérez, A. Echevarría, J. Elguero, *Inorg. Chem.* **1998**, *37*, 6606−6614.
[26] F. Gómez-de la Torre, A. de la Hoz, F. A. Jalón, B. R. Manzano, A. M. Rodríguez, J. Elguero, M. Martínez-Ripoll, *Inorg. Chem.* **2000**, *39*, 1152−1162.
[27] N. Arroyo, F. Gómez-de la Torre, F. A. Jalón, B. R. Manzano, B. Moreno-Lara, A. M. Rodríguez, *J. Organomet. Chem.* **2000**, *603*, 174−184.
[28] M. C. Carrión, A. Díaz, A. Guerrero, F. A. Jalón, B. R. Manzano, A. Rodríguez, R. L. Paul, J. C. Jeffery, *J. Organomet. Chem.* **2002**, *650*, 210−222.
[29] S. Hansson, P-O. Norrby, M. P. T. Sjögren, B. Åkermark, M. E. Cucciolito, F. Giordano, A. Vitagliano, *Organometallics* **1993**, *12*, 4940−4948.
[30] J. Sprinz, M. Kiefer, G. Helmchen, M. Reggelin, G. Huttner, O. Walter, L. Zsolnai, *Tetrahedron Let.* **1994**, *35*, 1523−1526.
[31] [31a] J. G. P. Delis, J. H. Groeen, K. Vrieze, P. W. N. M. van Leeuwen, N. Veldman, A. L. Spek, *Organometallics* **1997**, *16*, 551−562. [31b] L. Canovese, F. Visentin, P. Uguagliati, G. Chessa, V. Lucchini, G. Bandoli, *Inorg. Chim. Acta* **1998**, *275/276*, 385−394.
[32] R. J. van Haaren, K. Goubitz, J. Fraanje, G. P. F. Van Strijdonck, H. Oevering, B. Coussens, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Inorg. Chem.* **2001**, *40*, 3363−3372.
[33] J. W. Faller, H. L. Stokes-Huby, M. A. Albrizzio, *Helv. Chim. Acta* **2001**, *84*, 3031−3042.
[34] M. A. Pericàs, C. Puigjaner, A. Riera, A. Vidal-Ferran, M. Gómez, F. Jiménez, G. Muller, M. Rocamora, *Chem. Eur. J.* **2002**, *8*, 4164−4178.
[35] A. M. Guerrero, F. A. Jalón, B. R. Manzano, R. M. Claramunt, M. D. Santa María, C. Escolástico, J. Elguero, A. M. Rodríguez, M. A. Maestro, J. Mahía, *Eur. J. Inorg. Chem.* **2002**, 3178−3189.
[36] J. Catalán, J.-L. M. Abboud, J. Elguero, *Adv. Heterocycl. Chem.* **1987**, *41* 187−274.
[37] J. Elguero, A. Guerrero, F. Gómez de la Torre, A. de la Hoz, F. A. Jalón, B. R. Manzano, A. Rodríguez, *New. J. Chem.* **2001**, *25*, 1050−1060.
[38] [38a] L. A. Oro, M. Esteban, R. M. Claramunt, J. Elguero, C. Foces-Foces, F. H. Cano, *J. Organomet. Chem.* **1984**, *276*, 79−97. [38b] M. A. Esteruelas, L. A. Oro, M. C. Apreda, C. Foces-Foces, F. H. Cano, R. M. Claramunt, C. López, J. Elguero, M. Begtrup, *J. Organomet. Chem.* **1988**, *344*, 93−108.
[39] [39a] M. Fajardo, A. de la Hoz, E. Díez-Barra, F. A. Jalón, A. Otero, A. Rodríguez, J. Tejeda, D. Belletti, M. Lanfranchi, M. A. Pellinghelli, *J. Chem. Soc., Dalton Trans.* **1993**, 1935−1939. [39b] F. A. Jalón, B. R. Manzano, A. Otero, M. C. Rodríguez-Pérez, *J. Organomet. Chem.* **1995**, *494*, 179−185.
[40] M. Brookhart, B. Grant, A. F. Volpe Jr., *Organometallics* **1992**, *11*, 3920−3922.
[41] J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, London, **1982**.
[42] W. T. Dent, R. Long, G. Wilkinson, *J. Chem. Soc.* **1964**, 1585−1588.

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