The 3,5-Dichlorotrifluorophenyl Ligand, a Useful Tool for the Study of Coordination Modes and Dynamic Behavior of Complexes of Palladium and Platinum

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The square-planar complexes $[MR_2L_2]$ (M = Pd, Pt; R = 3,5-$C_6Cl_2F_3$) [L_2 = $OPPyPh_2$ (Py = 2-pyridyl); $SPPyPh_2$; $OPPy_2Ph$; DMBI (3,3′-dimethyl-2,2′-biindazole); OPPyPh(NHTol-*p*); *p*-TolNPPy_2Ph] have been prepared by treating *cis*-$[MR_2(THF)_2]$ (THF = tetrahydrofuran) with the appropriate chelate ligands. The ^{19}F-NMR spectra of these complexes show the presence of intramolecular through-space F-F couplings between *ortho*-fluorine atoms of nonequivalent R groups, which provide information for the assignment of the different *ortho*-fluorine signals and can be used to study the dynamic behavior of the mentioned complexes such as: a) Rotation of the R group in either Pd or Pt complexes, at the same or at different rates for each R groups depending on the neutral ligand; and b) exchange of the coordination sites of the chelating ligand, either by Berry or by turnstile mechanisms. The activation parameters for some of the processes are given.

Introduction

Fluoroaryl ligands have been profusely used in organometallic chemistry because of the stability of their complexes, which enables the isolation of compounds not easily obtained with nonfluorinated analogs[1]. The thermal stability of the complexes obtained is such that it allows not only their use as models in mechanistic studies, but also the synthesis of some thermotropic metal-containing liquid crystals[2]. Another advantage of fluoroaryl ligands is the simplicity of their ^{19}F-NMR spectra relative to the usually blurred ^{1}H-NMR aromatic region. Although higher field NMR instruments have decreased the importance of this second advantage, for detailed mechanistic and dynamic studies fluoroaryl ligands, particularly the pentafluorophenyl group, are still preferred[3].

However, the simplicity of the ^{19}F-NMR spectra of C_6F_5 derivatives is often deceptive. In the course of our work on asymmetric *cis*-bis(pentafluorophenyl) derivatives of palladium and platinum we have used systematically ^{19}F-^{19}F COSY-NMR experiments to help with the assignment of the two sets of ^{19}F signals of the two nonequivalent C_6F_5 rings. This methodology permits to observe the presence of scalar coupling cross-peaks between the *ortho*-fluorine signals of different C_6F_5 groups, although clear observation of the splitting pattern due to these couplings is possible only for few complexes, by selective-decoupling experiments on the F_{meta} nuclei when these have almost coincident chemical shifts. The observation of through-space coupling is not uncommon in ^{19}F-NMR spectroscopy, and it has been reported that the magnitude of the coupling depends on the distance between the interacting nuclei[4]. A detailed study of these *J*(F-F) has been carried out for the different atropisomers of $[Pd(2\text{-}C_6BrF_4)_2L_2]$ and $[Pd(3\text{-}C_6BrF_4)_2L_2]$ (L_2 = $OPPy_2Ph$, 2 tht, etc.), establishing that through-space interactions contribute importantly to them[5]. This study revealed that the magnitude of the coupling between *ortho*-fluorine atoms at the same side of the coordination plane (*syn*) in *cis*-bis(polyfluorophenyl) complexes is larger than that for *ortho*-fluorine atoms at different sides (*anti*) (Figure 1). Hence, even if the ^{19}F-NMR spectra show well-separated chemical shifts and well-resolved signals for each inequivalent nucleus (which is a quite common case), in complexes with two or more fluoroaryl rings coordinated to the same metallic center the presence of through-space F-F couplings prevents easy simulation of the spin system, measurement of *J*(F-F) values, and the use of line-shape analysis (LSA) for quantitative measurement of dynamic processes when pentafluorophenyl or tetrafluorophenyl groups are used.

Figure 1. F-F coupling constants measured in $[Pd(2\text{-}C_6BrF_4)_2L_2]$ complexes

In order to minimize this undesired complication we have started to use 3,5-dichlorotrifluorophenyl instead of the pentafluorophenyl[6]. In this group the spin system is very simple: The coupling between the fluorine atoms in position

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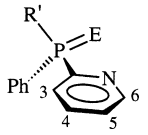
2 and 4, and between those in 4 and 6, is usually less than the half-height band width; then any multiplicity observed in the signals in the ^{19}F-NMR spectra is due only to intra-ring or inter-ring coupling of nuclei in the *ortho* position to the metal center (F_{ortho}). We will show here that this allows more stereochemical and dynamic information to be obtained than with the pentafluorophenyl rings, since the changes in the spin system due to the maintenance or not of the through-space coupling is an additional source of information. Another important advantage is that the longitudinal relaxation times T_1 for the F nuclei of 3,5-$C_6Cl_2F_3$ (1.5 to more than 3 s) are much longer than for C_6F_5, thus increasing the range of validity of the magnetization-transfer (MT) experiments for low exchange rates[7].

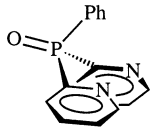
Results

The complexes $[MR_2L_2]$ (M = Pd, **a** or Pt, **b**; R = 3,5-$C_6Cl_2F_3$) [L_2 = $OPPyPh_2$ (Py = 2-pyridyl), **1**; $SPPyPh_2$, **2**; $OPPy_2Ph$, **3**; DMBI (3,3′-dimethyl-2,2′-biindazole), **4**; OPPyPh(NHTol-*p*), **5**; *p*-TolNPPy_2Ph, **6**] were obtained by substitution of tetrahydrofuran in *cis*-$[MR_2(THF)_2]$ under gentle conditions (Figure 2).

Figure 2. Ligands used to prepare complexes **1**−**6**



1 (E = O, R′ = Ph), **2** (E = S, R′ = Ph),
5 (E = O, R′ = NHTol-*p*),
6 (E = NTol-*p*, R′ = Py)



3

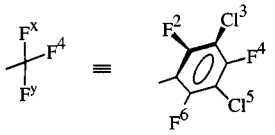
4

The solid-state IR spectra for all the isolated complexes show the characteristic infrared absorptions of the R group, and the presence of a split band in the region 710−670 cm^{-1} is in accordance with the presence of a *cis*-MR_2 arrangement[6a]. The shift to lower wavenumbers observed for ν(P=E) [E = O, S, N(C_6H_4Me-*p*)] for complexes **1**, **2**, **5**, and **6** relative to those of the free ligands[8][9] (see Experimental Section) suggests that, at least in the solid state, they are acting as E,N(Py) chelates. This is confirmed for their solutions by molecular-mass determinations with a vapor-pressure osmometer, which indicate monomeric species, and by the ^{31}P{^{1}H}-NMR spectra which show the presence of only one isomer. However, the $OPPy_2Ph$ ligand behaves as N,N chelate in complexes **3**, as found for the C_6F_5 analogues[9b].

In the 300-MHz ^{1}H-NMR spectra of complexes **1**, **2**, **3**, **5**, and **6** the resonances due to the Py groups can be detected, although in some cases they overlap with Ph peaks. The analysis of the Py first-order subspectra is trivial[10]. The H^6 (the atom on C^6 in the Py groups) signal corresponds to a multiplet slightly broadened by the quadrupolar effect of the ^{14}N nucleus. Its chemical shift is very sensitive to coordination of the group and, when coordinated, to the *cis* ligand[9][11]. For a coordinated Py group in these complexes H^6 has a negative coordination-induced shift value, indicating its close proximity to the shielding zone of the adjacent R ring. The same effect is observed in the ^{1}H-NMR spectrum of **4**, where the H^7 (and $H^{7'}$) signal of the coordinated DMBI shows a clear upfield shift relative to the free ligand[12].

The complexes studied here have different symmetry elements giving rise to different chemical or magnetic equivalence situations in the ^{19}F-NMR spectra in a static situation. Moreover, they undergo some dynamic processes. Altogether they constitute good models of the possible static and dynamic circumstances that can occur in square-planar coordination, and illustrate how the 3,5-$C_6Cl_2F_3$ groups behave, or how they reflect these circumstances. Each situation is discussed in turn in the following. A schematic representation of the group, as shown in Figure 3, is used in the figures.

Figure 3. Schematic representation of the 3,5-$C_6Cl_2F_3$ group

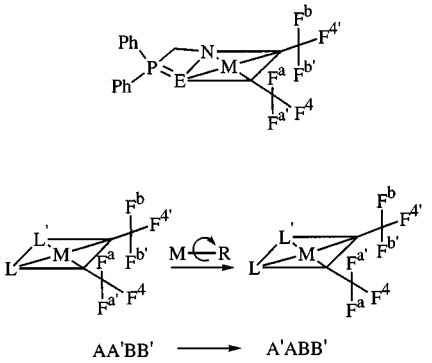


Complexes of Type I: $[MR_2(OPPyPh_2)]$ (1) and $[MR_2(SPPyPh_2)]$ (2)

These complexes have been studied both in $CDCl_3$ and [D_6]acetone solutions. The ligands $OPPyPh_2$ and $SPPyPh_2$ are coordinated through the pyridine nitrogen and the oxygen (in **1**) or the sulfur atom (in **2**) in an almost planar chelate ring. We have shown previously that there is a fast envelope-shift movement of the chelating ring, with a very low activation energy, which allows us to consider the five-membered metallacycle as planar for the rest of the discussion[9]. Thus, in a static situation the complexes have a C_s symmetry and the four F_{ortho} should give rise to an AA′BB′ spin system (Figure 4). The rotation of the R groups around the Pd−C bond in these complexes would produce exchange of chemically equivalent but magnetically inequivalent F_{ortho} nuclei.

Variable-temperature studies of **1a** and **1b** in $CDCl_3$ reveal that at room temperature the rotation of at least one of the R groups (most probably that *cis* to the oxygen atom, R^a, according to the results obtained for the related complexes **5**; see later) is fast, but on cooling the rotation is arrested. Thus, the appearance of the F_{ortho} signals changes from multiplets at low temperature, corresponding to an AA′BB′ spin system with J(AA′) and J(BB′) ≈ 0, to triplets (A_2B_2 system) as a result of the rotation of R^a which

Figure 4. Static structure of complexes of type I, and interconversion of the F_{ortho} as a result of the rotation of R[a]



interconverts the *ortho*-fluorine atoms as shown in Figure 4.

It is possible to obtain kinetic data for the rotation of R by LSA provided that the different J values can be estimated by simulation of the static spectrum (Table 1). However, the variation of the coupling constants with temperature observed, and the short range of temperatures in which the line-shape changes are detectable [which is related to J(AB) − J(AB′)] prevent accurate calculation of activation parameters other than $\Delta G^{\neq}$. With these limitations, only the spectra of **1a** in $CDCl_3$ and [D_6]acetone at 235.2 K have been simulated, yielding similar values of $\Delta G^{\neq}$ (Table 2). For **1b** we could not obtain numerical values of $\Delta G^{\neq}$, but the change in the appearance of the F_{ortho} signals shows that it is probably in the same order of magnitude.

The room temperature ^{19}F-NMR spectra of **2a** and **2b** in $CDCl_3$ and [D_6]acetone show that their F_{ortho} signals give rise to an AA′BB′ spin system indicating a rigid structure for these complex in which the R groups are not rotating around the Pd−C bond. However, on raising the temperature from 293 K to 332 K the appearance of the *ortho*-fluorine signals undergoes changes characteristic of the rotation of at least one of the R groups (Figure 5). These changes are more evident for **2b** in a shorter temperature interval, showing the smaller difference between J(AB) and J(AB′) (Table 1) which average their values in the fast exchange limit. The values of $\Delta G^{\neq}$ calculated for **2a** ([D_6]acetone) and **2b** ($CDCl_3$) at 324.7 K are in accordance with the higher steric hindrance imposed by the bulkier S atom (or the Py group) compared to the O atom[9b].

Another possible process in compounds of type I is that N and O (in **1**) or S (in **2**) exchange their sites. In the fast-exchange limit all the F_{ortho} signals of both R groups should average, and also their F_{para} signals. In practice, this limit is not reached for any of the complexes, but above 282 K this exchange is easily detected for **1a** in [D_6]acetone by the broadening of all the signals. The temperature dependence of the exchange rate, measured by MT experiments and

Table 1. ^{19}F-NMR data for the *ortho*-fluorine region of selected complexes

Complex Solvent, T [K]	δ^{19}F (J_{FPt} [Hz]) F^a, F^b F^c, F^d	J_{FF} [Hz] J_{ab}, J_{ac}, J_{ad} J_{bc}, J_{bd}, J_{cd}
[PdR_2(OPPyPh$_2$)] (**1a**) $CDCl_3$, 208.4	−91.21, −91.21 −89.71, −89.71	0.0, 8.3, 3.8 3.8, 8.3, 0.0
[PtR_2(OPPyPh$_2$)] (**1b**) $CDCl_3$, 208.4	−94.16 (423), −94.16 (423) −93.19 (504), −93.19 (504)	$J_{ac}+J_{ad}=8.3$ $J_{bc}+J_{bd}=8.3$[a]
[PdR_2(SPPyPh$_2$)] (**2a**) [D_6]acetone, 293	−86.95, −86.95 −87.88, −87.88	0.0[b], 9.1, 3.2 3.2, 9.1, 1.7[b]
[PtR_2(SPPyPh$_2$)] (**2b**) $CDCl_3$, 293	−91.70 (420), −91.70 (420) −92.55 (427), −92.55 (427)	0.0[b], 5.3, 3.2 3.2, 5.3, 0.5[b]
[PdR_2(OPPy$_2$Ph)] (**3a**) $CDCl_3$, 208.4	−88.36, −91.48 −88.36, −91.48	0.7, J_{ac}[c], 1.6 1.6, J_{bd}[c], 0.7
[PtR_2(OPPy$_2$Ph)] (**3b**) $CDCl_3$, 208.4	−90.56 (390), −93.81 (399) −90.56 (390), −93.81 (399)	0.7, J_{ac}[c], 1.6 1.6, J_{bd}[c], 0.7
[PdR_2(DMBI)] (**4a**) $CDCl_3$, 293	−86.79, −91.05 −91.05, −86.79	−1.8, 8.2, 0.6[d] 4.8[d], 8.2, −1.8
[PdR_2{OPPyPh(NHTol-*p*)}] (**5a**) [D_6]acetone, 208.4	−89.42, −88.48 −87.80, −88.04	0.0, 6.4, 3.8 3.8, 7.0, 0.0
[PtR_2{OPPyPh(NHTol-*p*)}] (**5b**) [D_6]acetone, 208.4	−92.11, −90.92 −90.96, −91.13[e]	[a]
[PdR_2(*p*-TolNPPy$_2$Ph)] (**6a**) [D_6]acetone, 293	−88.44, −87.33 −86.72, −87.27	0.0, 11.1, 2.8 2.8, 14.8, 0.0
[PtR_2(*p*-TolNPPy$_2$Ph)] (**6b**) [D_6]acetone, 293	−90.50 (431), −89.10 (421) −89.32 (465), −89.88 (428)	2.4, 8.3, 2.4 2.4, 14.2, 2.4

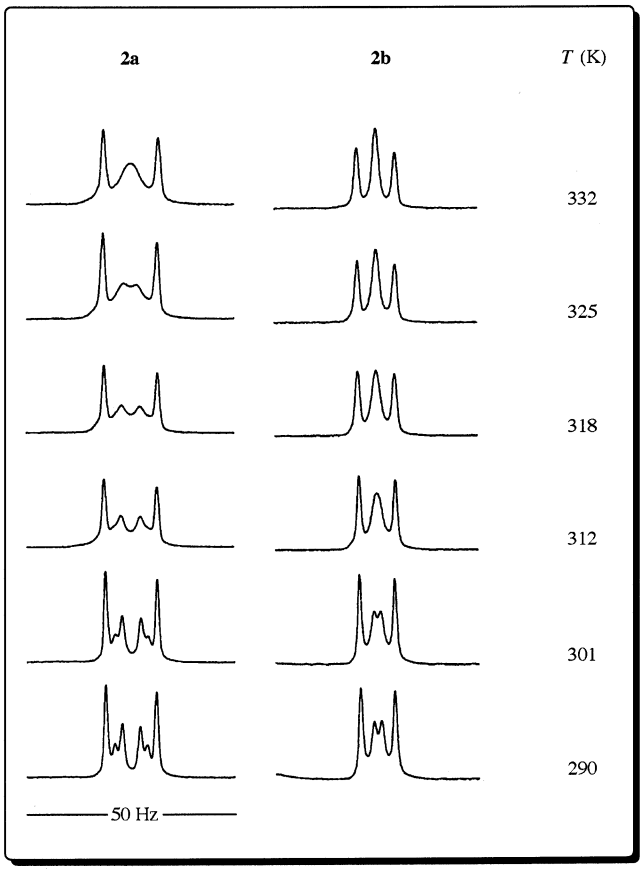
[a] It is not possible to estimate all the coupling constants. − [b] The spectrum is unaffected if these coupling constants are interchanged. − [c] The magnitude of these coupling constants does not affect significatively the appearance of the spectrum. − [d] The spectrum is unaffected by the interchange of these coupling constants and their values reflect probably some distortions. − [e] Two broad satellites.

Table 2. Activation parameters for the different processes observed for complexes **1−6** (standard deviations in parentheses)

Complex	Process	Method	$\Delta G_{298}^{\neq}$ [kJ mol^{-1}][a]	$\Delta H^{\neq}$ [kJ mol^{-1}]	$\Delta S^{\neq}$ [J K^{-1} mol^{-1}]
1a[b]	rotation R^a	LSA	53.6 (0.3)[d]		
1a[b]	exchange $R^a \rightleftharpoons R^b$	MT + LSA	65.5 (0.5)	53.1 (0.4)	−41.5 (1.3)
1a[c]	rotation R^a	LSA	54.4 (0.5)[d]		
1a[c]	exchange $R^a \rightleftharpoons R^b$	MT	77.9 (0.8)[e]		
2a[b]	rotation R^a	LSA	75.1 (0.5)[f]		
2a[b]	exchange $R^a \rightleftharpoons R^b$	MT	79.42 (0.12)[e]		
2b[c]	rotation R^a	LSA	74.9 (0.5)[f]		
3a[c]	rotation R	MT and LSA	60.8 (0.7)	57.6 (0.5)	−10.7 (1.6)
3b[c]	rotation R	MT and LSA	60.2 (0.2)	56.3 (0.1)	−13.4 (0.5)
4[c]	rotation R	MT	85.92 (0.07)[g]		
5a[b]	rotation R^a	MT and LSA	55.1 (0.7)	45.4 (0.4)	−32.6 (1.8)
5a[b]	exchange $R^a \rightleftharpoons R^b$	MT and LSA	68.3 (0.6)	54.0 (0.4)	−48.1 (1.4)
5b[b]	rotation R^a	LSA	52.4 (1.3)	42.9 (0.8)	−32 (3)
6a[b]	exchange $R^a \rightleftharpoons R^b$	MT	75.95 (0.04)[e]		
6b[b]	rotation R^a	LSA	69 (2)	59.4 (1.7)	−32 (6)

[a] Unless otherwise stated. − [b] In [D_6]acetone. − [c] In $CDCl_3$. − [d] Measured only at 235.2 K. − [e] Measured only at 298 K. − [f] Measured only at 324.7 K. − [g] Measured only at 329.1 K.

Figure 5. Temperature dependence of the AA′ part in the range 290−332 K for **2a** ([D_6]acetone) and **2b** ($CDCl_3$)



LSA on the F_{para} signals, allows us to calculate the activation parameters collected in Table 2. The exchange is solvent-dependent, and in $CDCl_3$ it is clearly much slower. The behavior of **2a** in [D_6]acetone is similar but with a lower rate; although the signals do not become broad it has been possible to measure k_{exch} at 298 K by MT experiments. In the platinum complexes, **1b** and **2b**, the exchange is not observed by MT.

The most plausible interpretation of this dependence on both the solvent and the metal center is a double substitution mechanism in which the solvent substitutes the weaker end of the chelating ligand (the oxygen atom in **1** or the sulfur or the Py nitrogen atom in **2**) at a rate measurable only in the kinetically labile Pd^{II} complexes, followed by the intramolecular substitution of the Py by the O or S atom, or by a reorganization in a pentacoordinate intermediate and the extrusion of the solvent molecule. However, the data available do not unequivocally support this hypothesis.

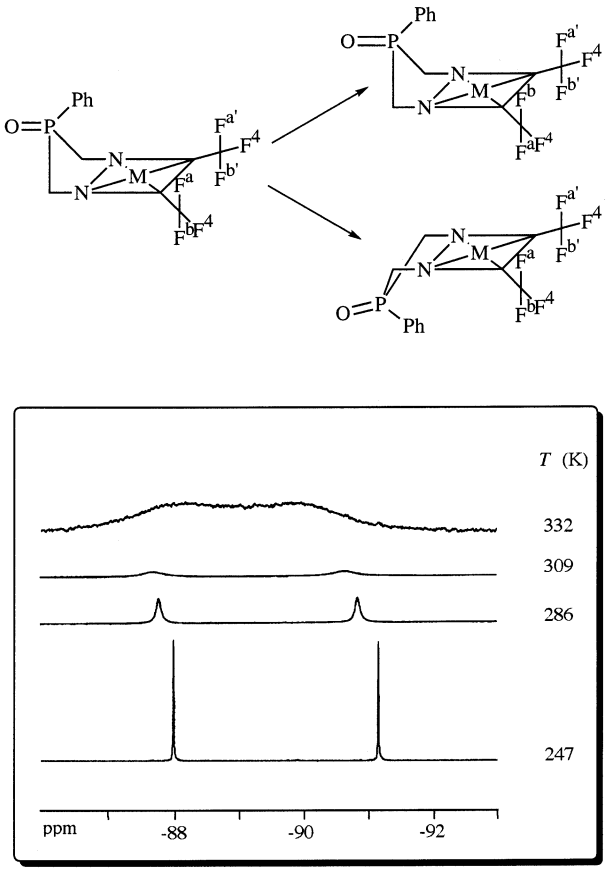
Complexes of Type II: [$MR_2(OPPy_2Ph)$] (3)

A detailed study of the related complexes [$M(C_6F_5)_2(OPPy_2Ph)$] has been recently published[9b]. The complexes [$MR_2(OPPy_2Ph)$] (**3**) have a C_s symmetry. In the slow-exchange limit the spin system of the F_{ortho} nuclei is AA′BB′ although the signals appear as broad singlets (approximately 4 Hz band width at half-height). The exchange, produced indistinctly by R rotation or by N,N exchange, renders equivalent the two sides above and below the coordination plane. Thus, in the fast-exchange limit the spin system becomes A_4 (Figure 6). In the case of **3**, the exchange is due to R rotation in the square-planar species without dissociation, which was measured and quantified by MT experiments or by LSA (Table 2).

Complexes of Type III: [$PdR_2(DMBI)$] (4a)

These complexes have a C_2 symmetry, common in enantiomerically pure ligands. With the ligand DMBI only the palladium compound has been studied, since with platinum an insoluble product was formed. The spin system of the F_{ortho} nuclei is again AA′BB′, but now the stereochemically

Figure 6. Interconversion of the F_{ortho} as a result of the rotation of R or by N,N exchange, and variable temperature ^{19}F-NMR spectra of [PdR_2($OPPy_2Ph$)] (**3a**) in the F_{ortho} region



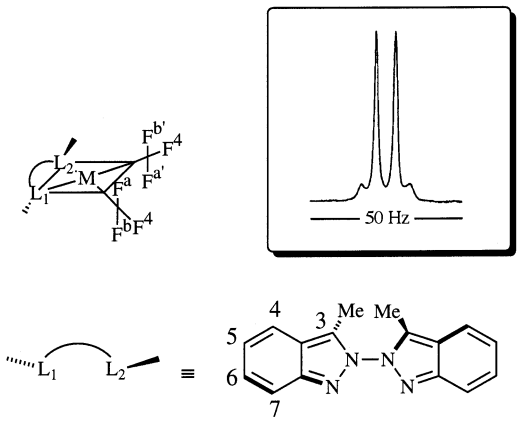
inequivalent nuclei are at the same side of the coordination plane (Figure 7). The origin of the nonplanarity of the coordinated DMBI is the methyl-methyl interaction. The twist of both indazole moieties about the N−N bond brings the protons H^7 and $H^{7'}$ close to the upfield F_{ortho} nuclei, which show some unresolved coupling (it can be removed by ^{1}H irradiation).

In this type of complexes the rotation of the aryl group should produce the equivalence of the *ortho*-fluorine nuclei (A_4). On the other hand, the two R groups (or their F_{para}) are equivalent by symmetry, so any exchange between the N coordination sites will not produce any observable effect, unless it occurs with concurrent R rotation. The latter should be the case if the exchange of coordination sites involved ligand dissociation, since R rotation becomes faster in a three-coordinate intermediate. The very slow exchange of the *ortho*-fluorine nuclei detected by MT at 329.1 K (Table 2) indicates a quite hindered rotation of the R groups in the tetracoordinate species.

Complexes of Type IV: [MR_2{OPPyPh(NHTol-*p*)}] (5) and [MR_2(*p*-TolNPPy_2Ph)] (6)

Complexes of type IV have the lowest symmetry, and in all the fluorine atoms are chemically inequivalent, giving

Figure 7. Static structure of complexes type III, and the AA′ part of the AA′BB′ spin system of the F_{ortho} for **4a** ($CDCl_3$, 293 K)



rise to an ABCD spin system in the low-exchange limit. The rotation of each group can be studied separately and also the stereochemistry of the exchange of the coordination sites of the chelated ligand.

As we have already mentioned, IR and ^{1}H- and ^{31}P{^{1}H}-NMR data indicate that the ligand OPPyPh(NHTol-*p*) is acting as O,N(Py) chelate in complexes **5**, like $OPPyPh_2$ in complexes **1**. In addition, only one stereoisomer is detected in solution for both complexes **5**, due to a rapid amine inversion process. Accordingly, four signals are expected in their ^{19}F-NMR spectra for the nonequivalent F_{ortho} nuclei. However, their ^{19}F-NMR spectra in [D_6]acetone at 293 K show only three signals in the F_{ortho} region, two of them with some splitting and the other very broad, in an intensity ratio of 1:1:2. This indicates that the two complexes behave similarly with one of the R groups (R^a) rotating fast at room temperature around the M−C bond, and the other apparently static. This is illustrated in Figure 8. The exchange interconverts the *ortho*-fluorine atoms according to the scheme ABCD ⇌ BACD, and F^4 and $F^{4'}$ remain unaffected.

Irradiation at room temperature of the broad signals assigned to R^a in **5a** and **5b** (F^a and F^b in Figure 8) led to the following results: For **5a** a simplification of the signals corresponding to R^b (the nonrotating group) from triplets to singlets is observed, which shows that for R^b $J(F^c$-$F^{4'})$ and $J(F^d$-$F^{4'})$ are smaller than the half-height band width. If the irradiation is used to presaturate the signal, a remarkable loss of intensity is observed in the others, confirming that a slow exchange is occurring between R^a and R^b. This last process will be further analyzed below considering the *para*-fluorine signals. For **5b** a simplification in R^b signals also occurs. Irradiation gives rise to two doublets from which it is possible to measure $J(F^c$-$F^d) = 2.8$ Hz.

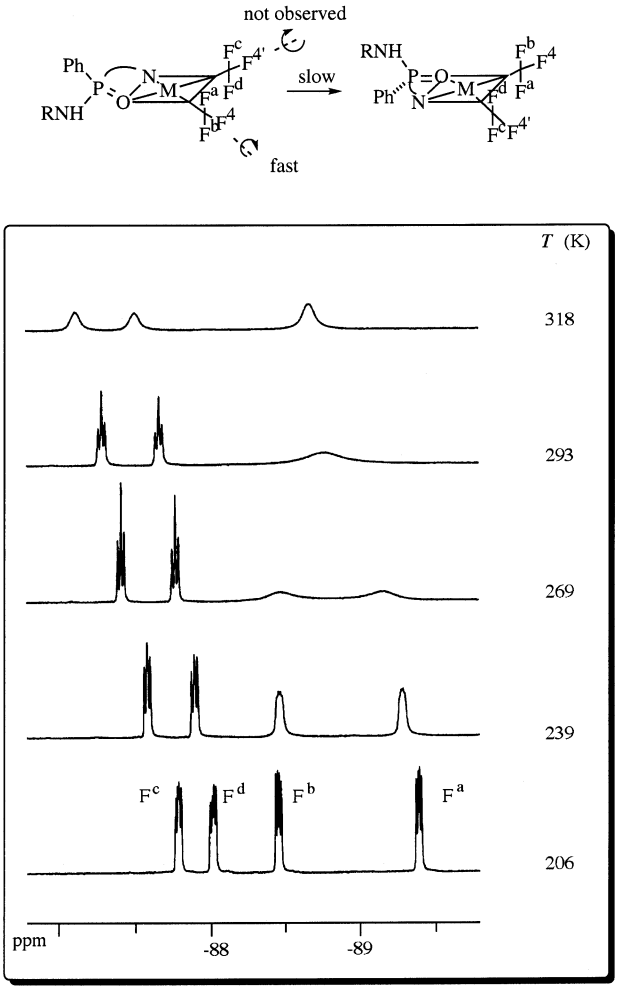
At low temperature the rotation of the R^a group is arrested leading to inequivalence of its two F_{ortho} nuclei. The coalescence temperatures for **5a** and **5b** are 281 and 269 K, respectively.

For **5a** at temperatures below 258 K there is a change in the appearance of the signals; the *ortho*-fluorine atoms of R^b change from triplets in system A_2CD, with $J(CD) = 0$

Hz] to doublets of doublets [ABCD with $J(AB) = J(CD) = 0$ Hz]. Thus, in the slow-exchange limit the spectrum of the palladium complex **5a** consists of four doublets of doublets (Table 1, Figure 8). The signal assignment of the fluorine atoms on the same side of the coordination plane is straightforward considering the relative magnitudes of their coupling constants. Unfortunately, ^{1}H-^{19}F NOE experiments do not give clear results and it is not possible to tell F^a and F^c from F^b and F^d.

The activation parameters for the rotation of R^a in **5a** (Table 2) were determined by MT experiments and LSA in the range 200−282 K. The exchange between the N and O coordination sites in **5a** is also observable (Figure 8), and it has been possible to perform kinetic studies by MT experiments and LSA in the range 275−330 K in the F_{para} region, to determine the corresponding activation parameters.

Figure 8. Illustration of the rotation of R^a and the exchange between the N and O coordination sites for complexes **5**, and variable-temperature ^{19}F-NMR spectra of [PdR_2{OPPyPh(NHTol-*p*)}] (**5a**) in the F_{ortho} region

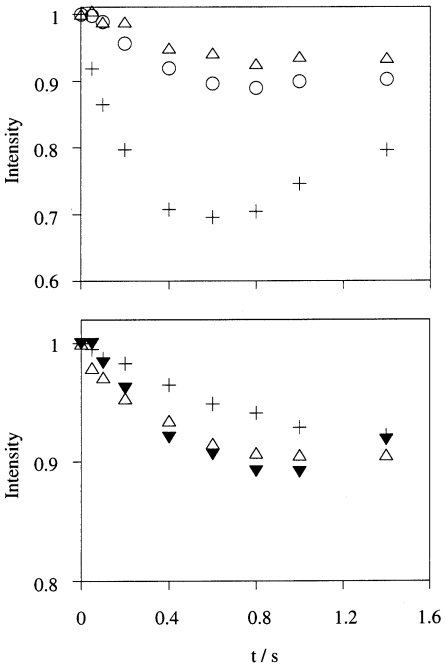


For the platinum complex **5b** LSA was performed in the temperature range in which the F_{ortho} signals are broad. There is no detectable exchange between R^a and R^b in this complex. The values of $^3J(^{195}Pt$-$^{19}F)$ measured in this complex confirm the assignment of R^a and R^b made in **5a**[6a][9b][13].

The room-temperature ^{1}H-NMR spectra of **6a** and **6b** in [D_6]acetone display the signals expected for two nonequivalent Py groups, one of them coordinated, and the ^{19}F-NMR spectra reveal four distinct fluorine environments associated with the F_{ortho} of the two nonequivalent R groups, which corresponds to a static structure for both complexes. Thus, their room-temperature spectra resemble the low-temperature spectra of **5a** and **5b** but with larger through-space coupling constants. When the temperature was increased **6a** and **6b** behaved differently. For **6b** a noticeable broadening of two F_{ortho} signals was observed and although the fast-exchange limit was not reached, this feature corresponds to the rotation of one of the R groups (R^a). Accordingly, the fine structure of the F_{ortho} signals of the nonrotating group (R^b) modified its appearance due to averaging of the couplings with the F_{ortho} of the rotating ring, in agreement with the simulated spectra. A good set of simulated band shapes was obtained for the spectra recorded, and the activation parameters derived are given in Table 2. Neither exchange between R^a and R^b, nor between the nonequivalent Py groups was detected for **6b** up to 325 K.

For **6a** only a slight broadening of the F_{ortho} signals was observed at 325 K, being the aryl rotation slow in the *J* time scale. MT experiments on ^{1}H Py signals and on ^{19}F F^4 signals of **6a** at 298 K confirm the slow exchanges between R^a and R^b [$k_{exch}(R^a \rightarrow R^b) = 0.30 \pm 0.01$] and between the nonequivalent Py groups [$k_{exch}(Py_{free} \rightarrow Py_{coord}) = 0.38 \pm 0.06$]. The similarity of both k_{exch} values (identical within the error limit) suggests that the two exchanges are produced by the same mechanism. The MT experiments on the *ortho*-fluorine nuclei at 298 K show a multi-step transfer (Figure 9). After the selective inversion of F^a, the intensity of the F^b signal decreased 30% after 0.6 s due to the rotation of the R group. There is also MT to F^c, which decreased 10% after 0.8 s, and to a smaller extent to F^d, which decreased 5% after 0.8 s (using the same numbering scheme as for complexes **5** in Figure 8). This experiment shows that the rotation of R^a is faster than the exchange between the N and N′ sites, and that the N,N′ exchange is stereoselective, since the magnetization is transferred from F^a preferentially to F^c. When the same experiment was performed by inversion of F^c there was simultaneous transfer to F^d and F^a, which decreased 10% after 1 s, while the transfer to F^b was slower and the signal decreased 7% after 1.4 s. Then the rotation of R^b has a rate comparable to the N,N′ exchange. The very low transfer of magnetization from F^a to F^d in the first experiment, or from F^c to F^b in the second, seems to be due to the fact that there is no transfer form the selectively inverted signal, but from the others when the MT has affected them. This selectivity supports a faster rotation for one of the aryl groups than for the other, as observed for **6b** and also for complexes **5**. It also suggests that the exchange between aryl groups takes place by a turnstile mechanism, with coordination of the free Py group to produce a square-pyramidal intermediate, supporting our previous observation that

Figure 9. Top: evolution of the signals of F^d (△), F^c (○) and F^b (+) after the selective inversion of F^a (▼) in complex **6a** ([D_6]acetone, 298 K); bottom: the same experiment by selective inversion of F^c



turnstile mechanisms are preferred to Berry mechanism for ligands favoring square-pyramidal geometry[14].

Conclusions

The compounds described in this paper allow the study of the inter-ring F-F coupling constants in *cis*-bis(3,5-dichlorotrifluorophenyl)palladium and -platinum units. In addition, they show that the use of this partially fluorinated ligand greatly facilitates their characterization and the study of their behavior in solution, which reveals the occurrence of the following processes: (a) fluoroaryl rotation, and (b) exchange between the coordination sites of the chelating ligand. The $\Delta G^{\neq}$ values associated with the aryl rotation processes (Table 2) reinforce our previous ideas suggesting that the rate of aryl rotation in square-planar complexes depends mainly on the steric hindrance by the atoms (or groups of atoms) coordinated to the metal center *cis* to the aryl ligand[9b].

Conversely, the patterns observed for the fluorine signals can be used to assign the coordination mode of the neutral ligands, or to detect some dynamic processes they might be undergoing. Thus, exchange between the coordination sites of the chelating ligand has been observed for the palladium complexes **1a**, **2a**, **5a**, and **6a**, and the low values of $\Delta S^{\neq}$ for **1a** and **5a** suggest an associative mechanism by a pentacoordinate mechanism. An incoming solvent does not impose any geometric restriction in the pentacoordinate intermediate, so a Berry mechanism seems most probable[15], but when the pentacoordination is achieved with the aid of one arm of the chelating ligand with a small bite angle (as for **6a**), the turnstile mechanism seems to be preferred[14].

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Experimental Section

General Considerations: All reactions were performed under nitrogen in deoxygenated solvents, although subsequent manipulations were carried out in air, except where otherwise stated. Solvents were dried by standard methods and freshly distilled under nitrogen prior to use[16]. − C,H,N analyses were obtained with a Perkin-Elmer 2400B microanalyzer. − Molecular-mass determinations were carried out with a Knauer vapour-pressure osmometer, in $CHCl_2CHCl_2$ at 303 K (the solubility of **3b**, **4a**, and **5b** was too low to carry out this determination). − IR spectra were recorded (in the range 4000−200 cm^{-1}) with a Perkin-Elmer 883 spectrophotometer using samples mulled in Nujol between polyethylene films. − ^1H-, ^{19}F-, and $^{31}P\{^1H\}$-NMR spectra were recorded with a Bruker ARX 300 spectrometer (300.13, 282.35, and 121.44 MHz, respectively) equipped with a VT-100 variable-temperature unit. Temperature calibration was performed before measurements using the temperature-dependent chemical shift differences of the ^1H resonances of methanol (175−313 K) or ethylene glycol (310−410 K)[17]. Chemical shifts are relative to TMS (^1H), $CFCl_3$ at 293 K (^{19}F), or external 85% H_3PO_4 (^{31}P), with downfield values reported as positive. In some of the kinetic studies the magnetization transfer from a selective inverted peak was observed as a function of time. The selective excitation was executed using the known 1-1 sequence or with a Gaussian-shaped soft pulse, and the data analysis was carried out as described in the literature[18]. The computer simulation of the variable-temperature NMR spectra was carried out by line-shape analysis using the standard DNMR 6 program[19]. − The following starting materials were prepared according to published procedures: $OPPyPh_2$[20], $SPPyPh_2$[21], $OPPy_2Ph$[20], DMBI[22], *cis*-$[MR_2(THF)_2]$[6a]. The monophosphazene (*p*-MeC_6H_4)$NPPy_2Ph$ was synthesized by reaction of equimolar amounts of PPy_2Ph (made as reported for PPy_3[23], but starting from $PPhCl_2$) and the organic azide[24] in toluene. Hydrolysis in chloroform of this monophosphazene produced the ligand $OPPyPh\{NH(C_6H_4Me\text{-}p)\}$.

Preparation of the Complexes [MR_2L_2]: To a solution of *cis*-$[MR_2(THF)_2]$ (0.2 mmol) in 20 ml of $CHCl_3$ was added 0.2 mmol of the ligand ($OPPyPh_2$: 56 mg; $SPPyPh_2$: 60 mg; $OPPy_2Ph$: 56 mg; DMBI: 53 mg; OPPyPh(NHTol-*p*): 62 mg; *p*-$TolNPPy_2Ph$: 74 mg). The solution was stirred for 1 h and then concentrated to ca. 5 ml and stored at 243 K. Yellow or white crystals precipitated which were filtered off, washed with diethyl ether, and vacuum-dried.

[$PdR_2(OPPyPh_2)$] (**1a**): Yield: 132 mg (84%). − IR (cm^{-1}): $\tilde{\nu}$ = 1134 (P=O) (free ligand 1203), 706, 692 (R). − ^1H NMR ($CDCl_3$, 293 K): δ = 7.99 (m, 1 H, H^6 Py), 7.95 (m, 1 H, H^4 Py), 7.90−7.45 (12 H). − ^{19}F NMR ($CDCl_3$, 293 K): δ = −88.91 (t, *J* = 7 Hz, 2 F, F_{ortho}), −90.68 (t, *J* = 7 Hz, 2 F, F_{ortho}), −118.68 (s, 1 F, F_{para}), −119.68 (s, 1 F, F_{para}). − $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 49.8 (free ligand 21.5). − $C_{29}H_{14}Cl_4F_6NOPPd$ (785.61): calcd. C 44.34, H 1.80, N 1.78; found C 44.49, H 1.90, N 1.76. − Molecular mass: calcd. 786; found 808.

[$PtR_2(OPPyPh_2)$] (**1b**): Yield: 149 mg (85%). − IR (cm^{-1}): $\tilde{\nu}$ = 1134 (P=O) (free ligand 1203), 708, 695 (R). − ^1H NMR ($CDCl_3$,

293 K): δ = 8.30 (m, J_{HPt} = 23 Hz, 1 H, H^6 Py), 8.06 (m, 1 H, H^4 Py), 7.77 (m, 1 H, H^5 Py), 7.71−7.59 (10 H, Ph), 7.53 (m, 1 H, H^3 Py). − ^{19}F NMR ($CDCl_3$, 293 K): δ = −92.33 (t, J = 4.4 Hz, J_{FPt} = 505 Hz, 2 F, F_{ortho}), −93.44 (t, J = 4.4 Hz, J_{FPt} = 427 Hz, 2 F, F_{ortho}), −120.16 (s, 1 F, F_{para}), −120.67 (s, 1 F, F_{para}). − $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 55.2 (J_{PPt} = 37 Hz) (free ligand 21.5). − $C_{29}H_{14}Cl_4F_6NOPPt$ (874.30): calcd. C 39.84, H 1.61, N 1.60; found C 40.06, H 2.13, N 1.53. − Molecular mass: calcd. 874; found 887.

[PdR$_2$(SPPyPh$_2$)] (**2a**): Yield: 135 mg (84%). − IR (cm^{-1}): $\tilde{\nu}$ = 701, 686 (R), 631 (P=S) (free ligand 645). − ^{1}H NMR ($CDCl_3$, 293 K): δ = 8.20 (m, 1 H, H^6 Py), 7.90 (m, 1 H, H^4 Py), 7.85−7.60 (10 H, Ph), 7.46 (m, 1 H, H^5 Py), 7.36 (m, 1 H, H^3 Py). − ^{19}F NMR ($CDCl_3$, 293 K): δ = −89.31 (m, 2 F, F_{ortho}), −89.44 (m, 2 F, F_{ortho}), −118.75 (s, 1 F, F_{para}), −120.30 (s, 1 F, F_{para}). − $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 47.9 (free ligand 38.1). − $C_{29}H_{14}Cl_4F_6NPPdS$ (801.67): calcd. C 43.45, H 1.76, N 1.75; found C 43.79, H 1.93, N 1.84. − Molecular mass: calcd. 802; found 818.

[PtR$_2$(SPPyPh$_2$)] (**2b**): Yield: 103 mg (58%). − IR (cm^{-1}): $\tilde{\nu}$ = 698, 687 (R), 629 (P=S) (free ligand 645). − ^{1}H NMR ($CDCl_3$, 293 K): δ = 8.48 (m, J_{HPt} = 28 Hz, 1 H, H^6 Py), 8.00 (m, 1 H, H^4 Py), 7.85−7.55 (10 H, Ph), 7.45 (m, 1 H, H^5 Py), 7.34 (m, 1 H, H^3 Py). − ^{19}F NMR ($CDCl_3$, 293 K): δ = −91.70 (m, J_{FPt} = 419 Hz, 2 F, F_{ortho}), −92.55 (m, J_{FPt} = 427 Hz, 2 F, F_{ortho}), −119.85 (s, 1 F, F_{para}), −121.37 (s, 1 F, F_{para}). − $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 47.2 (J_{PPt} = 82 Hz) (free ligand 38.1). − $C_{29}H_{14}Cl_4F_6NPPtS$ (890.36): calcd. C 39.12, H 1.59, N 1.57; found C 38.94, H 1.83, N 1.33. − Molecular mass: calcd. 890; found 865.

[PdR$_2$(OPPy$_2$Ph)] (**3a**): Yield: 134 mg (85%). − IR (cm^{-1}): $\tilde{\nu}$ = 1216 (P=O) (free ligand 1207), 703, 688 (R). − ^{1}H NMR ($CDCl_3$, 293 K): δ = 8.76−8.62 (4 H, H^6 + H^3 Py), 8.13 (m, 2 H, H^4 Py), 7.84−7.59 (m, 5 H, Ph), 7.55 (m, 2 H, H^5 Py). − ^{19}F NMR ($CDCl_3$, 293 K): δ = −87.75 (br., 2 F, F_{ortho}), −90.79 (br., 2 F, F_{ortho}), −118.49 (s, 2 F, F_{para}). − $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 20.7 (free ligand 17.7). − $C_{28}H_{13}Cl_4F_6N_2OPPd$ (786.60): calcd. C 42.76, H 1.67, N 3.56; found C 42.72, H 1.99, N 3.40. − Molecular mass: calcd. 787; found 773.

[PtR$_2$(OPPy$_2$Ph)] (**3b**): Yield: 145 mg (83%). − IR (cm^{-1}): $\tilde{\nu}$ = 1217 (P=O) (free ligand 1207), 708, 689 (R). − ^{1}H NMR ($CDCl_3$, 293 K): δ = 8.87 (m, J_{HPt} = 33 Hz, 2 H, H^6 Py), 8.71 (m, 2 H, H^3 Py), 8.17 (m, 2 H, H^4 Py), 7.80−8.50 (7 H). − ^{19}F NMR ($CDCl_3$, 293 K): δ = −90.06 (br., J_{FPt} = 386 Hz, 2 F, F_{ortho}), −93.07 (br., J_{FPt} = 394 Hz, 2 F, F_{ortho}), −119.32 (s, 2 F, F_{para}). − $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 22.3 (J_{PPt} = 166 Hz) (free ligand 17.7). − $C_{28}H_{13}Cl_4F_6N_2OPPt$ (875.29): calcd. C 38.42, H 1.50, N 3.20; found C 38.51, H 1.70, N 3.26.

[PdR$_2$(DMBI)] (**4a**): Yield: 138 mg (90%). − IR (cm^{-1}): $\tilde{\nu}$ = 700, 693 (R). − ^{1}H NMR ($CDCl_3$, 293 K): δ = 7.56 (d, J = 8.6 Hz, 2 H, $H^{4,4'}$ DMBI), 6.84 (dd, J = 8.6 and 6.6 Hz, 2 H, $H^{5,5'}$ DMBI), 6.50 (dd, J = 8.8 and 6.6 Hz, 2 H, $H^{6,6'}$ DMBI), 5.53 (d, J = 8.8 Hz, 2 H, $H^{7,7'}$ DMBI), 3.12 (s, 6 H, Me DMBI). − ^{19}F NMR ($CDCl_3$, 293 K): δ = −86.79 (m, 2 F, F_{ortho}), −91.05 (m, 2 F, F_{ortho}), −118.31 (s, 2 F, F_{para}). − $C_{28}H_{14}Cl_4F_6N_4Pd$ (768.65): calcd. C 43.75, H 1.84, N 7.29; found C 43.81, H 1.91, N 7.15.

[PdR$_2${OPPyPh(NHTol-p)}] (**5a**): Yield: 114 mg (70%). − IR (cm^{-1}): $\tilde{\nu}$ = 3341 (N−H), 1143 (P=O) (free ligand 1202), 704, 693 (R). − ^{1}H NMR ([D$_6$]acetone, 293 K): δ = 8.53 (d, J_{HP} = 12.4 Hz, 1 H, NH), 8.38−8.27 (3 H), 8.18 (m, 1 H, H^4 Py), 8.08 (m, 1 H, H^6 Py), 7.87−7.65 (4 H), 7.40−7.08 (m, 4 H, C_6H_4), 2.24 (s, 3 H, Me). − ^{19}F NMR ([D$_6$]acetone, 293 K): δ = −87.27 (t, J = 6.2 Hz, 1 F, F_{ortho}), −87.64 (t, J = 6.4 Hz, 1 F, F_{ortho}), −88.72 (vbr., 2 F, F_{ortho}), −119.49 (s, 1 F, F_{para}), −120.03 (s, 1 F, F_{para}). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 293 K): δ = 37.7 (free ligand 11.6). − $C_{30}H_{17}Cl_4F_6N_2OPPd$ (814.65): calcd. C 44.23, H 2.10, N 3.44; found C 43.88, H 2.24, N 3.25. − Molecular mass: calcd. 815; found 779.

[PtR$_2${OPPyPh(NHTol-p)}] (**5b**): Yield: 128 mg (71%). − IR (cm^{-1}): $\tilde{\nu}$ = 3342 (N−H), 1139 (P=O) (free ligand 1202), 705, 689 (R). − ^{1}H NMR ([D$_6$]acetone, 293 K): δ = 8.76 (d, J_{HP} = 13 Hz, 1 H, NH), 8.40−8.20 (5 H), 7.88−7.65 (4 H), 7.40−7.06 (m, 4 H, C_6H_4), 2.23 (s, 3 H, Me). − ^{19}F NMR ([D$_6$]acetone, 293 K): δ = −90.40 (m, J_{FPt} = 508 Hz, 1 F, F_{ortho}), −90.71 (m, J_{FPt} = 512 Hz, 1 F, F_{ortho}), −91.26 (br., J_{FPt} = 424 Hz, 2 F, F_{ortho}), −121.32 (s, 1 F, F_{para}), −121.37 (s, 1 F, F_{para}). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 293 K): δ = 44.6 (broad satellites) (free ligand 11.6). − $C_{30}H_{17}Cl_4F_6N_2OPPt$ (903.34): calcd. C 39.89, H 1.90, N 3.10; found C 39.91, H 1.96, N 3.21.

[PdR$_2$(p-TolNPPy$_2$Ph)] · CHCl$_3$ (**6a**·$CHCl_3$): Yield: 119 mg (60%). − IR (cm^{-1}): $\tilde{\nu}$ = 1270 (P=N) (free ligand 1316), 699, 689 (R). − ^{1}H NMR ([D$_6$]acetone, 293 K): δ = 8.95 (m, 1 H, H^6 Py_{free}), 8.67 (m, 1 H, H^3 Py_{free}), 8.30−8.15 (3 H), 8.10−8.00 (m, 2 H, Ph), 8.02 (s, 1 H, $CHCl_3$), 7.97 (m, 1 H, H^3 Py_{coord}), 7.83−7.70 (3 H), 7.67−7.58 (m, 2 H, Ph), 6.73−6.52 (m, 4 H, C_6H_4), 1.97 (s, 3 H, Me). − ^{19}F NMR ([D$_6$]acetone, 293 K): δ = −86.72 (dd, J = 11.1 and 2.8 Hz, 1 F, F_{ortho}), −87.27 (m, J = 14.8 and 2.8 Hz, 1 F, F_{ortho}), −87.33 (m, J = 14.8 and 2.8 Hz, 1 F, F_{ortho}), −88.44 (dd, J = 11.1 and 2.8 Hz, 1 F, F_{ortho}), −119.95 (s, 1 F, F_{para}), −121.93 (s, 1 F, F_{para}). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 293 K): δ = 27.7 (free ligand −6.1). − $C_{35}H_{20}Cl_4F_6N_3PPd\cdot CHCl_3$ (995.12): calcd. C 43.45, H 2.13, N 4.22; found C 43.79, H 2.22, N 4.04. − Molecular mass: calcd. 876; found 850.

[PtR$_2$(p-TolNPPy$_2$Ph)]·0.5 CHCl$_3$ (**6b**·0.5 $CHCl_3$): Yield: 124 mg (61%). − IR (cm^{-1}): $\tilde{\nu}$ = 1273 (P=N) (free ligand 1316), 711, 701 (R). − ^{1}H NMR ([D$_6$]acetone, 293 K): δ = 8.96 (m, 1 H, H^6 Py_{free}), 8.73 (m, 1 H, H^3 Py_{free}), 8.55 (m, J_{HPt} = 29 Hz, 1 H, H^6 Py_{coord}), 8.30 (m, 1 H, H^4 Py_{coord}), 8.25 (m, 1 H, H^4 Py_{free}), 8.10−7.98 (m, 2 H, Ph), 8.02 (s, 0.5 H, $CHCl_3$), 7.93 (m, 1 H, H^3 Py_{coord}), 7.81 (m, 1 H, H^5 Py_{free}), 7.78−7.68 (2 H), 7.65−7.57 (m, 2 H, Ph), 6.84−6.54 (m, 4 H, C_6H_4), 1.98 (s, 3 H, Me). − ^{19}F NMR ([D$_6$]acetone, 293 K): δ = −89.10 (dt, J = 14.2 and 2.4 Hz, J_{FPt} = 428 Hz, 1 F, F_{ortho}), −89.32 (dt, J = 8.3 and 2.4 Hz, J_{FPt} = 458 Hz, 1 F, F_{ortho}), −89.88 (dt, J = 14.2 and 2.4 Hz, J_{FPt} = 430 Hz, 1 F, F_{ortho}), −90.50 (dt, J = 8.3 and 2.4 Hz, J_{FPt} = 434 Hz, 1 F, F_{ortho}), −121.53 (s, 1 F, F_{para}), −123.11 (s, 1 F, F_{para}). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 293 K): δ = 31.2 (J_{PPt} = 67 Hz) (free ligand −6.1). − $C_{35}H_{20}Cl_4F_6N_3PPt\cdot 0.5\ CHCl_3$ (1024.12): calcd. C 41.64, H 2.02, N 4.10; found C 41.48, H 2.06, N 4.10. − Molecular mass: calcd. 964; found 949.

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