Articles

Dynamic Behavior of $[Pd(C_6F_5)_2(SPPy_nPh_{3-n})]$ Complexes: Evidence for a Turnstile Mechanism in Intramolecular Exchange

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The synthesis of the complexes $[PdR_2(SPPy_nPh_{3-n})]$ (**1**, $n = 1$, R = C_6F_5; **2**: $n = 2$, R = C_6F_5; **3**, $n = 2$, R = $C_6F_3Cl_2$; **4**, $n = 3$, R = C_6F_5; Py = 2-pyridyl) is reported. **2**−**4** show N,N- and N,S-bonded isomers in slow equilibrium. For the N,S-bonded isomers of **2** and **3**, the intramolecular nature of the substitution process observed (pendant Py group for coordinated Py group), together with the restricted rotation of the fluoroaryl ligands, allows the determination of the relative directions of the entering and leaving ligands with respect to the metal center and the simultaneous motion of the $SPPy_nPh_{3-n}$ ligand with respect to the fluoroaryl rings. This information supports the occurrence of a turnstile mechanism in a square-pyramidal intermediate, rather than the common Berry pseudorotation in a trigonal-bipyramidal intermediate. This is probably induced by the disinclination of the ligands to coordinate in the latter geometry.

Introduction

Associative substitution reactions in square-planar complexes via pentacoordinated intermediates is a very well studied topic. Usually, the stereochemistry is maintained and the entering ligand occupies the position of the leaving ligand. Scheme 1 shows some ligand exchange processes in which the entering ligand L′ does not occupy the place of the leaving ligand L^a after the substitution and the cis stereochemistry is maintained. This result is usually explained by the "Berry pseudorotation" mechanism (Scheme 1a). However, there are other possible mechanisms for the isomerization on the pentacoordinated intermediate,[1] such us the "turnstile mechanism" (Scheme 1b) proposed by Ugi *et al.*[2] Also, a bizarre pentacoordinated planar intermediate has been proposed for the intramolecular ligand exchange of rigid tridentate ligands (Scheme 1c).[3]

When $R^a = R^b$, there is no electronic preference for one or another coordination position for L′ since both are degenerate. All these mechanisms produce the same complex, and it is difficult to obtain any experimental evidence about which one is preferred. Recent *ab initio* calculations show that the turnstile mechanism is an energetically allowed pathway for isomerization in some pentacoordinated palladium(II) complexes,[4] but to the best of our knowledge, there is no experimental evidence supporting the occurrence of this mechanism.[5]

Here we report the synthesis and the study of the dynamic behavior of the complexes $[PdR_2(SPPy_nPh_{3-n})]$ (**1**, $n = 1$, R = C_6F_5; **2**, $n = 2$, R = C_6F_5; **3**, $n = 2$, R = $C_6F_3Cl_2$; **4**, $n = 3$, R = C_6F_5; Py = 2-pyridyl). The intramolecular nature of the substitution process observed in the N,S isomers of **2** and **3** (pendant Py group for coordinated Py group), together with the restricted rotation of the fluoroaryl ligands, allows us to determine the relative directions of the entering and leaving ligands with respect to the metal center and the simultaneous

Scheme 1

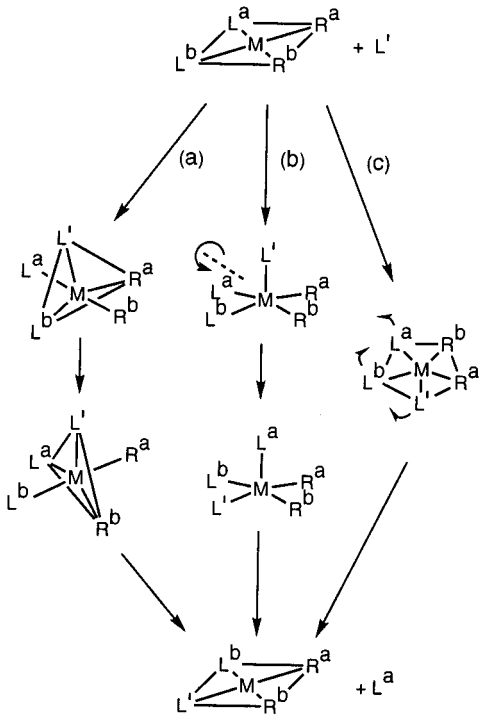

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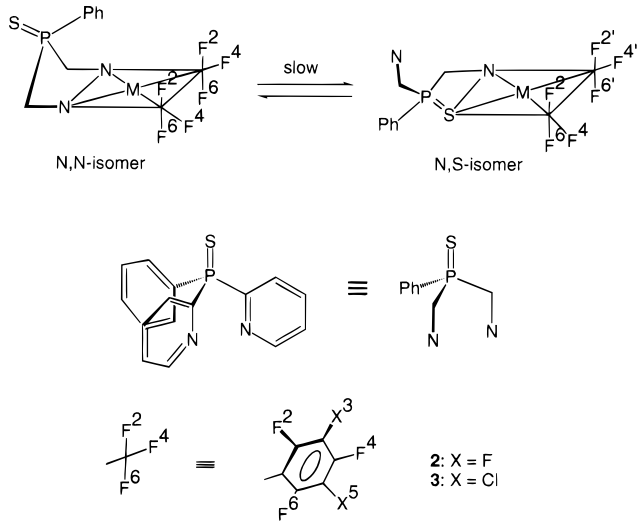
Table 1. ^{19}F NMR Data ($CDCl_3$; δ in ppm Referred to $CFCl_3$)

no.	compd	*T*/K	F_o	F_p	F_m
1	$[Pd(C_6F_5)_2(SPPyPh_2)]$	298	−115.8, −116.3	−160.7, −162.1	−163.0, −164.8
2a	$[Pd(C_6F_5)_2(SPPy_2Ph\text{-}N,N)]$	213	−117.4, −114.9	−159.9	−163.0, −163.3
2b	$[Pd(C_6F_5)_2(SPPy_2Ph\text{-}N,S)]$	213	−117.5, −116.7, −116.2, −115.7	−160.1, −161.3	−162.1, −162.8, −163.7, −163.8
3a	$[Pd(C_6F_3Cl_2)_2(SPPy_2Ph\text{-}N,N)]^a$	213	−87.8, −91.4	−118.6	
3b	$[Pd(C_6F_3Cl_2)_2(SPPy_2Ph\text{-}N,S)]^a$	213	−89.0, −89.9, −90.6, −90.9	−118.7, −119.9	
4a	$[Pd(C_6F_5)_2(SPPy_3\text{-}N,N)]$	213	−115.4, −117.4	−159.8	−162.1, −163.0
4b	$[Pd(C_6F_5)_2(SPPy_3\text{-}N,S)]$	213	−116.2, −116.5	−159.9, −161.1	−162.2, −163.8

[a] Solvent: acetone-d_6.

Scheme 2



motion of the $SPPy_nPh_{3-n}$ ligand with respect to the fluoroaryl rings. This information supports the occurrence of a turnstile mechanism.

Results and Discussion

Complexes **1**−**4** have been characterized by ^1H, ^{19}F, and ^{31}P NMR (Table 1), and the connectivity in the fluoroaryl rings has been established by ^{19}F COSY experiments, at the temperature at which the equilibrium is slow in each compound. They are either N,S-chelated (in the case of **1**) or a mixture of N,N- and N,S-chelated isomers (in the case of **2**−**4**). The structures of such isomers, shown in Scheme 2, are based on those found for closely related complexes by X-ray diffraction.[6,7]

Compound **1** is a stereochemically rigid N,S-chelated complex. A magnetization transfer experiment between the F_{ortho} atoms of the two aryl groups showed that there is no observable exchange at room temperature between these inequivalent rings (*trans* to S and *trans* to N) or between the N and S sites of the chelating ligand. Moreover, when an excess of $SPPyPh_2$ was added to a solution of **1**, the ^{31}P NMR spectrum of the mixture showed the signals of the complex and those of the free ligand at the same chemical shift found for pure samples, excluding any stereoselective exchange between free and coordinated ligands.

Complexes **2** and **3** exist in solution as mixtures of N,S and N,N coordination isomers in slow equilibrium (Scheme 2). The former is predominant in a ratio of N,S/N,N = 2.4 at 213 K. Upon an increase in temperature, the concentration of the N,N isomer decreases, and at room temperature its signal is not observable in the ^{31}P NMR spectrum. There is no coalescence between the two signals within this range of temperature.

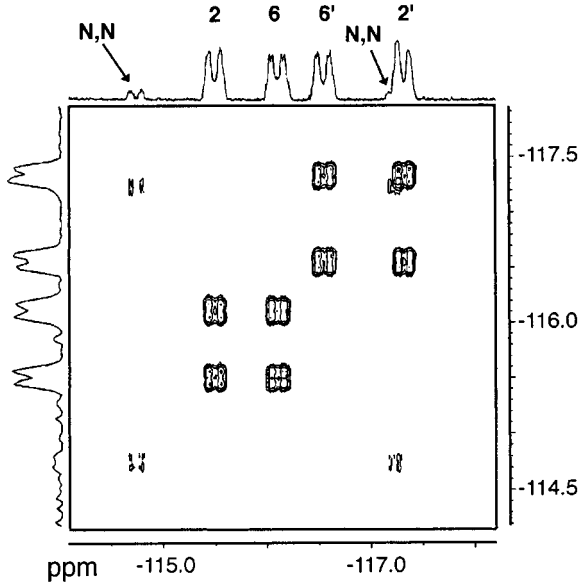


Figure 1. Phase-sensitive NOESY of **2** in $CDCl_3$ at 250 K. Only the F_{ortho} signals are shown. The numbered signals correspond to the N,S isomer (the assignment above or below the coordination plane, i.e. 2−6 or 2′-6′, is arbitrary). Arrows indicate the minor N,N isomer.

In addition to this slow process, both isomers show intramolecular dynamic processes. The ^{19}F phase-sensitive NOESY spectrum of **2** at 250 K (Figure 1) in $CDCl_3$ shows that at this temperature all the F_{ortho} atoms of the fluoroaryl ligands are involved in an intramolecular exchange process but there is no exchange between the N,N and N,S isomers. The two inequivalent F_{ortho} atoms of the N,N isomer are exchanging in a process of slow rotation of the C_6F_5 group around the C−Pd bond, as previously seen in the analogous complexes $[M(C_6F_5)_2(OPPy_nPh_{3-n})]$.[6] More interestingly, in the N,S isomer the exchange correlates in pairs F_{ortho} atoms in different C_6F_5 rings, while there are no cross peaks between atoms of the same C_6F_5 group. This means that the right and left halves of this isomer are exchanging but not the upper and lower halves. In fact, the equivalence of the F_{para} atoms is observed at higher temperature (the coalescence temperature in ^{19}F NMR is 321 K), and simultaneously the coordinated and uncoordinated Py groups are exchanging, and the coalescence of their signals is observed in their ^1H and ^{13}C NMR spectra (see Experimental Section).[8]

The same process is observed in the N,S isomer of **3**. Although the very low solubility of this product precludes the use of 2D experiments or ^{13}C NMR spectroscopy, in the ^{19}F NMR spectrum of this complex it is possible to measure the coupling constants involving the four F_{ortho} atoms, as well as the exchange pattern, by saturation transfer experiments. This

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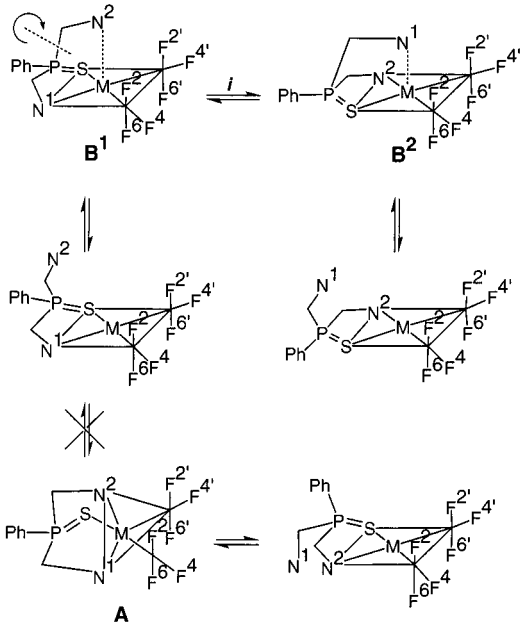
(7) Casares J. A.; Coco, S.; Espinet, P.; Lin Y.-S. *Organometallics* **1995**, *14*, 3058.
(8) The expected coalescence of the F_{ortho} by pairs cannot be reached in a 300 MHz apparatus (only broadening of the signals is observed at the highest temperature accessible), but it can be seen in an 80 MHz apparatus.

Scheme 3



allows us to confirm that the nuclei involved in the exchange are on the same face of the coordination plane.[9] The same applies to **2**, as its COSY spectrum shows cross-peaks between the F_{ortho} atoms on the same face of the complex but on different C_6F_5 groups. Thus, in this process the N and S ends of the chelate ring exchange their positions with simultaneous exchange of the coordinated and uncoordinated Py groups, in a substitution reaction in which the incoming and the leaving Py groups do not occupy the same coordination site in the square-planar complex.

An exchange mechanism involving Py dissociation can be discounted, because the four *ortho*-F atoms should be involved in the exchange *via* easy rotation of the fluoroaryl groups about the Pd−C bond in the tricoordinated intermediate.[7] Hence, an associative mechanism must considered (Scheme 3). In the classical substitution pathway, a trigonal-bipyramidal pentacoordinated intermediate is proposed in which both the incoming and the leaving ligands are in the equatorial plane. In complexes **2** and **3**, this intermediate (**A** in Scheme 3) makes the two Py groups equivalent and renders the two *ortho*-F atoms on the same ring equivalent (i.e., F^2 and F^6 or $F^{2'}$ and $F^{6'}$), contrary to the observed exchange (which is F^2 and $F^{2'}$ or F^6 and $F^{6'}$). Thus the classical substitution pathway has to be discarded also.

However, if the intermediate has a square-pyramidal geometry with one Py in the apical position (**B¹** or **B²** in Scheme 3), both Py groups are not equivalent, but can exchange their positions by a "twist" of the bis-chelating tridentate ligand (***i***, Scheme 3; as a matter of fact this is a racemization equilibrium). In this way, the exchange of the Py group and the exchange of the coordination site of the sulfur are produced in the same process, and the decoordination of the apical Py group takes place from the same face of the coordination plane of the metal where the incoming ligand attacked. This gives rise to the observed exchange pattern.

Finally, complex **4** shows a fluxional behavior very similar to that of **2** and **3**. At 213 K, the N,N and N,S isomers are in a ratio of N,N/N,S = 3.5. The exchange of the Py groups and the sulfur atom in the N,S isomer is much faster than in **2**: At 233 K, the F_{ortho} resonances are in coalescence, and in the ^{1}H NMR the Py signals of this isomer are very broad at 213 K. In this complex, the coordination plane is a symmetry plane; hence in the ^{19}F NMR, it is only possible to observe the exchange between both perfluoroaryl groups. In the N,N isomer, there is exchange between the coordinated and uncoordinated Py groups, as observed for the structurally analogous $[Pd(C_6F_5)_2(OPPy_3)]$.[6] As for complexes **2** and **3**, the N,N to N,S equilibrium is slower and affects the ^{1}H NMR spectrum only above room temperature. In the ^{31}P NMR spectrum, the signals of these two isomers have not reached coalescence yet at 323 K.

Conclusions

The N,S isomers of compounds **2** and **3** fulfill two conditions that allow the complete study of the mechanism of intramolecular substitution, namely: (a) the coordinated $SPPy_2Ph$ ligand is chiral, making all the fluorine nuclei diastereotopic, and (b) the rotation of the fluoroaryl ligands is very slow. This allows us to conclude that the substitution of the Py groups in this isomer takes place by a turnstile mechanism in a pentacoordinated intermediate and not by the usual trigonal-bipyramidal intermediate proposed for other ligands. Probably this mechanism is a singularity produced by this special ligand and is due to the fact that its geometry makes the trigonal-bipyramidal coordination very strained, whereas there is no strain in a square-pyramidal coordination, as even simple models show.[10]

Experimental Section

General Methods. ^{1}H NMR (300.16 MHz), ^{19}F NMR (282.4 MHz), and ^{31}P NMR (121.4 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with a VT-100 variable-temperature probe. Chemical shifts are reported in ppm from tetramethylsilane (^{1}H), CCl_3F (^{19}F), or H_3PO_4 (85%) (^{31}P), with positive shifts downfield, and at ambient probe temperature unless otherwise stated. ^{19}F EXSY experiments were carried out with a standard NOESY program operating in the phase-sensitive mode, with a 5% of random variation of the evolution time to avoid COSY cross-peaks. Details about the magnetization transfer experiments have been described in a previous paper.[7] Combustion CHN analyses were made on a Perkin-Elmer 2400 CHN microanalyzer. $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$,[11] *cis*-$[Pd(C_6F_3Cl_2)_2(COD)]$ (COD = 1,5-cyclooctadiene),[12] the phosphines,[13] and their sulfides[14] were also made by methods in the literature.

Synthesis of the Complexes. (a) $[Pd(C_6F_5)_2(SPPyPh_2)]$ (1). $SPPyPh_2$ (0.096 g, 0.33 mmol) was added to a suspension of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ (0.25 g, 0.165 mmol) in ethanol (20 mL). The mixture was stirred for 2 h and then concentrated to 10 mL. The resulting white precipitate, **1**, was filtered off, washed with ethanol, and dried. Yield: 0.220 g, 91%. Anal. Calcd: C, 47.33; H, 1.92; N, 1.90. Found: C, 47.26; H, 1.85; N, 1.84. ^{1}H NMR ($CDCl_3$): δ 8.22 (d, coord Py, 1H), 7.91 (m, coord Py, 1H), 7.78 (m, Ph, 6H), 7.65 (m, Ph, 4H), 7.46 (m, Py, 1H), 7.37 (t, Py, 1H). ^{31}P NMR: δ 47.4.

(b) $[Pd(C_6F_5)_2(SPPy_2Ph)]$ (2). This complex was prepared as described for **1**, but by starting from $SPPy_2Ph$ (0.097g, 0.33 mmol) instead of $SPPyPh_2$. Yield: 0.211 g (87%). Anal. Calcd: C, 45.64;

(9) In another paper, we have shown that the direct inter-ring coupling between *ortho*-F nuclei on mutually *cis* fluoroaryl rings allows this asignment to be made: Albéniz, A. C.; Casado, A. L.; Espinet, P. *Inorg. Chem.*, submitted for publication.

(10) This can also be seen in the X-ray structure of $[Mo(CO)_4(SPPy_2Ph)]$, where the tridentate ligand takes three *mer* positions in an octahedral environment with little distortion of the ideal geometry: Casares, J. A.; Espinet, P.; Hernando, R.; Iturbe, G.; Villafañe, F.; Ellis, D. D.; Orpen, A. G. *Inorg. Chem.* **1997**, *36*, 44.

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H, 1.76; N, 3.80. Found: C, 45.69; H, 1.72; N, 3.75. ^{1}H NMR (213 K, $CDCl_3$): N,S isomer δ 8.78 (d, 1H), 8.71 (m, 1H), 8.16 (m, 1H), 8.02 (m, 1H), 7.98 (m, 1H), 7.94 (m, 1H), 7.72 (m, 1H), 7.64 (m, 5H), 7.43 (m, 1H); N,N isomer δ (in part hidden by N,S signals) 9.09 (m, 2H), 8.69 (m, 2H), 8.17 (m, 2H), 8.05 (m, 2H), 7.38 (m, 2H). ^{31}P NMR: δ 42.3 (N,N isomer), 40.8 (N,S isomer). ^{13}C NMR (264 K; in parentheses $J_{^{13}C-^{13}P}$/Hz, quaternary carbons excluded): Py δ 121.9 (4), 122.8 (<2), 125.0 (in part overlapped with the phenyl ring signals), 125.6 (23), 133.0 (14) (two carbons, T_c at 213 K), 145.3 (16), 148.3 (13); phenyl δ 124.6 (13), 128.0 (9), 129.2 (5). At 315 K, ^{13}C NMR Py signals: δ 126.8, 129.9, 137.7, 152 (very broad); phenyl signals remain unchanged.

(c) $[Pd(C_6F_3Cl_2)_2(SPPy_2Ph)]$ (3). To a suspension of $[Pd(C_6F_5)_2(COD)]$ (0.185 g, 0.30 mmol) in dichloromethane (15 mL) was added $SPPy_2Ph$ (0.097 g, 0.33 mmol). The mixture was stirred for 2 h, *n*-hexane was added (10 mL), and the mixture was concentrated to 10 mL. The resulting white product, **3**, was filtered off, washed with *n*-hexane, and dried. Yield: 0.230 g, 95%. Anal. Calcd: C, 41.92; H, 1.62; N, 3.63. Found: C, 41.91; N, 3.60; H, 1.73. ^{1}H NMR (acetone-d_6), N,S/N,N ratio 9.5: N,S isomer δ 8.92 (d, Py, 1H), 8.65 (m, Py, 1H), 8.28 (m, 3H), 8.0 (m, 3H), 7.88 (m, 2H), 7.74 (m, 3H); N,N isomer δ 9.10 (m, 2H), 8.85 (m, 2H), 8.27 (m, 2H), 7.56 (m, 4H), other signals are hidden by the N,S isomer. ^{31}P NMR: δ 46.3 (N,N isomer), 44.07 (N,S isomer). ^{19}F NMR: δ data in Table 1. Each *ortho*-fluorine signal of the N,S isomer is a multiplet due to the coupling with the other three nuclei. By selective irradiation experiments, the *J* coupling constants (in Hz) have been obtained (see Scheme 2 for numbering): $J_{2-2'} = 8.5$, $J_{6-6'} = 7.2$, $J_{2-6'} = 2.8$, $J_{2'-6} = 2.6$, $^4J_{2-6} = 1.4$, $^4J_{2'-6'} = 1.8$.

(d) $[Pd(C_6F_5)_2(SPPy_3)]$ (4). This complex was prepared as described for **1**, but by starting from $SPPy_3$ (0.981 mg, 0.33 mmol) instead of $SPPyPh_2$. Yield: 0.202 g (83%). Anal. Calcd: C, 43.95; H, 1.64; N, 5.70. Found: C, 43.77; H, 1.65; N, 5.62. ^{1}H NMR (213 K, $CDCl_3$): N,N isomer δ 9.18 (m, 2H), 8.82 (m, 1H), 8.73 (m, 2H), 8.21-(m, 2H), 7.96 (m, 1H), 7.61 (broad m, 4H); N,S isomer δ 8.90, 8.39, 8.12, 7.60 (all broad multiplets). ^{31}P NMR: δ 39.1 (N,N isomer), 37.6 (N,S isomer).

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