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Five Different Fluxional Processes in Polyfluorophenyl Palladium(II) Complexes with 2,4,6-Tris(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine. The Driving Effect of the Solvent

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The polydentate N-donor ligand 2,4,6-tris(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine (Me_2-TpzT) has been used to synthesize the new palladium derivatives $Pd(R)_2(Me_2\text{-TpzT})$, R = C_6F_5, **1**; R = *m*-C_6ClF_4, **2**. In the case of complex **2**, four different atropisomers have been detected at low temperature. The new complexes exhibit a rich dynamic behavior, including three metallotropic processes (metal-hurdling, 1,4-metallotropic shifts, and an intermolecular process) and two processes involving restricted rotation of aromatic rings (the polyfluorophenyl groups and the uncoordinated pyrazole group adjacent to the metal fragment). The fluxional behavior has been studied by ^1H and ^{19}F NMR spectroscopy using variable temperature NMR studies and $^1H,^1H$ and $^{19}F,^{19}F$ EXSY experiments. The study of solutions of **2** in 1,1′,2,2′-tetrachloroethane-d_2 gave the following order for the free energy of activation: pyrazole rotation < 1,4-metallotropic shift < intermolecular exchange < polyfluorophenyl rotation. The process of metal hurdling was not found in this solvent. However, in acetone-d_6 such a process was detected and was found to be of lower energy than the 1,4-metallotropic shift. In dilute acetone-d_6 or 1,1′,2,2′-tetrachloroethane-d_2 solutions, the intermolecular process was not observed. Conclusions concerning the different mechanisms have been deduced from the data obtained.

Introduction

Fluxional processes are very common in coordination and organometallic chemistry. Very frequently these processes are accompanied by rupture of metal−atom bonds and also by conformational changes in the molecule. We have recently been interested in fluxional processes in palladium complexes containing N-donor ligands. In these types of derivatives we and others have found evidence of Pd−N bond rupture processes[1−11] with correlation, in some cases, between the free energy of activation and the strength of the bond to be broken.[6] In the work reported here we chose the ligand 2,4,6-tris(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine (Me_2-TpzT) (see Chart 1), mainly because of the rich fluxional behavior that

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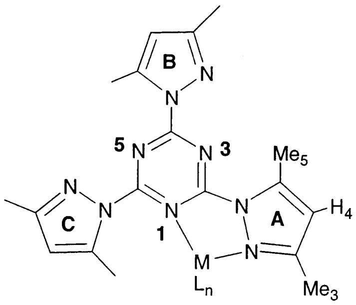
Chart 1



their metal derivatives could exhibit. This ligand possesses six bidentate coordination sites, and when the ligand is coordinated to a single metallic fragment, it is possible that six identical (degenerate) isomers can exist. If we denote the three pyrazole rings as A, B, and C, the three nitrogen atoms of the triazine as 1, 3, and 5, and consider the nitrogen atoms that are coordinated, we can designate these isomers as A1, A3, B3, B5, C5, and C1 (see Chart 1, isomer A1 is represented as an example). Orrell et al. have studied in detail the fluxional behavior of Re complexes of this ligand[12] as well as different coordination complexes (including palladium derivatives[8-11]) and similar ligands such as pyrazolylpyridines,[13] pyrazolylbipyridine,[14] 2,4,6-tris(pyrazolyl)pyrimidines,[15] 2,2′:6′,2′′-terpyridine[8,9,11] and 2,4,6-tris(2-pyridyl)-pyrimidine.[10] Processes involving 1,4-metallotropic shifts were described for these types of systems.[8-17]

In the case of our ligand this would imply, for example, changing from the A1 to the C1 isomer. There has been some controversy regarding the mechanism of this process, and both associative[8,10-15] and dissociative[17] pathways have been proposed. Orrell et al.,[9] by means of a study with asymmetric terpyridine ligands coordinated to palladium or platinum fragments, demonstrated that the mechanism is associative—implying a quasi-terdentate ligand intermediate and a “tick-tock” motion of the metal moiety. When the appropriate coordination sites are available, Orrell also found another process in palladium or platinum derivatives called metal hurdling,[10] which implies partial dissociation of the metal fragment by cleavage of a metal−nitrogen bond ($M-N_{triazine}$ in our case) followed by 180° rotation of the metallic group bonded to the other nitrogen (pyrazole in our case) about the C−N bond and, finally, recoordination to the new nitrogen (triazine) atom. In our case such a process would involve, for example, the change from the A1 to the A3 isomer. Restricted rotation of uncoordinated pyrazole[12] or pyridine[8,10,11] rings adjacent to the metal center has been found to occur at low temperature. In our complexes with our ligand it is possible for the two aforementioned metallotropic processes to occur. The metal-hurdling process requires the Pd−N(triazine) bond to be broken and not the Pd−N(pyrazole) bond, while the 1,4-metallotropic shift involves cleavage of at least the M−N(pyrazole) bond. For this reason, we chose a ligand with two heterocycles of different basicity and, consequently, Pd−N bonds of different strengths in an attempt to obtain different free energies of activation for the two processes. When comparing these two processes, we were interested in evaluating the influence of the coordinating ability of the solvent, a factor that has not been studied previously and could give a greater insight into the possible mechanisms.

The restricted rotation of the uncoordinated pyrazole ring adjacent to the metal center was also a possible process, and this would be favored by the presence of the methyl substituents on pyrazolyl groups. Another aim of our work was to analyze the possible presence of intermolecular processes similar to those that we detected in allyl−palladium derivatives with similar ligands.[7] The metallic fragments chosen were bis(polyfluorophenyl)palladium systems because they usually give Pd−C bonds of high stability and also because ^{19}F NMR could give supplementary information about this system. We also studied other fragments, such as allylpalladium(II), with these types of ligands, but in these cases hydrolysis of the ligand occurred.[6] In addition, the reaction of $Pd(C_6F_5)_2(cod)$ (cod = 1,5-cyclooctadiene) with 2,4,6-tris(4-methylpyrazol-1-yl)-1,3,5-triazine was previously studied and was found to give complex mixtures.[6] For this reason, we chose the ligand with a dimethylpyrazolyl group in order to obtain a more basic heterocycle that could stabilize the final complex. The presence of polyfluorophenyl groups in the new derivatives also led to the possibility of analyzing any possible process involving restricted rotation of these rings, an area that has been previously studied in a wide variety of systems.[8,10,18] Besides the bis(pentafluorophenyl) derivative, we also synthesized the corresponding complex with the *m*-C_6ClF_4 group. This ring, which contains two different sides, in the case of restricted rotation could give rise to the formation of atropisomers—thus providing supplementary information about the fluxional processes.

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Experimental Section

General Comments. All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. The preparation of the ligand Me_2-TpzT has been described previously.[19] $[Pd(C_6F_5)_2(cod)]$ and $[Pd(m\text{-}C_6ClF_4)_2(cod)]$ were synthesized as described in the literature for similar complexes.[20] Elemental analyses were performed using a Thermo Quest FlashEA 1112 microanalyzer. IR spectra were recorded in Nujol mulls on a Perkin-Elmer 883 (200−4000 cm^{-1} range) spectrophotometer. NMR spectra were recorded on a VARIAN UNITY 300 spectrometer operating at 299.980 MHz for ^1H: bs = broad singlet; dm = doublet of multiplets. Spectra were recorded at the temperature indicated (±0.1 K) with a probe calibrated with methanol. The standard VARIAN pulse sequence was used (VNMR 6.1 software, COSY and EXSY pulse sequences). The NOE difference spectra were recorded with the following conditions: 4000 Hz; acquisition time, 3.744 s; pulse width, 90°; relaxation delay, 5 s; irradiation power, 5−10 dB. $^{19}F,^{19}F$ COSY spectra were acquired using a 30604 kHz spectral width; 24 transients of 4096 data points were collected for each 240 t_1 increments. A 1 s relaxation delay, a 12 μs (45°) pulse width, and a 0.134 s acquisition time were used. A second $^{19}F,^{19}F$ COSY spectrum was acquired using a 2572 kHz spectral width; 8 transients of 512 data points were collected for each 214 t_1 increments. A 1 s relaxation delay, a 12 μs (45°) pulse width, and a 0.19 s acquisition time were used. The data were processed using zero filling and sine-bell functions in both dimensions before Fourier transformation. The 2D exchange spectra (EXSY) were acquired in the phase-sensitive mode using the States Haberkorn method.[21] Typically for $^1H,^1H$ EXSY, a 2130 kHz spectral width and 16 transients of 512 data points were collected for each 176 t_1 increments. A 1 s relaxation delay, a 23 μs (90°) pulse width, and a 0.24 s acquisition time were used. For $^{19}F,^{19}F$ EXSY experiments, a 2692 kHz spectral width and 16 transients of 512 data points were collected for each 112 t_1 increments. A 1 s relaxation delay, a 20 μs (90°) pulse width, and a 0.19 s acquisition time were used. The free induction decays were processed with square cosine-bell filters in both dimensions, and zero filling was applied prior to double Fourier transformation.

Determination of the kinetic parameters required two experiments with mixing times of 1 s (optimized from 1 to 2 s in order to find the value that gives the cross-peaks with higher intensity) for the exchange experiment and 0.02 s for the nonexchange spectra. The cross-peak/diagonal ratio was determined by integrating the volume under the peaks.

Free energies of activation were calculated[22] from the coalescence temperature (T_c) and the frequency difference between the coalescing signals (extrapolated at the coalescence temperature) with the formula $\Delta G_c^{\ddagger} = aT[9.972 + \log(T/\delta\nu)]$, $a = 1.914 \times 10^{-2}$. The spectra were recorded each 10° and each 1° in the proximities of the coalescence temperature. We have only considered the signals separated with $\delta\nu$ high enough to make the calculations accurate. In the EXSY experiments the formula $\Delta G^{\ddagger} = aT[10.319 + \log(T/k)]$, $a = 1.914 \times 10^{-2}$, was used. The estimated error in the calculated free energies of activation is ± 1.0 kJ·mol^{-1}. We have tried to dry the deuterated solvents as much as possible in order to avoid any effect of water. In any case, the results are reproducible.

Preparation of Complexes. (a) $[Pd(C_6F_5)_2(Me_2$-TpzT)] (1). To a solution of Me_2-TpzT (63.2 mg, 0.17 mmol) in tetrahydrofuran (THF; 35 mL) was added $Pd(C_6F_5)_2(cod)$ (95.5 mg, 0.17 mmol). The mixture was stirred for 2 h at room temperature, and the solution was partially evaporated and hexane added. The resulting pale yellow solid obtained was separated by filtration and washed with hexane (2 × 10 mL). Yield: 89.2 mg (65%). Anal. Calcd for $C_{30}H_{21}F_{10}N_9Pd$: C, 44.82; H, 2.63; N, 15.68. Found: C, 44.65; H, 2.55; N, 15.43. ^{13}C NMR (1,1′,2,2′-tetrachloroethane-d_2, room temp) δ 162.6 (s, C_{quat}, triazine), 162.4 (s, 2C, C_{quat}, triazine), 157.0 (bs, C_3), 155.9 (s, C_3), 153.7 (bs, C_3), 147.0 (dm, $^1J_{CF}$ = 225 Hz, C_{ortho}, C_6F_5), 146.9 (bs, C_5), 144.5 (s, C_5), 142.4 (bs, C_5), 135.1 (dm, $^1J_{CF}$ = 240 Hz, C_{meta}, C_6F_5), 114.0 (bs, C_4), 114.0 (s, C_4), 111.0 (bs, C_4), 15.5 (s), 15.4 (bs), 14.0 (s), 13.0 (s, 2C), 12.1 (bs) (Me_3 and Me_5), the C_{ipso} and C_{para} of the C_6F_5 groups have not been observed. IR (Nujol): 799 and 785 cm^{-1} (C_6F_5).

(b) $[Pd(m\text{-}C_6ClF_4)_2(Me_2$-TpzT)]·1/4$C_6H_{14}$ (2·1/4C_6H_{14}). To a solution of Me_2-TpzT (40.0 mg, 0.11 mmol) in acetone (30 mL) was added $Pd(C_6ClF_4)_2(cod)$ (64.0 mg, 0.11 mmol). The mixture was stirred for 2 h and the solution evaporated to dryness. The resulting white solid was washed with pentane (2 × 10 mL). Yield: 52.0 mg (57%). The solid could be recrystallized from dichloromethane/hexane. Anal. Calcd for $C_{31.5}H_{24.5}Cl_2F_8N_9Pd$: C, 44.08; H, 2.88; N, 14.69. Found: C, 44.18; H, 2.71; N, 14.75. The hexane found in the elemental analysis is also observed in the ^1H NMR spectrum. ^{13}C NMR (1,1′,2,2′-tetrachloroethane-d_2, room temp): δ 162.6 (s, C_{quat}, triazine), 161.4 (s, 2C, C_{quat}, triazine), 158.1 (bs, C_3), 155.9 (s, C_3), 153.8 (bs, C_3), 146.8 (bs, C_5), 144.4 (s, C_5), 142.6 (bs, C_5), 114.1 (bs, C_4), 114.0 (s, C_4), 111.0 (bs, C_4), 15.6 (s), 15.4 (bs), 14.0 (s), 13.1 (s, 2C), 12.4 (bs) (Me_3 and Me_5), the carbons of the C_6ClF_4 group have not been observed. IR (Nujol): 802 and 751 cm^{-1} (C_6ClF_4).

Preparation of the NMR Samples for the 2D EXSY Experiments. A saturated acetone solution of **2** was prepared by stirring 10 mg of the complex in 0.5 mL of acetone-d_6. The solution was filtered and introduced into an NMR tube and the sample used for 2D EXSY (^1H and ^{19}F) experiments. A more dilute solution was prepared by taking 0.25 mL of the aforementioned solution and adding an additional acetone-d_6 (0.25 mL) to the NMR tube. A $^1H,^1H$ EXSY experiment was performed on this sample.

A solution of **2** in 1,1′,2,2′-tetrachloroethane-d_2 was prepared in an NMR tube with 7.5 mg of the complex and 0.5 mL of the deuterated solvent. The diluted solution was prepared with 3.5 mg of the complex and 0.5 mL of the solvent. 2D EXSY (^1H and ^{19}F) experiments were performed on these solutions.

Results and Discussion

Synthesis and Characterization. The reaction of 2,4,6-tris(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine, Me_2-TpzT, with

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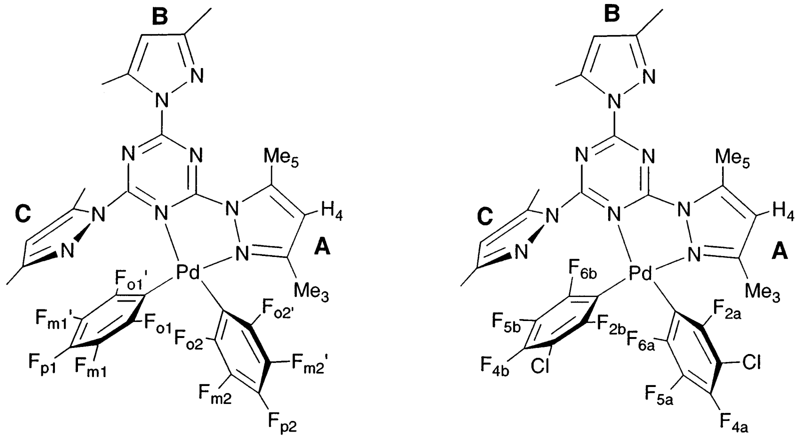
Chart 2



1

2

Table 1. ^{1}H NMR Chemical Shifts (δ, ppm) of Me$_2$-TpzT, [Pd(C$_6$F$_5$)$_2$(Me$_2$-TpzT)] (**1**) and [Pd(*m*-C$_6$ClF$_4$)$_2$(Me$_2$-TpzT)] (**2**)[a]

deriv	solvent	*T* (K)	pyrazole A			pyrazole B			pyrazole C		
			H$_4$	Me$_3$	Me$_5$	H$_4$	Me$_3$	Me$_5$	H$_4$	Me$_3$	Me$_5$
Me$_2$-TpzT	acet-d_6	298	6.22 (q) $^4J_{HH} = 1.0$	2.26 (s)	2.84 (d)						
1	acet-d_6	298	6.66 (bs)	1.84 (bs)	2.96 (bs)	6.44 (bs)	2.28 (bs)	2.76 (bs)	5.87 (bs)	2.09 (bs)	2.51 (bs)
1	acet-d_6	253	6.62 (s)	1.85 (s)	2.98 (s)	6.41 (s)	2.30 (s)	2.77 (s)	5.85 (s)	2.11 (s)	2.55 (s)
1	tetra-d_2	253	6.25 (s)	1.80 (s)	2.84 (s)	6.22 (s)	2.33 (s)	2.66 (s)	5.66 (s)	2.16 (s)	2.46 (s)
2	acet-d_6	253	6.61 (s)	1.84 (s)	2.98 (s)	6.40 (s)	2.29 (s)	2.77 (s)	5.82 (s)	2.12 (s)	2.54 (s)
2	tetra-d_2	253	6.24 (s)	1.78 (s)	2.83 (s)	6.22 (s)	2.32 (s)	2.66 (s)	5.66 (s)	2.15 (s)	2.46 (s)

[a] Acet-d_6 = acetone-d_6; tetra-d_2 =1,1′,2,2′-tetrachloroethane-d_2.

Pd(R)$_2$(cod) (R = C$_6$F$_5$, *m*-C$_6$ClF$_4$) in a 1:1 ratio led to the new derivatives Pd(R)$_2$(Me$_2$-TpzT), R = C$_6$F$_5$, **1**, *m*-C$_6$ClF$_4$, **2** (see Chart 2).

The solids are air-stable in the solid state as well as in acetone or 1,1′,2,2′-tetrachloroethane solutions and can be kept for several weeks under a nitrogen atmosphere without evidence of decomposition. In addition, there is no evidence of decomposition even after heating the tetrachloroethane solutions at 373 K. The complexes are soluble in acetone and in most chlorinated solvents but insoluble in hexane. The IR spectra show two bands in the X-sensitive region,[23,24] which indicates the presence of two different polyfluorophenyl groups.

(a) ^{1}H and ^{13}C NMR Spectra. The ^{1}H NMR spectra (acetone-d_6 or 1,1′,2,2′-tetrachloroethane-d_2) of **1** and **2** at room temperature, although some signals are slightly broad, show signals consistent with the presence of three types of pyrazolyl group. This is in accordance with the expected structure, which contains a *cis*-PdR$_2$ fragment coordinated to one pyrazole and one *N*-triazine donor atom. At 253 K all signals were narrow (see Table 1). The use of NOE experiments on H$_4$ allowed the assignment of the Me$_3$ and Me$_5$ signals of each pyrazole ring. The more deshielded resonances for H$_4$ and Me$_5$ were assigned to the coordinated pyrazole ring (A in Chart 2). Note that the Me$_3$ signal of this pyrazole was particularly shielded as a consequence of the ring current anisotropy of the pentafluorophenyl group[25] situated in close proximity. This effect has been previously described in the literature,[11,26] and we have also found it in several other types of complex.[7,27] The differentiation between pyrazolyl groups B and C was made on the basis of the higher shielding expected for Me$_3$ (and also for the Me$_5$ if rotation of the free pyrazolyl groups at room temperature is assumed) of ring C due to the anisotropy effects of the proximal pentafluorophenyl ring. Besides, as one would expect, the resonances of pyrazole B are the most similar to those in the free ligand (see Table 1). In the aforementioned NOE experiments, transfer of magnetization between protons of pyrazoles C and B was observed in acetone-d_6 solution, while the same effect between protons of A and C pyrazoles was detected in 1,1′,2,2′-tetrachloroethane-d_2 for both derivatives. This effect will be explained below in the section concerning fluxional behavior. Such interchanges were used to differentiate the Me$_3$ and Me$_5$ resonances of pyrazoles B and C once the signals of pyrazole A had been assigned. This situation is in accordance with the expected chemical shifts.

The ^{13}C NMR data (room temperature, 1,1′,2,2′-tetrachloroethane-d_2, see Experimental Section) are consistent with the presence of three different pyrazolyl groups. The assignment

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Table 2. ^{19}F NMR Chemical Shifts Data for Complexes **1** and **2**[a]

compd	T (K)	F_{o1}/F_{o1}'	F_{o2}/F_{o2}'	F_{m1}/F_{m1}'	F_{m2}/F_{m2}'	F_{p1}	F_{p2}'
1[b]	343	−116.2 (m)		−165.6 (m)		−129.5 (t; $^3J_{FF}$ = 21.3)	
1[b]	293	−115.7 (bs)	−119.2 (bs)	−164.8 (m)	−166.0 (m)	−161.4 (t)	−163.4 (t)
1[b]	253	−115.7 (m)	−116.8 (m)	−164.5 (m)[d]	−165.5 (m)	−161.1 (t)	−163.2 (t)
		−116.1 (m)	−119.8 (m)		−166.3 (m)		
1[c]	213	−115.4 (m)	−117.1 (m)	−166.0 (m)	−167.1 (m)	−163.1 (t)	−163.2 (t)
		−116.2 (m)	−118.9 (m)	−166.4 (m)	−168.1 (m)	$^3J_{FF}$ = 19.8	$^3J_{FF}$ = 19.8
		F_2		F_6		F_4	F_5
2[b]	253	−94.2 (m) (1)	−95.9 (bs) (5+6)	−110.4 (dd)	−111.6 (d; J = 17)	−140.9 (d; J = 21.4)	−164.6 (m)
		−94.5 (m) (2)	−98.6 (s) (7)	J = 31.6, 21.3.	−111.7 (d; J = 18.3)	−142.9 (d; J = 21.4)	−165.5 (m)
		−95.0 (s) (3)	−98.8 (s) (8)	−110.7 (m)	−114.6 (d; J = 36.6)		−166.3 (m)
		−95.1 (m) (4)		−111.2 (d; J = 23)	−114.7 (d; J = 36.6)		
				−111.3 (d; J = 27.5)			

[a] The labeling of ring 1 and 2 for complex **1** could be the reverse. [b] 1,1′,2,2′-tetrachloroethane-d_2. [c] Acetone-d_6. [d] Signals overlapped.

of the triazine[7] or pyrazole carbons was made according to literature.[7,28] The signals corresponding to two pyrazoles are slightly broad, while those of the other pyrazole are narrow. This assignment is in accordance with the behavior observed in the variable temperature ^{1}H NMR studies.

(b) ^{19}F NMR Spectra. The ^{19}F NMR spectrum of **1** in 1,1′,2,2′-tetrachloroethane-d_2 at room temperature (see Table 2) confirmed the existence of two different pentafluorophenyl rings by the appearance of two triplets for the F_{para} atoms. Two broad signals for the F_{ortho} and another two for the F_{meta} atoms were also observed. However, at low temperature (213 K) four different signals were observed for the F_{ortho} atoms and another four for the F_{meta}. The resonances corresponding to fluorine atoms of the same ring (rings 1 and 2, see Chart 2 and Table 2) were assigned on the basis of ^{19}F,^{19}F COSY spectra. Besides the intraannular couplings, an interannular coupling was observed between F_{ortho1}' and F_{ortho2}. For the two F_{ortho} or the two F_{meta} atoms of the same ring to be chemically different, not only is a restricted rotation of the pentafluorophenyl rings necessary but also the absence of planarity in the ligand. On considering the reported data concerning similar ligands containing pyridyl[8,10,11] or pyrazolyl rings,[12] we propose that at low temperature there is a restricted rotation of the uncoordinated pyrazole ring C. In contrast to pyrazole B, this ring should experience some degree of steric hindrance due to the adjacent pentafluorophenyl ring. The most plausible conformation for this compound (and also for **2**) is that in which the planes of the polyfluorophenyl groups and pyrazole C approximate a mutually parallel arrangement that is orthogonal to the coordination plane, with pyrazole B parallel to this latter plane.

The ^{19}F NMR spectrum of **2** at room temperature (1,1′,2,2′-tetrachloroethane-d_2) contains broad signals, whereas the same spectrum at 253 K shows narrow signals. The assignment of the different types of fluorine atoms was made on the basis of bibliographic references (see, for example, ref 29 for a similar system) and by means of a ^{19}F,^{19}F COSY spectrum. Cross-peaks were observed between the signals of F_5 and those of F_4 and F_6. Some interannular couplings were observed between F_2−F_6 and F_2−F_2 resonances, and these will be discussed in more detail below. Although only two or three resonances appeared for the F_4 and F_5 atoms, respectively, the regions containing F_2 (seven signals) and F_6 (eight signals) were more informative. This number of signals indicates the existence of eight different phenyl rings. Considering that two different tetrafluorophenyl groups are expected for each species, four isomeric forms must be present in solution at this temperature, a situation that is in accordance with the existence of four atropisomers (see Chart 3 for a schematic view of the possible rotamers considering an averaged perpendicular orientation of the C_6ClF_4 groups). To justify the presence of four different atropisomers, and in a way similar to complex **1**, not only must there be a restricted rotation of the phenyl rings but also the planarity of the ligand must be broken—a direct consequence of the restricted rotation of pyrazole C. In the case of a free rotation of the uncoordinated pyrazole rings, isomers I and II, on one side, and III and IV, on the other side, would be enantiomers and would not be distinguishable by NMR (Chart 3). This problem of restricted rotation of the pyrazole ring C and the polyfluorophenyl rings will be discussed in the section concerning fluxional behavior.

Chart 3

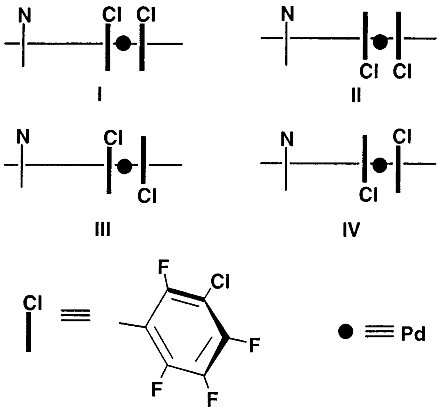

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Table 3. Calculated Free Energy of Activation for Some Processes in Complex **1** in 1,1′,2,2′-Tetrachloroethane-d_2[a]

nucleus	Pz interchange	T (K)	$\delta\nu$ (Hz)	ΔG_c[a] (kJ mol^{-1})	process
^{1}H	$A \rightleftharpoons C\ (H_4)$	325	164.9	63.9	1,4-metallotropic shift
^{1}H	$A \rightleftharpoons C\ (Me_3)$	319	108.5	63.7	1,4-metallotropic shift
^{1}H	$A \rightleftharpoons C\ (Me_5)$	321	126.9	63.7	1,4-metallotropic shift
^{19}F	$F_{para1} \rightleftharpoons F_{para2}$	343	540.1	64.2	1,4-metallotropic shift
^{19}F	$F_{ortho1} \rightleftharpoons F_{ortho1}'$	287	130.1	56.6	pyrazole rotation
^{19}F	$F_{meta1} \rightleftharpoons F_{meta1}'$	293	267.6	56.1	pyrazole rotation

[a] ±1 kJ mol^{-1}.

The detailed assignment of the F_2 resonances to the four atropisomers will be covered in a separate section after a discussion of the information obtained from the study of the fluxional behavior.

The effect of the atropisomerism on the chemical shifts of the pyrazole protons should be very small. The presence of the four atropisomers is not detected in the ^{1}H NMR spectra of the 1,1′,2,2′-tetrachloroethane-d_2 solution, probably due to the similarity of the chemical shifts. However, small splittings of the Me_3 ($CDCl_3$) or H_4 signals (acetone-d_6) were observed at low temperature (183−213 K). The $\delta\nu$ measured were too small, and consequently the calculation of free energies of activation from these data is not considered in the following section of fluxional behavior.

Fluxional Behavior. (a) Complex 1. To gain a deeper insight into the fluxional behavior of complex **1**, several variable temperature ^{1}H NMR studies in acetone-d_6 and 1,1′,2,2′-tetrachloroethane-d_2 were undertaken. The study in acetone-d_6 started at 253 K, and in this case all signals were narrow. However, when the temperature was increased, the coalescence of signals due to the uncoordinated pyrazolyl rings [Me_3(B)−Me_3(C) and Me_5(B)−Me_5(C)] was observed. As the temperature was increased further, the corresponding signals that emerge after the coalescences were observed to broaden along with the resonances of the coordinated pyrazole ring (A), but the coalescence of these signals was not achieved due to the limit of the boiling point of the solvent. The corresponding free energies of activation were not calculated because the concomitant broadening of the signals due to the presence of at least two processes made these calculations inaccurate. The spectra of the samples in 1,1′,2,2′-tetrachloroethane-d_2 at 253 K also contained narrow signals. An increase in temperature led to the coalescence of resonances due to pyrazoles A and C (Me_3, Me_5, and H_4), but the signals of pyrazole B were narrow even at 413 K. In this case we observed only one process, so the corresponding free energies of activation were calculated (see Table 3). One conclusion that can be drawn from these data is that the 1,4-metallotropic shift process that involves interconversion of pyrazole rings A and C takes place in 1,1′,2,2′-tetrachloroethane-d_2 and, very probably, also in acetone-d_6. However, the interconversion of pyrazoles B and C, which would take place via a "metal-hurdling" process, is only observed in acetone-d_6.

To evaluate the influence of the coordinating ability of the solvent, a variable temperature ^{1}H NMR study in acetone-d_6/1,1′,2,2′-tetrachloroethane-d_2 (1:1) was performed. The coalescence of the signals due to pyrazole A and C was observed in a way similar to that described for the 1,1′,2,2′-tetrachloroethane-d_2 solution. However, a clear broadening of the pyrazole B signals was observed when the temperature was increased. The limit of the boiling point of the acetone prevented the achievement of signal coalescences. It is possible to conclude that the process of "metal hurdling" is only observed when acetone is present, presumably due to its coordinating ability.

A variable temperature ^{19}F NMR study was also undertaken in 1,1′,2,2′-tetrachloroethane-d_2 in the case of compound **1**. As we have previously reported, four F_{ortho}, four F_{meta}, and two F_{para} resonances were observed at low temperature. When the temperature was increased, the coalescence between the F_{ortho} and F_{meta} resonances of the same ring was achieved (F_{o1}−F_{o1}', F_{o2}−F_{o2}', F_{m1}−F_{m1}', F_{m2}−F_{m2}'). A further increase in the temperature led to the coalescence of the signals of ring 1 with those of ring 2. Consequently, F_{ortho} or F_{meta} signals undergo two types of interchange, while those of F_{para} experience only one. Thus, in the latter case it was possible to calculate the free energy of activation without interference, while in the former case only two barriers (F_{o1}−F_{o1}', F_{m1}−F_{m1}', first process) were calculated; these corresponded to coalescence temperatures that were low enough that the broadening due to the second process could be considered negligible. The data for these studies are given in Table 3. In principle, the possible processes that lead to interconversion of signals due to atoms in the same ring that are of lower energy could be the following: (i) a rotation of pyrazole C, (ii) a rotation of both pentafluorophenyl groups, or (iii) a combination of both types of rotation. We propose alternative i on the basis that this type of process has been found to be of low energy in similar systems.[8,10−12] Besides, from the data obtained for complex **2** (see below), in which similar behavior is expected, it is possible to conclude that rotation of both polyfluorophenyl groups with a similar energy barrier does not take place. The interchange of atoms of different rings indicates that they interconvert their positions with respect to the pyrazole or triazine rings, and this is possible via the 1,4-metallotropic shift. Coincidentally, the $\Delta G_c^{\ddagger}$ value obtained from the ^{19}F NMR spectra fits well with those obtained for this process from the ^{1}H NMR spectra (see Figure 1) and, consequently, we can conclude that in this metallotropic shift not only does the interchange of pyrazoles A and C take place but the polyfluorophenyl rings also exchange their positions.

(b) Complex 2. Variable temperature ^{1}H NMR studies (acetone-d_6 or 1,1′,2,2′-tetrachloroethane-d_2 solutions) on complex **2** showed similar behavior to that found for **1**. However, in the case of the ^{19}F NMR spectra, the large number of signals made it extremely difficult to determine which pairs of resonances coalesced at each temperature. At high temperature only one resonance was observed for each type of fluorine atom, indicating that all the atropisomers interconverted and, in addition, that the two tetrafluorophenyl groups (trans to pyrazole or triazine) interchange their environments. For this reason we decided to carry out 2D

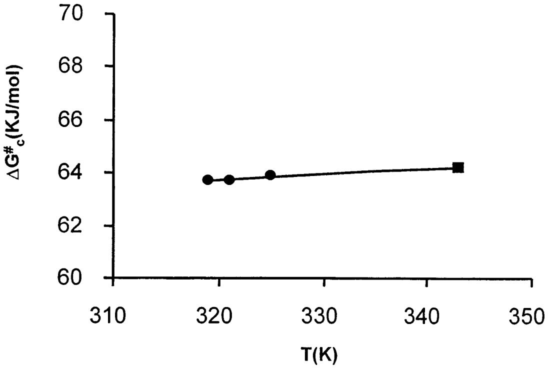

Figure 1. $\Delta G_c^{\ddagger}$ versus T_c for complex **1** for the 1,4-metallotropic shift process in 1,1′,2,2′-tetrachloroethane-d_2 obtained after the coalescence temperatures: (●) from ^{1}H NMR spectra; (■) from ^{19}F NMR spectra ($R^2 = 0.9579$).

Table 4. Calculated Free Energy of Activation for the Different Processes Detected in **2** from 2D EXSY Studies[a]

entry	solvent	nucleus	Pz inter-change	ΔG (kJ mol^{-1})[b]	process
1	tetra-d_2	^{19}F		60.5	pyrazole rotation
2	acet-d_6	^{1}H	$B \rightleftharpoons C$	63.3	metal hurdling
3	acet-d_6[c]	^{1}H	$B \rightleftharpoons C$	63.9	metal hurdling
4	tetra-d_2	^{1}H	$B \rightleftharpoons C$	d	metal hurdling
5	acet-d_6	^{1}H	$A \rightleftharpoons C$	66.2	1,4-metallotropic shift
6	acet-d_6[c]	^{1}H	$A \rightleftharpoons C$	68.1	1,4-metallotropic shift
7	tetra-d_2	^{1}H	$A \rightleftharpoons C$	65.7	1,4-metallotropic shift
8	tetra-d_2	^{19}F	$A \rightleftharpoons C$	65.4	1,4-metallotropic shift
9	acet-d_6	^{1}H	$A \rightleftharpoons B$	72.0	intermolecular metal interchange
10	tetra-d_2	^{1}H	$A \rightleftharpoons B$	70.6	intermolecular metal interchange
11	acet-d_6[c]	^{1}H	$A \rightleftharpoons B$	d	intermolecular metal interchange
12	tetra-d_2[c]	^{1}H	$A \rightleftharpoons B$	d	intermolecular metal interchange
13	tetra-d_2	^{19}F		74.5[e]	C_6F_4Cl rotation

[a] Tetra-d_2 = 1,1′,2,2′-tetrachloroethane-d_2; acet-d_6 = acetone-d_6. [b] ±1 kJ mol^{-1}. [c] Half-concentration. [d] Not detected. [e] Determined by the coalescence temperature.

EXSY experiments on this compound. In this method each single process is separated in the 2D map and interference between processes are therefore avoided.[30] A special feature of 2D EXSY is that the kinetic constant for each independent process is deduced from the data in the NMR spectra. More recently, 1D EXSY techniques have been introduced.[31] The essential feature of a quantitative 2D EXSY experiment is the relationship between the intensity of a cross-peak and the rate constants for chemical exchange. Cross-peaks in the spectrum correspond to nuclei that exchange from one site to another. The intensities of those cross-peaks do not correspond directly to the exchange matrix but to its exponential form.[30]

Rate constants can be deduced from the spectrum according to the following equation:

$$R = -(\ln A)/\tau_m = -X(\ln \Lambda)X^{-1}/\tau_m$$

where $A_{ij} = I_{ij}/M_j$ and τ_m is the mixing time. $I_{ij}(\tau_m)/M_j$ and X are the square matrix of eigenvectors of A_i such that $X^{-1}AX - \Lambda = \mathrm{diag}(\lambda_i)$, with λ_i being the i^{th} eigenvalue of A. I_{ij} can be deduced by measuring the volume of each peak intensity directly from the spectrum. M_j is the volume of the diagonal peak of the spectrum registered with a mixing time close to 0, without any chemical exchange.

An essential feature of the process is that

$$K_{ij}p_i = K_{ji}p_j$$

where K_{ij} and K_{ji} are the rate constants of processes $i \rightarrow j$ and $j \rightarrow I$, respectively, and p_i is the relative population of the i^{th} site.

Considering the coalescence of all signals, as detected in the variable temperature ^{19}F NMR spectra, a maximum of 56 correlations is expected in the 2D map in the well-resolved F_2 region. These experiments were performed in 1,1′,2,2′-tetrachloroethane-d_2 solution for ^{1}H and ^{19}F and also in acetone-d_6 for ^{1}H (in all cases at 253 K). The ^{1}H NMR spectrum in acetone contained cross-peaks corresponding to three different processes with three energy barriers: (i) interchange of pyrazoles B and C with $\Delta G^{\ddagger} = 63.3$ kJ·mol^{-1} (entry 2, Table 4), (ii) interchange of pyrazoles A and C with $\Delta G^{\ddagger} = 66.2$ kJ·mol^{-1} (entry 5), and (iii) interchange of pyrazoles A and B with $\Delta G^{\ddagger} = 72.0$ kJ·mol^{-1} (entry 9). The first interchange must be due to a metal-hurdling process and the second to a 1,4-metallotropic shift. The metal-hurdling process has a lower energy barrier than the 1,4-metallotropic shift in this solvent (entries 2 and 5). The third process has not been detected in similar systems.[10,12] We considered the possibility that the interchange between pyrazoles A and B could be due to an intermolecular process. To verify this hypothesis, we performed a 2D EXSY experiment in acetone-d_6 solution with half-concentration. Interestingly, the first two processes took place with barriers similar to those found for the former solution (compare entries 2 and 3 and also 5 and 6) and were not markedly affected by the dilution. However, the interchange between pyrazoles A and B was not observed in the dilute solution (entries 9 and 11), which is a clear indication of an intermolecular process.

^{1}H,^{1}H EXSY studies were also performed in 1,1′,2,2′-tetrachloroethane-d_2 solution. In this case, only two processes were observed and these correspond to (i) interchange of pyrazoles A and C with an energy barrier of 65.7 kJ·mol^{-1} (entry 7) and (ii) interchange of pyrazoles A and B with an energy barrier of 70.6 kJ·mol^{-1} (entry 10). The first process must be due to a 1,4-metallotropic shift, and the second, if we take into account the results obtained in acetone, must be the intermolecular interchange. It is noteworthy that in this noncoordinating solvent the process of metal-hurdling is not observed (entry 4), a situation in agreement with the results obtained from the monodimensional spectra. In this case, cross-peaks between pyrazoles B and C are not observed while the intermolecular process is present. Therefore, this process cannot involve complete dissociation of the metal fragment from the Me_2-TpzT ligand followed by recombination, because such a process would lead to interchange of all pyrazolyl groups. Confirming the results

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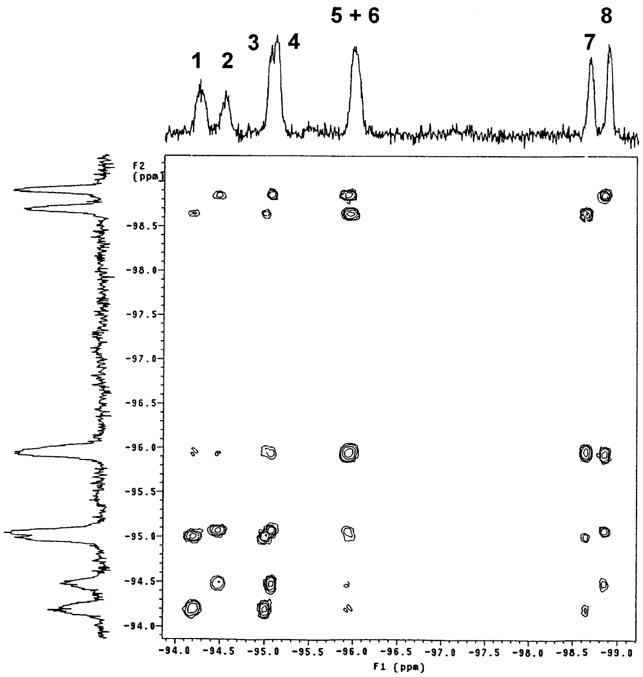

Figure 2. ^{19}F,^{19}F EXSY experiment in the region of F_2 for complex **2**.

obtained in acetone, the intermolecular process is not observed when a 1,1′,2,2′-tetrachloroethane-d_2 solution with half-concentration is measured (entry 12).

^{19}F,^{19}F EXSY studies were performed for F_2 because the signals of this fluorine atom do not show large couplings and are simpler than those of F_6, which appear as doublets. If we number the signals from 1 to 8 (5 and 6 overlapped) in order of increasing field, a first process of lower energy ($\Delta G^{\ddagger} = 60.5$ kJ·mol^{-1}) (entry 1, Table 4) with cross-peaks between the pairs 1−3, 2−4, 5−8, and 6−7 is observed (see Figure 2). A second process ($\Delta G^{\ddagger} = 65.4$ kJ·mol^{-1}, entry 8), in which the pair of signals 1 and 3 interchange with the pair 6 and 7 on one side and also the pair 2 and 4 with the pair 5 and 8 on the other side, is also observed (see Scheme 1, right). On the basis of this correlation, the eight signals are classified into two blocks that do not correlate with one another. The first process, which has no equivalence in any interchange observable in the ^{1}H ,^{1}H EXSY study, should be the rotation of one ring (we must assume that the atropisomers have not been observed separately in the ^{1}H NMR spectra in 1,1′,2,2′-tetrachloroethane-d_2 solution). This process could be (i) the restricted rotation of the pyrazole C or (ii) the restricted rotation of one of the polyfluorophenyl rings (the rotation of both C_6ClF_4 rings would lead to a larger number of cross-peaks). We propose that this process corresponds to the first possibility on the basis of systems described previously[8,10−12] and by analogy to the results found for complex **1**. The second process, which has an energy barrier similar to that found in the ^{1}H NMR study (compare entries 7 and 8), must correspond to the 1,4-metallotropic shift. It is unreasonable to believe that a process observed by ^{1}H NMR is not present in the corresponding study by ^{19}F NMR.

Despite the fact that the ^{19}F,^{19}F EXSY study at 253 K did not reveal any other exchange process, we must consider that the variable temperature ^{19}F NMR study showed, after several coalescences, only one signal for each type of fluorine atom. Consequently, at a relatively high temperature, the fluorine atoms for the two blocks described above experience an interchange. The corresponding barrier calculated for the F_2 atoms by the coalescence method ($T_c = 348$ K) is 74.5 kJ·mol^{-1} (entry 13). This process must imply the rotation of one or two polyfluorophenyl groups. In this case it is meaningless to consider whether the rotation of the two rings has the same energy barrier or not, because they are interconverting by the 1,4-metallotropic shift—a process that is of lower energy.

Assignment of Atropisomers. Assignment of the ^{19}F NMR signals to atropisomers I−IV and the determination of their relative ratios was undertaken by considering the long-range through-space correlations in the ^{19}F,^{19}F COSY spectra and interconversions detected in the ^{19}F,^{19}F EXSY spectra (in all cases we used the F_2 signal).

As discussed above, the ^{19}F NMR spectra for F_2 would be expected to show eight signals, although only seven are observed due to the overlapping of signals 5 and 6.

Pyrazole rotation interchanges signals 1−3, 2−4, 6−7, and 5−8 and interconverts atropisomers I−II (with the chlorine atoms in syn dispositions) and III−IV (with the chlorine atoms in anti dispositions) (Scheme 1). This means that each of the stated pairs of signals correspond to resonances of different isomers with the same relative disposition of the chlorine atoms and with the same heterocycle (triazine or pyrazole) in a trans arrangement.

1,4-Metallotropic shift exchanges the pairs 1−3 with 6−7 and 2−8 with 4−5. Although this process does not interconvert atropisomers, both C_6F_4Cl groups in each compound interchange their positions. Consequently, it is possible to define two blocks of signals: 1,3,6,7 and 2,4,5,8—with each block corresponding to the same orientation for the chlorine atoms (see Scheme 1). In the ^{19}F,^{19}F COSY spectra (253 K), where the long-distance correlations can be observed, a cross-peak between signals 2 and 5 of F_2 has been found. It is necessary to consider that the magnitude of this through-space coupling is correlated with the nonbonding F···F distance,[32] and, consequently, it indicates that the resonances belong to one atropisomer that contains the chlorine atoms in a syn disposition. The same reasoning should be applicable to signals 4 and 8. If we take into account the values of the integrals in the ^{19}F spectrum, it is possible to deduce that one of these isomers has an abundance of 21% (signals 2 and 5) and the other of 28% (signals 4 and 8). After analyzing molecular models, it is apparent that a greater degree of steric hindrance would exist between Me_3 and the chlorine atom in isomer I (see Chart 2) and, consequently, we propose that this isomer corresponds to that indicated in Table 5 and with

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Scheme 1. Analogy between the Expected Reduction in the Number of Haloarene Rings (left) and the Resonance Groups Correlated in the $^{19}F,^{19}F$ EXSY Experiment of **2** (Right)

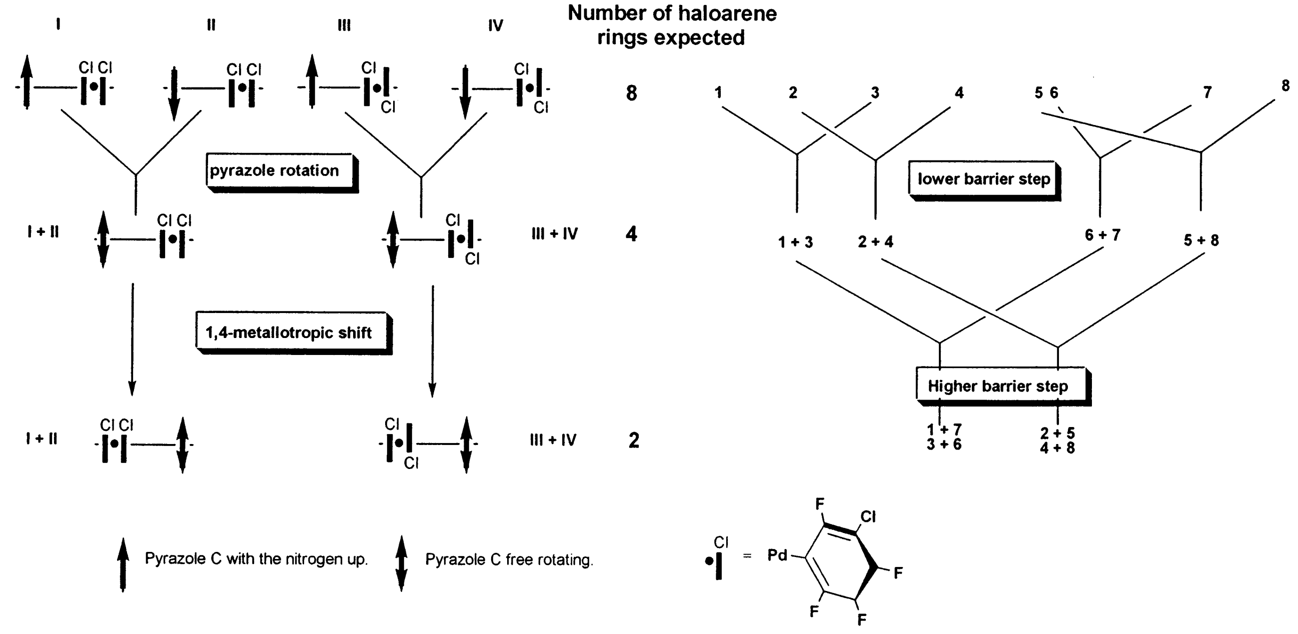
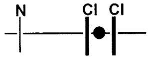
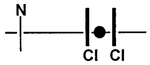
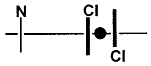
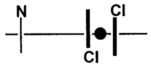


Table 5. Assignment of the F_2 Resonances of Complex **2** to the Four Atropisomers and Their Abundance

Atropisomer	F_2 Resonances	Assignment	Ratio (%)
I	2 and 5		21
II	4 and 8		28
III	3 and 6		24
IV	1 and 7		26

signals 2 and 5. The assignment of signals 4 and 8 to isomer II is straightforward.

If we consider isomers III and IV (block of signals 1, 3, 6, 7), it is envisaged that cross-peaks between the resonances of F_2 and F_6 should be observed in the COSY spectrum. In fact, this situation was found for signals 1 and 6 of F_2 with other resonances of F_6 (−111.6 and −110.6, respectively). These two couplings probably correspond to two different isomers because one of the two possible couplings between the F_{ortho} atoms of two rings is usually higher than the other due to the tilting of the two polyfluorophenyl rings.[29] This led to the conclusion that the resonances 1, 7 on one side and 3, 6 on the other side belonged to the same isomer. Although the integral values are not markedly different, it is possible to conclude that they are in accordance with the assigned pairs of signals. On the basis of the same argument applied to isomers I and II, we tentatively assign signals 3 and 6 (with an abundance of 24%) to isomer III.

Mechanistic Considerations. The conclusions reached from the study of the dynamic behavior of complexes **1** and **2** give a greater insight into the mechanisms involved in the different processes.

It is clear that the 1,4-metallotropic shift is an intramolecular process that does not need the presence of a coordinating solvent. Besides, the process is not accompanied by the rotation of any of the tetrafluorophenyl rings; otherwise a unique block of all correlated signals would be obtained in the $^{19}F,^{19}F$ EXSY spectrum of complex **2**. Given the fact that we have found the same energy barrier for the interconversion of pyrazoles A and C and the interchange of the relative positions of the two polyfluorophenyl rings with respect to the heterocyclic ligands, this process should involve the "tick-tock" motion of the PdR_2 moiety. All these data are in accordance with the associative mechanism proposed by Orrell,[9] which involves a pentacoordinate intermediate containing a terdentate ligand, as shown in Scheme 2. We must consider that in the first and the last step of the process it is necessary to rotate one uncoordinated pyrazole ring. However, considering our data, this rotation can take place with a lower energy barrier.

We have demonstrated for the first time that the coordinating ability of the solvent has a dramatic influence on the process of metal hurdling. In fact, this phenomenon is not observed in tetrachloroethane solutions. The accelerating effect of species with coordinating ability (solvent, counteranions, added ligands, etc.) has been used as an argument supporting both dissociative[33] (formation of threecoordinate intermediates) or associative[34] (formation of pentacoordinate intermediates) pathways. When kinetic measurements have been made (for example in isomerization, substitution reactions, etc.; see, for example, ref 35), it has been found that pentacoordinate intermediates are normally involved. We therefore propose that the prior coordination of the solvent is necessary to give a pentacoordinate intermediate, which

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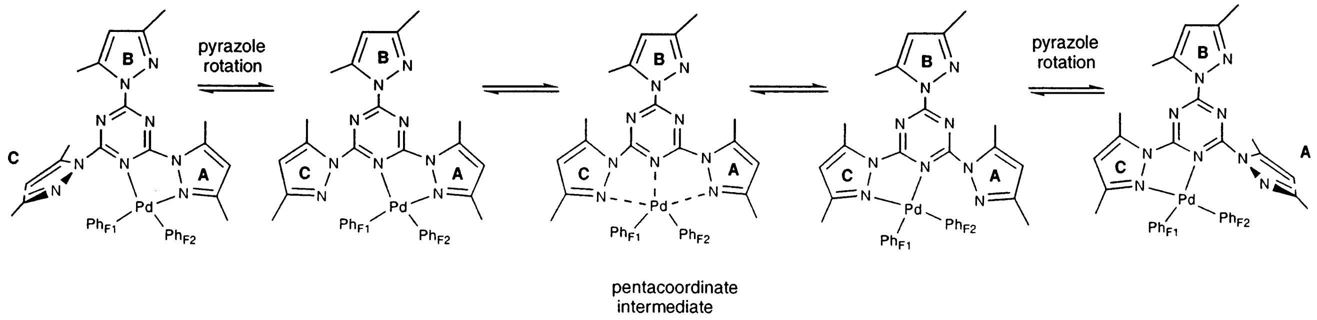
(33) Gogoll, A.; Örnebro, J.; Grennberg, H.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 3631.

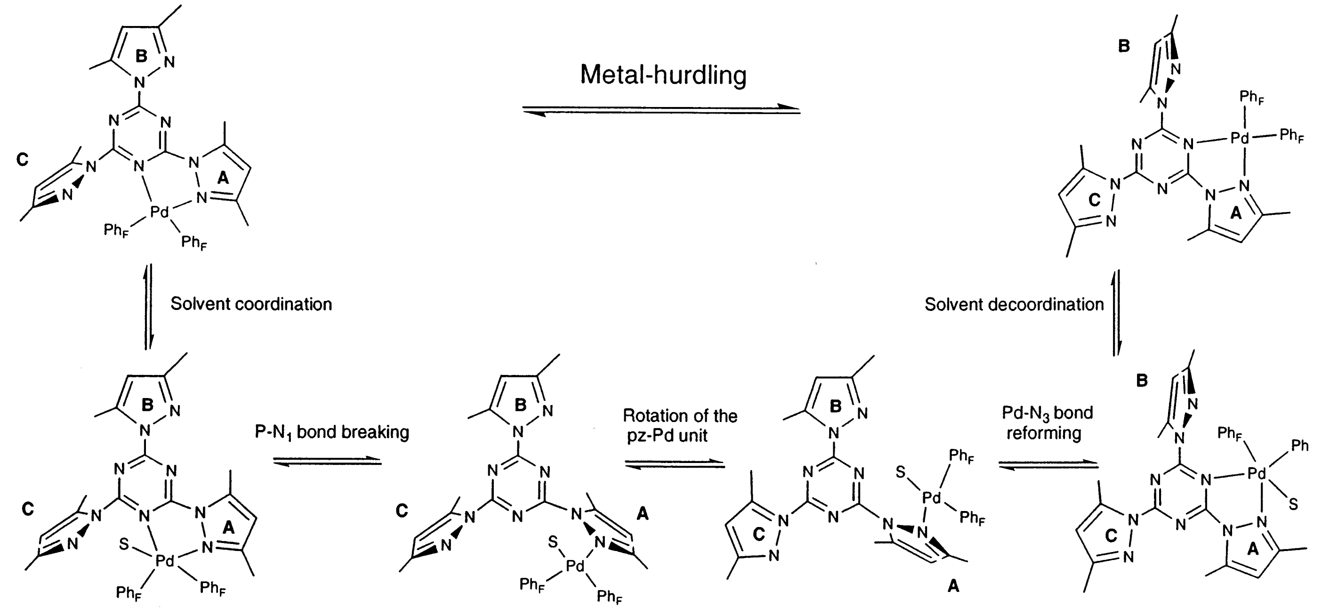
(34) Hansson, S.; Norrby, P. O.; Sjögren, M. P. T.; Åkermark, B.; Cucciolito, M. E.; Giordano, F.; Vitagliano, A. *Organometallics* **1993**, *12*, 4940.

(35) Espinet, P. *Comprehensive in Organometallic Chemistry*; Pergamon Press: Oxford, U.K., 1982; Vol. 6, pp 235 and 412.

Scheme 2. Proposed Mechanism for the 1,4-Metallotropic Shift



Scheme 3. Proposed Mechanism for the Process of Metal Hurdling



subsequently suffers rupture of the Pd$-$N$_1$(triazine) bond. This process is then followed by a 180° rotation of the metal-bound pyrazole group around the C(triazine)$-$N(pyrazole) axis, formation of the Pd$-$N$_3$(triazine) bond, and dissociation of the solvent (see Scheme 3). An alternative mechanism implying a three-coordinate intermediate formed after rupture of the Pd$-$N$_1$(triazine) bond and stabilized with the solvent cannot be completely ruled out. The fact that the process of metal hurdling has a lower energy barrier in acetone solutions than the 1,4-metallotropic shift may be related with the Pd$-$N(triazine) bond being weaker than the Pd$-$N(pyrazole) bond due to the lower basicity of the triazine heterocycle.

As far as the intermolecular process that interconverts pyrazoles A and B is concerned, we have already explained that this cannot involve complete dissociation of the metallic fragment. Bearing in mind the dramatic effect of dilution, we propose that an interaction exists between two molecules of the complex in such a way that a pentacoordinate intermediate is also formed, but this time with the participation of one uncoordinated pyrazole from the other molecule (the less crowded ring will be pyrazole B). This would lead to the rupture of the Pd$-$N(triazine) bond and finally to the concerted transfer of the metallic fragment from one molecule to the other.

Conclusions

We have synthesized the new complexes Pd(R)$_2$(Me$_2$-TpzT), Me$_2$-TpzT = 2,4,6-tris(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine, R = C_6F_5, **1**; R = C_6ClF_4, **2**. Four different atropisomers have been detected at low temperature in complex **2**. The fluxional behavior in acetone-d_6 or 1,1′,2,2′-tetrachloroethane-d_2 solutions of the new derivatives has been analyzed in detail by means of ^{1}H and ^{19}F one- and two-dimensional NMR techniques. Five different processes have been found, three of which involve metallotropy (namely, metal hurdling, 1,4-metallotropic shift, and an intermolecular process) and two of restricted rotation of aromatic rings (the uncoordinated pyrazole ring adjacent to the metal center and the polyfluorophenyl groups). The 1,4-metallotropic shift takes place in both solvents. The coordinating ability of the solvent has a dramatic effect on the metal-hurdling process in the sense that it is not observed in tetrachloroethane solutions while in acetone solutions was present. In this solvent, it was of lower energy than the 1,4-metallotropic shift. These two processes (especially the metal hurdling) are not significantly affected by the concentration, whereas the intermolecular process is not observed in dilute acetone solutions. In tetrachloroethane solutions of complex **2** the following order for the free energy of activation was found:

pyrazole rotation < 1,4-metallotropic shift < intermolecular exchange < polyfluorophenyl rotation. Considering these obtained data, we propose that the three metallotropic processes proceed through associative mechanisms via pentacoordinate intermediates, implying coordination of the solvent (metal hurdling), the N atom of the adjacent pyrazole (1,4-metallotropic shift), or the pyrazole N atom of another molecule (intermolecular process). The data from the ^{19}F,^{19}F EXSY and COSY experiments allowed complete assignment of the F$_2$ resonances to the different atropisomers of **2**.

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