Pd(II) Complexes with Polydentate Nitrogen Ligands. Molecular Recognition and Dynamic Behavior Involving Pd−N Bond Rupture. X-ray Molecular Structures of [{Pd(C_6HF_4)$_2$}(bpzpm)] and [{Pd(η^3-C_4H_7)}$_2$(bpzpm)] (CF_3SO_3)$_2$ [bpzpm = 4,6-Bis(pyrazol-1-yl)pyrimidine]

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The ligands 4,6-bis(pyrazol-1-yl)pyrimidine (bpzpm) and 4,6-bis(4-methylpyrazol-1-yl)pyrimidine (Me−bpzpm) were synthesized and their reactions with some palladium derivatives explored. Mononuclear or dinuclear neutral or cationic complexes were obtained by reaction of the ligands with 1 or 2 equiv of Pd(C_6XF_4)$_2$(cod) (cod = 1,5-cyclooctadiene; X = F, H) or the palladium fragment [Pd(η^3-2-Me-C_3H_4)(S)$_2$]$^+$ (S = acetone). The reaction of the dinuclear derivatives with 1 equiv of the respective free ligand immediately led to the regeneration of the mononuclear complexes. Except in the case of the synthesis of [{Pd(C_6HF_4)$_2$}{Pd(C_6F_5)$_2$}(bpzpm)], where two similar metallic groups are present, all attempts to obtain dinuclear asymmetric complexes with two different palladium fragments failed. Instead, the dinuclear symmetric complexes were formed. This result could be considered as an example of molecular recognition with the ligand acting as a ditopic receptor. This behavior is comparable to chemical symbiosis but in this case applied to the ligand rather than to the metal center as occurs normally. The polyfluorophenyl rings are situated on average in a perpendicular orientation with respect to the coordination plane. Their restricted rotation results in several atropoisomers for the complexes with *m*-C_6HF_4. Different cross-reaction experiments were carried out, and these showed the mobility of the metallic fragments, with the more difficult process being that involving the more strongly bonded polyfluorophenyl palladium groups. By means of ^{1}H NMR variable temperature studies, the interconversion of the two isomers of [{Pd(η^3-C_4H_7)}$_2$-(bpzpm)]Tf_2 (Tf = CF_3SO_3) was analyzed. In the case of [{Pd(η^3-C_4H_7)}(bpzpm)]Tf the existence of two processes, an intramolecular apparent allyl rotation and an intermolecular exchange of the allylpalladium fragments, has been demonstrated. Different $\Delta G_c^{\ddagger}$ values at the coalescence temperatures have also been determined. An X-ray single-crystal analysis was carried out on [{Pd(η^3-C_4H_7)}$_2$(bpzpm)]Tf_2, which crystallizes in the monoclinic system, space group *I*2/*m*, with a = 9.368(2), b = 16.191(3), c = 20.228(6) Å, β = 101.26(3), and Z = 4. Compound [{Pd(C_6HF_4)$_2$}(bpzpm)] crystallized in the triclinic system, space group $P\bar{1}$, with a = 8.845(6), b = 12.6609(9), c = 12.826(3) Å, α = 88.45(2), β = 74.36(3), γ = 89.32(2), and Z = 2.

Introduction

Polydentate ligands with sp^2-hybridized nitrogen atoms have been frequently used, for instance, polypyrazolylborates[1,2] and polypyridines.[2−16] More related to the ligands of the present work, other aromatic polydentate N-donor ligands, such as TPT (2,4,6-tris-2-pyridyl-1,3,5-triazine)[17−27] and pyrazolylpyridines,[28−38]

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have also been the subject of many studies, especially charge-transfer studies and related properties. On the other hand, triazines[39−42] or pyrimidines[43,44] bearing pyrazol-1-yl substituents have received much less attention.

Orrell et al.[45,46] have reported the fluxional behavior of new palladium and platinum derivatives containing 2,4,6-tris(2-pyridyl)-1,3,5-triazine and 2,4,6-tris(2-pyridyl)pyrimidine ligands. An intramolecular mechanism based on a 1,4-metallotropic shift coupled to the metal hurdling along the coordination positions of the N-donor ligand has been proposed. There have been some controversy about the mechanism of the 1,4-metallotropic shift process, and both associative[47] and dissociative[48] pathways have been proposed. Recently, Orrell et al.,[9] in an elegant study with asymmetric terpyridine ligands coordinated to palladium and platinum fragments, have shown that the 1,4-metallotopic shift pursues an associative mechanism where the role of the N atom in the central pyridine ring is essential.

In a previous paper[49] we have reported the synthesis and study of the dynamic behavior of new allylpalladium derivatives coordinated to pyrazolyltriazine ligands where the metallic group interchanges between the different coordination positions of the ligand. As in Orrell's examples,[45,46] but with energy barriers low enough to observe several coalescences in the ^{1}H NMR spectra, we have measured two different free activation energies whose difference lies correctly with the expected strengths of the Pd−N bonds, which are necessarily broken in each step. This implies the existence of Pd−N bond rupture in the two processes. The N_5 atom of the triazine ring could assist the palladium group in the 1,4-metallotropic shift (see Scheme 5 of ref 49), making the process intramolecular.

To extend our previous work and to evaluate the role of the triazine central nitrogen atom, we have now synthesized two similar ligands, 4,6-bis(pyrazol-1-yl)pyrimidine[44] (bpzpm) and 4,6-bis(4-methylpyrazol-1-yl)pyrimidine (Me−bpzpm) (see Scheme 1), that lack the N_5 atom, making impossible an intramolecular 1,4-metallotropic shift of the metal. Because these ligands still possess two identical asymmetric chelating coordination sites, if the palladium fragments are able to jump from one position to the other, a different pathway must be involved.

Another goal we have pursued in this work was to explore the possibility of synthesizing asymmetric dinuclear derivatives and to study the mutual influence of the two metallic groups through the ligand core. In this context different reactions have been performed with the bpzpm and Me−bpzpm ligands, with the metallic complex $Pd(C_6F_5)_2(cod)$ or $Pd(C_6HF_4)_2(cod)$, and with the solvato $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(S)_2]Tf$.

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. Pyrazole, 4-methylpyrazole, 4,6-dichloropyrimidine, and $AgCF_3SO_3$ were purchased from Aldrich. $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(\mu\text{-}Cl)]_2$[50,51] was prepared as described in the literature. $[Pd(C_6F_5)_2(cod)]$ and $[Pd(C_6HF_4)_2(cod)]$ were synthesized as described in the literature for similar complexes.[52] The ligand 4,6-bis(pyrazol-1-yl)-1,3-pyrimidine (bpzpm) has been previously described.[44] Elemental analyses were performed with a Perkin-Elmer 2400 microanalyzer. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian Unity 300 spectrometer using, unless specified, acetone-d_6 as solvent. Standard experimental conditions were employed.[49] Free energies of activation were calculated[53] 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 estimated error in the calculated free energies of activation is 0.5 kJ mol^{-1}.

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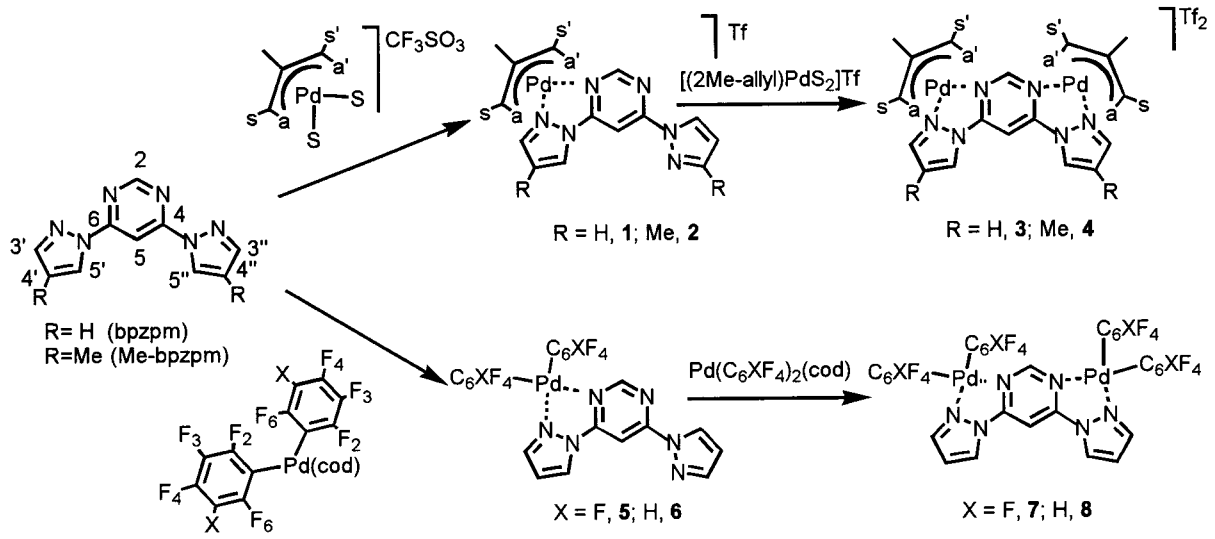
Scheme 1



Preparation of Compounds. (a) 4,6-Bis(4-methylpyrazol-1-yl)-1,3-pyrimidine (Me−bpzpm). To a solution of 4-methylpyrazole (1.21 g, 14.7 mmol) in 50 mL of THF was added $NaNH_2$ (0.573 g, 14.7 mmol). The solution was stirred at room temperature for 1 h, and evolution of NH_3 was observed. 4,6-Dichloropyrimidine (1.094 g, 7.35 mmol) was then added to the reaction mixture. The pale-brown solution was left stirring for 10 h, and the mixture was evaporated to dryness. The product was extracted three times with 30 mL of toluene. The toluene was removed, and the white solid obtained was dissolved in dichloromethane. Layering the resulting solution with pentane led to the precipitation of traces of pyrazole. Me−bpzpm was obtained after filtration and evaporation to dryness of the resulting solution. The solid was recrystallized from dichloromethane/pentane. Yield: 67%. Anal. Calcd for $C_{12}H_{12}N_6$ (240.27): C, 59.99; H, 5.03; N, 34.98. Found: C, 60.16; H, 4.95; N, 35.02.

(b) [{Pd(η^3-C_4H_7)}(4,6-bis(pyrazol-1-yl)pyrimidine)]CF_3SO_3 (1). To a solution of [Pd(η^3-C_4H_7)(μ-Cl)]$_2$ (74.2 mg, 0.19 mmol) in 20 mL of acetone was added $AgCF_3SO_3$ (96.8 mg, 0.38 mmol). The solution was protected from light and stirred at room temperature for 4 h, and the resulting suspension was filtered off. The compound bpzpm (80 mg, 0.38 mmol) was added to the filtrate. After the mixture was stirred for 15 min, the colorless solution formed was evaporated to dryness. The solid was recrystallized from acetone/diethyl ether. Yield: 82%. Anal. Calcd for $C_{15}H_{15}F_3N_6O_3PdS$ (522.80): C, 34.46; H, 2.89; N, 16.08. Found: C, 34.33; H, 2.97; N, 15.85. The data for $\Delta G_c^{\ddagger}$ of complex **1** at different concentrations were obtained by preparing the more concentrated solution and diluting consecutively with addition of 1,1,2,2-tetrachloroethane-d_2, and all the data were collected in the same NMR session.

(c) [{Pd(η^3-C_4H_7)}(4,6-bis(4-methylpyrazol-1-yl)pyrimidine)]CF_3SO_3 (2). This compound was prepared in a way similar to the preparation of **1**. Yield: 77%. Anal Calcd for $C_{17}H_{19}F_3N_6O_3PdS$ (550.85): C, 37.07; H, 3.48; N, 15.25. Found: C, 36.92; H, 3.36; N, 14.97.

(d) [{Pd(η^3-C_4H_7)}$_2$(4,6-bis(pyrazol-1-yl)pyrimidine)]$(CF_3SO_3)_2$ (3). (d.1) Method 1. To a solution of [Pd(η^3-C_4H_7)(μ-Cl)]$_2$ (148.5 mg, 0.38 mmol) in 20 mL of acetone was added $AgCF_3SO_3$ (194.0 mg, 0.76 mmol). The solution was protected from light and stirred at room temperature for 4 h, and the resulting suspension was filtered off. The compound bpzpm (80 mg, 0.38 mmol) was added to the filtrate. After the mixture was stirred for 15 min, the colorless solution was evaporated to dryness. Yield: 77%.

(d.2) Method 2.To a solution of [Pd(η^3-C_4H_7)(acetone)$_2$]CF_3SO_3, prepared from [Pd(η^3-C_4H_7)(μ-Cl)]$_2$ (74.2 mg, 0.19 mmol) as specified in method 1, a solution of **1** (98 mg, 0.19 mmol) in acetone (10 mL) was added. Workup identical to that of method 1 led to **3**. Yield: 90%. Anal. Calcd for $C_{20}H_{22}F_6N_6O_6Pd_2S_2$ (833.38): C, 28.82; H, 2.66; N, 10.08. Found: C, 28.65; H, 2.73; N, 9.77. Crystals suitable for X-ray analysis were obtained from acetone/pentane.

(e) [{Pd(η^3-C_4H_7)}$_2$(4,6-bis(4-methylpyrazol-1-yl)pyrimidine)]$(CF_3SO_3)_2$ (4). This compound was prepared in a way similar to the preparation of **3.** For method 1, the yield was 75%. For method 2, the yield was 82%. Anal. Calcd for $C_{22}H_{26}F_6N_6O_6Pd_2S_2$ (861.44): C, 30.67; H, 3.04; N, 9.76. Found: C, 30.17; H, 3.27; N, 9.43.

(f) {Pd(C_6F_5)$_2$}(4,6-bis(pyrazol-1-yl)pyrimidine) (5). To a solution of Pd(C_6F_5)$_2$(cod) (100.0 mg, 0.18 mmol) in 20 mL of acetone was added bpzpm (38.9 mg, 0.18 mmol). The solution was stirred at room temperature for 5 h. The colorless solution was evaporated to dryness. The white solid was recrystallized from dichloromethane/pentane. Yield: 90%. Anal. Calcd for $C_{22}H_8F_{10}N_6Pd\cdot 2CH_2Cl_2$ (822.62): C, 35.04; H, 1.47; N, 10.22. Found: C, 34.94; H, 1.09; N, 10.61. ^{19}F NMR: δ −112.25 (m, F_{ortho}), −158.53 (t, J_{FF} = 20.0, F_{para}), −158.92 (t, J_{FF} = 20.0, F_{para}), −161.09 (m, F_{meta}), −161.45 (m, F_{meta}) ppm.

(g) {Pd(C_6HF_4)$_2$}(4,6-bis(pyrazol-1-yl)pyrimidine) (6). To a solution of Pd(C_6HF_4)$_2$(cod) (124.7 mg, 0.24 mmol) in 20 mL of acetone was added bpzpm (51.6 mg, 0.24 mmol). The solution was stirred at room temperature for 4 h. The colorless solution formed was evaporated to dryness. The product was recrystallized from dichloromethane/pentane. Crystals suitable for X-ray structure determination were obtained using these solvents. Yield: 61%. Anal. Calcd for $C_{22}H_{10}F_8N_6$-Pd (616.75): C, 42.84; H, 1.63; N, 13.63. Found: C, 42.85; H, 1.23; N, 13.76. ^{19}F NMR: δ −92.13 (bs, 3F, F_6), −92.21 (bs, 1F, F_6), −111.50 (d, J_{FF} = 27.5, 2F, F_2), −111.71 (d, J_{FF} = 24.4, 1F, F_2), −111.80 (d, J_{FF} = 21.4, 1F, F_2), −143.72 (d, J_{FF} = 18.3, 1F, F_4), −143.76 (d, J_{FF} = 21.4, 1F, F_4), −144.19 (d, J_{FF} = 21.4, 1F, F_4), −144.23 (d, J_{FF} = 18.3, 1F, F_4), −170.91 (m, 2F, F_3), −171.18 (m, 2F, F_3) ppm.

(h) {Pd(C_6F_5)$_2$}$_2$(4,6-bis(pyrazol-1-yl)pyrimidine) (7).

(h.1) Method 1. To a solution of Pd(C_6F_5)$_2$(cod) (120.5 mg, 0.22 mmol) in 20 mL of acetone was added bpzpm (23.3 mg, 0.11 mmol). The solution was stirred at room temperature for 5 h. The colorless solution was evaporated to dryness. The white solid was recrystallized from dichloromethane/pentane. Yield: 80%.

(h.2) Method 2. To a solution of **5** (120 mg, 0.14 mmol) in acetone (20 mL), Pd(C_6F_5)$_2$(cod) (80 mg, 0.14 mmol) was added. Workup similar to that of method 1 led to **7**. Yield: 86%. Anal. Calcd for $C_{34}H_8F_{20}N_6Pd_2\cdot(^1/_2)CH_2Cl_2$ (1171.21): C, 36.49; H, 0.80; N, 7.40. Found: C, 36.25; H, 0.76; N, 6.92. ^{19}F NMR: δ −117.42 (d, J_{FF} = 24.3, F_{ortho}), −117.89 (d, J_{FF} = 24.3, F_{ortho}), −161.55 (t, J_{FF} = 15.2, F_{para}), −163.53 (t, J_{FF} = 18.9, F_{para}), −165.76 (m, F_{meta}), −166.29 (m, F_{meta}) ppm.

(i) {Pd(C_6HF_4)$_2$}$_2$(4,6-bis(pyrazol-1-yl)pyrimidine) (8).

(i.1) Method 1. To a solution of Pd(C_6HF_4)$_2$(cod) (100.4 mg, 0.20 mmol) in 20 mL of acetone was added bpzpm (20.8 mg, 0.10 mmol). The solution was stirred at room temperature for 4 h. The colorless solution was evaporated to dryness, and the resulting solid recrystallized from acetone/pentane. Yield: 68%.

(i.2) Method 2. To a solution of **6** (72.5 mg, 0.12 mmol) in acetone (15 mL), Pd(C_6HF_4)$_2$(cod) (60.3 mg, 0.12 mmol) was added. A workup

similar to that of method 1 led to **8**. Yield: 85%. Anal. Calcd for $C_{34}H_{12}F_{16}N_6Pd_2\cdot(^1/_2)(CH_3)_2CO$ (1050.36): C, 40.60; H, 1.44; N, 8.00. Found: C, 40.44; H, 0.97; N, 7.45. ^{19}F NMR: F_6, δ −91.80 (bs), −92.00 (bs), −92.16 (bs), ppm, 2:1:1 ratio; F_2, δ −111.0 to −111.35 ppm, complex signal; F_4, δ −140.9 to −141.2 (complex signal where at least three doublets are included), −142.95 to −143.1 (complex signal where three doublets, −143.00, J_{FF} = 18.0, −143.01, J_{FF} = 19.1, −143.04, J_{FF} = 19.1, are included) ppm, the ratio of the two complex signals is 1:1; F_3, δ −169.29 to −169.55 (m), −169.78 to −170.04 (m), −170.04 to −170.40 (m), ppm, 1:1:2 ratio.

(j) Reaction of 5 and Pd(C$_6$HF$_4$)$_2$(cod). To a solution of Pd(C$_6$HF$_4$)$_2$(cod) (55.9 mg, 0.11 mmol) in acetone (20 mL) complex **5** was added (71,1 mg, 0.11 mmol). The reaction was stirred at room temperature for 16 h. The resulting colorless solution was evaporated to dryness. ^{1}H NMR analyses showed that the reaction product was a mixture of **7**, **8**, and **9** in a 1:1:2 ratio. All attempts to purify the mixture by crystallization failed, and always an identical ratio of products was obtained. ^{19}F NMR of **9** (although the presence of signals of **9** can be supposed from a change in integrals, only the signals that appear in chemical shifts different from those of **7** and **8** are indicated): F_2, δ −110.93 (d, J_{FF} = 29) ppm; F_{ortho}, δ −117.5 to −117.75 (m) ppm; F_{para}, δ −161.41 (t, J_{FF} = 17.5), −161.47 (t, J_{FF} = 18.5), −163.63 (t, J_{FF} = 19.0) ppm; F_{meta}, δ −165.25 (m) ppm.

Cross Reactions in NMR Tube. (a) Cross Reaction Type 1. Reaction of 3 and bpzpm. The dinuclear compounds **3**, **4**, **7**, and **8** react with the corresponding free ligands to afford the mononuclear **1**, **2**, **5**, and **6**, respectively, in an apparent quantitative yield. The reactions were monitored by ^{1}H NMR. An example of the experimental procedure is the following. A solid sample of **3** (20 mg, 0.024 mmol) was solved in acetone-d_6 (0.7 mL). This solution was frozen with an external bath of liquid N_2, and then bpzpm was added (5.1 mg, 0.024 mmol). The tube was sealed and introduced into the NMR probe previously at 183 K. A ^{1}H NMR spectrum of pure **1** (compared with a pure sample of this compound at this temperature) was observed at 183 K. In a similar way **2** was also formed from the corresponding reactants (**4** and Me−bpzpm). Compounds **5** and **6** were also formed as pure products in the NMR tube at higher temperature (258 K) from the mixture of the corresponding reactants when the temperature was slowly raised. NMR spectra were recorded at intervals of 10 °C up to that for the complete reaction.

(b) Cross Reaction Type 2. Reaction of 1 and Pd(C$_6$F$_5$)$_2$(cod), 1:1 Ratio. Reactions of **1** with Pd(C$_6$F$_5$)$_2$(cod) or Pd(C$_6$HF$_4$)$_2$(cod) afforded equimolecular mixtures of the homodinuclear compounds **3** and **7** or **3** and **8**. An example of the experimental procedure is the following. A mixture of **1** (5.4 mg, 0.01 mmol) and Pd(C$_6$F$_5$)$_2$(cod) (5.7 mg, 0.01 mmol) was introduced in an NMR tube. Acetone-d_6 (0.7 mL) was added. When the reaction was monitored by ^{1}H NMR, the formation of an equimolecular mixture of **3** and **7** was observed, even at 183 K.

(c) Cross Reaction Type 3. Reaction of 1 and Pd(C$_6$F$_5$)$_2$(cod), 1:2 Ratio. Compound **1** (2.70 mg, 0.005 mmol) and 2 equiv of Pd(C$_6$F$_5$)$_2$(cod) (5.7 mg, 0.01 mmol) were introduced in a NMR tube, and they were made to react at room temperature in 0.7 mL of acetone-d_6. Formation of a mixture of **7** together with [Pd(η^3-C$_4$H$_7$)(cod)]CF$_3$SO$_3$ and free cod in a 1:1:1 ratio was observed. The ^{1}H NMR resonances of the products were compared with those of the corresponding free samples.

(d) Cross Reaction Type 4. Reaction of 1 and Me−bpzpm. In a procedure similar to that described for cross reaction type 1, Me−bpzpm and **1** where made to react. An equimolecular mixture of the starting materials, **2** and bpzpm, was observed at 183 K by ^{1}H NMR (comparison with pure samples of these products at this temperature was made). The mixture ratio was unaltered in the studied range of temperatures (183−323 K).

(e) Cross Reaction Type 5. Reaction of 7 and 8. In an NMR tube, **7** (0.45 mg, 0.38 mmol) and **8** (0.40 mg, 0.38 mmol) were made to react at room temperature in 0.7 mL of acetone-d_6. A new complex, **9**, appeared until finally a mixture of **7**, **8**, and **9** in a 1:1:2 ratio was established. Several spectra were made at different temperatures (183−323 K), and the ratio was unchanged.

Cross Exchange Experiments. In a procedure similar to that described for cross reaction type 1, the NMR tube was charged with equimolecular amounts of **1** and **2**, **3** and **4**, or **5** and **6** and introduced in the NMR probe. Spectra were recorded each 5 °C in the studied temperature range (193−323 K) except when coalescence of signals were observed. In this case the spectra were recorded each 1 °C in a range of ±10 °C over the coalescence temperatures.

X-ray Structural Determination of 3 and 6. Crystal, data collection, and refinement parameters are collected in Table 5. Suitable crystals were selected and mounted on fine glass fibers with epoxy cement. The unit cell parameters were determined from the angular setting of a least-squares fit of 25 strong high-angle reflections. The asymmetric unit for **3** contained a half independent molecule. Reflections were collected at 25 °C on a Nonius-Mach3 diffractometer equipped with a graphite monochromated radiation source (λ = 0.710 73 Å). None of the samples showed any significant intensity decay over the duration of the data collection.

Data were corrected in the usual fashion for Lorentz and polarization effects, and empirical absorption correction was not necessary (μ = 14.16 cm^{-1}, **3**, and 7.45 cm^{-1}, **6**). The space group was determined from the systematic absence in the diffraction data. The structures were solved by direct methods,[54] and refinements on F^2 were carried out by full-matrix least-squares analysis.[55] Anisotropic temperature parameters were considered for all non-hydrogen atoms, while hydrogen atoms were included in calculated positions but not refined. For the disordered F2 and F21 atoms in **6**, occupancies were refined initially and then both fixed at 0.5. Crystallographic data and selected bond parameters are collected in Tables 5 and 6, respectively.

Results and Discussion

Synthesis of Ligands and Complexes. Compounds bpzpm[44] and Me−bpzpm were prepared from the corresponding pyrazolate anion and 4,6-dichloropyrimidine. Reaction of 1 equiv of [Pd(η^3-2-Me-C$_3$H$_4$)(S)$_2$]CF$_3$SO$_3$ (S = acetone), prepared by reaction of [Pd(η^3-2-Me-C$_3$H$_4$)(μ-Cl)]$_2$ with AgCF$_3$SO$_3$ in acetone solution, with bpzpm or Me−bpzpm generated the mononuclear complexes [{Pd(η^3-C$_4$H$_7$)}(bpzpm)]CF$_3$SO$_3$ (**1**) and [{Pd(η^3-C$_4$H$_7$)}(Me−bpzpm)]CF$_3$SO$_3$ (**2**), respectively (Scheme 1). The homologous complexes with two coordinated allylpalladium fragments, [{Pd(η^3-C$_4$H$_7$)}$_2$(bpzpm)](CF$_3$SO$_3$)$_2$ (**3**) and [{Pd(η^3-C$_4$H$_7$)}$_2$(Me−bpzpm)](CF$_3$SO$_3$)$_2$ (**4**), were prepared when a 2:1 molar ratio was used. Under similar conditions the reaction of Pd(C$_6$F$_5$)$_2$(cod) (cod = 1,5-cyclooctadiene) or Pd(2,3,4,6-C$_6$HF$_4$)$_2$(cod) with bpzpm in a 1:1 molar ratio led to the complex [{Pd(C$_6$F$_5$)$_2$}(bpzpm)] (**5**) or [{Pd(C$_6$HF$_4$)$_2$}(bpzpm)] (**6**), whereas when a 2:1 molar ratio was used, the homologous complex [{Pd(C$_6$F$_5$)$_2$}$_2$(bpzpm)] (**7**) or [{Pd(C$_6$HF$_4$)$_2$}$_2$(bpzpm)] (**8**) was the corresponding reaction product.

The reaction of the mononuclear complexes **1**, **2**, **5**, or **6** with the corresponding Pd precursors led to the respective symmetric dinuclear complexes **3**, **4**, **7**, or **8**. The reaction of **3** or **4**, even at 183 K, with 1 equiv of the respective free ligand led instantaneously to the mononuclear complexes. Identical reactions with **7** or **8**, bearing the bis(polyfluorophenyl)palladium fragments, with bpzpm regenerated the mononuclear compounds only at higher temperatures (258 K).

When compound **5** was made to react with 1 equiv of Pd(C$_6$HF$_4$)$_2$(cod) in acetone solution, a 1:1:2 mixture (determined by NMR) of the symmetric complexes **7** and **8** and the asymmetric derivative [{Pd(C$_6$F$_5$)$_2$}{Pd(C$_6$HF$_4$)$_2$}(bpzpm)] (**9**)

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Table 1. ^{1}H NMR Data for bpzpm, Me−bpzpm Ligands, and Complexes **1**−**9**[a]

									2-Me−allyl[c]		
compound[b]	H_2	H_5	$H_{3'}$	$H_{4'}$	$H_{5'}$	$H_{3''}$	$H_{4''}$	$H_{5''}$	CH_3	H_a	H_s
bpzpm	8.89 d $J_{25} = 1.0$	8.41	7.92 dd $J_{34} = 1.5$	6.65 dd $J_{45} = 2.9$	8.69 dd $J_{53} = 0.7$						
Me−bpzpm	8.82 d $J_{25} = 1.0$	8.30	7.74	2.18[d]	8.44						
1	9.35 bs	8.52 bs	8.52 bs	7.12 bs	9.48 bs	8.06 bs	6.76 bs	8.74 bs	2.26	3.46 bs	4.62 bs
1 (193 K)	9.41 d $J_{25} = 1.0$	8.48	8.61 d $J_{34} = 2.0$	7.23 dd $J_{45} = 3.1$	9.66 d	8.20 d $J_{34} = 1.5$	6.84 dd $J_{45} = 2.7$	8.81 d	2.24	3.39(a) 3.49(a′)	4.57(s) 4.64(s′)
2	9.19 bs	8.34 bs	8.34 bs	2.29[d]	9.27 bs	7.90 bs	2.19[d]	8.48 bs	2.26	3.44 bs	4.58 bs
2 (193 K)	9.29	8.41	8.17	2.23[d]	9.29	7.98	2.12[d]	8.51	2.20	3.35(a) 3.45(a′)	4.54(s) 4.62(s′)
3	9.83	9.15	8.60 d $J_{34} = 2.0$	7.18 dd $J_{45} = 3.1$	9.28 d				2.27	3.52	4.71
3a (183 K)	10.0	9.22	8.72 d	7.30 d	9.18 d				2.16	3.42, 3.44(a)	4.61(2H,s)
3b (183 K)	10.0	9.22	8.72 d	7.30 d	9.18 d				2.18	3.48(2H,a′)	4.74, 4.79(s′)
4	9.73 d $J_{25} = 1.0$	8.92	8.46	2.29[d]	9.04				2.26	3.49	4.67
4a (183 K)	9.90	8.56	8.74 bs	2.22[d]	8.77 bs				2.18	3.45, 3.50(a)	4.62, 4.75(s)
4b (183 K)	9.92	8.56	8.74 bs	2.22[d]	8.77 bs				2.22	3.42, 3.49(a′)	4.61, 4.65(s′)
5	8.40	8.55	8.06 d $J_{34} = 2.2$	7.02 dd $J_{45} = 3.2$	9.50 d	7.84 d $J_{34} = 1.5$	6.73 dd $J_{45} = 2.9$	8.67 d			
6	8.33 d $J_{25} = 1.0$	8.54	8.05 d $J_{34} = 1.9$	6.99 dd $J_{45} = 3.1$	9.46 d	7.74 d $J_{34} = 1.7$	6.73 dd $J_{45} = 2.9$	8.69 d		C_6HF_4 6.67(bs)	
7	7.75	9.26	7.98 d $J_{34} = 2.1$	7.14 dd $J_{45} = 3.1$	9.19 d						
8	7.80	9.20	7.85 d $J_{34} = 2.0$	7.10 dd $J_{45} = 3.2$	9.16 d					C_6HF_4 6.46, 6.53, 6.63 (2H), (bs)	
9[e]	7.77	9.23	7.95 d $J_{34} = 2.0$	[7.14]	[9.19]	7.86 $J_{HH} = 2.0$	[7.10]	[9.16]		[6.50 (2H) (bs)] [6.63 (2H) (bs)]	

[a] $T = 293$ K if not indicated; δ, ppm; J, Hz; solvent = acetone-d_6. See Scheme 1 for numbering scheme. Unless specified the signals are singlets; d = doublet, bs = broad singlet. [b] **a** and **b** denote the two different stereoisomers (meso and dl pair). [c] $H_a = H_{anti}$, $H_s = H_{syn}$ (a, s, or s′, a′; see Scheme 1). [d] Me group on the $C_{4'}$ or $C_{4''}$ positions of the pyrazole. [e] The values in square brackets correspond to signals overlapping with those of complexes **7** and **8**. H_n'' corresponds to the protons of the pyrazol group coordinated to the fragment $[Pd(C_6HF_4)_2]$.

was obtained, which corresponds to a statistical distribution of the similar metallic fragments. All attemps to isolate **9** as a pure product failed, and always the thermodynamic mixture of **7**, **8**, and **9** was obtained. However, attempts to prepare asymmetric dinuclear complexes with both allyl and bispolyfluoroaryl fragments attached to the same ligand by reaction of the mononuclear complexes with a different Pd precursor failed as it was monitored by NMR. Equimolecular amounts of the corresponding symmetric dinuclear complexes were obtained in these reactions. Furthermore, reaction of complex **1** with 2 equiv of $Pd(C_6F_5)_2$(cod) (acetone-d_6, NMR tube) led to a complete and instantaneous displacement of the allylpalladium fragment with the formation of complex **7** and $[Pd(\eta^3\text{-}C_4H_7)(cod)]^+$ (see eq 1).

$$[\{Pd(\eta^3\text{-}C_4H_7)\}(bpzpm)]Tf\ (\mathbf{1}) + 2Pd(C_6F_5)_2(cod) \rightarrow [\{Pd(C_6F_5)_2\}_2(bpzpm)]\ (\mathbf{7}) + [Pd(\eta^3\text{-}C_4H_7)(cod)]Tf + cod \quad (1)$$

The following conclusions may be drawn from these results: (i) The bis(polyfluorophenyl)palladium groups are more strongly bonded than the allylpalladium cations. (ii) The bonds between the palladium fragments and the ligands are stronger in the mononuclear than in the dinuclear complexes as a consequence of the partial deactivation of the second coordination position of the ligand when the first one is implicated in the coordination. (iii) The asymmetric dinuclear complexes are less stable than the symmetric dinuclear species, and only when the two metallic fragments are very similar (i.e., $Pd(C_6F_5)_2$ and $Pd(C_6HF_4)_2$) is the asymmetric compound observed.

This last conclusion opens the possibility of considering the ligand as a ditopic receptor[56] that, after the coordination of the first metallic center, induces the bonding in the second coordination position of a near-identical metallic fragment. Consequently, homotopic (autotopic) cosystems[56] with identical subunits are formed against a statistical distribution of the fragments. This behavior is comparable to the chemical symbiosis[57] very often used in metallic complexes.[58] In our case, this phenomenon is driven by the ligand instead of being directed by the metal center.

Characterization of 1−9. Complexes **1**−**8** were characterized by NMR and IR spectroscopy and elemental analysis (**9** only by NMR). ^{1}H and ^{13}C NMR data of the complexes at room and low temperature, along with those of the starting ligands, are compiled in Tables 1 and 2. Although some ^{1}H NMR values of complex **9** are tentative because of overlapping with signals of **7** and **8**, some of these resonances have been seen separately at temperatures different from room temperature. The pyrazole protons $H_{3'}$ and $H_{5'}$ were assigned according to their different coupling constants with $H_{4'}$ ($J_{45} > J_{34}$).[59,60] The assignment of the pyrazole carbons was made on the basis of the general order in chemical shifts[59−61] $\delta_3 > \delta_5 > \delta_4$, which was confirmed in complex **7** by a ^{1}H−^{13}C shift-correlated spectrum.

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Table 2. ^{13}C {^1H} NMR Data for bpzpm, Me−bpzpm Ligands, and Complexes **1**−**9**[a]

												2-Me−allyl		
compound	C_2	C_4	C_5	C_6	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{3''}$	$C_{4''}$	$C_{5''}$	CH_3	CH_2	C	CH_3
bpzpm	159.3	159.7	95.7	159.7				145.0	110.1	128.4				
Me−bpzpm	159.1	159.2	94.6	159.2				146.0	120.7	126.6	8.9			
1	162.2	156.6	96.3	160.2	148.6	113.7	133.2	146.8	112.1	130.0		62.3	136.2	23.4
2	161.9	156.3	95.0	159.8	148.2	127.7	130.6	146.0	124.1	127.2	8.9	61.8	135.6	23.3
3	164.6	157.2	97.4	157.2	150.3	114.6	133.9					63.2	136.6	23.1
4	164.7	157.0	96.2	157.0	151.3	125.9	131.4				9.0	63.1	136.6	23.1
											Co	Cm	Cp	
5	160.0	157.0	96.0	159.2	146.0	112.8	132.9	146.2	111.6	129.7	148.5 bd	136.6 bd	138.5 bd	
											$^1J_{CF}$ = 240	$^1J_{CF}$ = 240	$^1J_{CF}$ = 240	
6	158.9	157.0	95.9	159.9	146.5	112.8	132.8	146.0	111.6	129.8	C_6HF_4(*C*H) = 99.0−100.0			
											Co	Cm	Cp	
7	156.5	159.1	96.8	159.1	148.0	114.5	133.3				148.4 bd	136.6 bd	138.4 bd	
											$^1J_{CF}$ = 240	$^1J_{CF}$ =240	$^1J_{CF}$ = 240	
8	157.3	159.0	96.7	159.0	147.5	114.2	132.9				C_6HF_4(*C*H) = 98.7−100.0			
9[b]	157.5	159.0	96.8	159.0	147.6	114.3	133.0	147.9	114.3	133.2	C_6HF_4(*C*H) = [98.7−100.0]			

[a] T = 295 K; δ, ppm; solvent = acetone-d_6. See Scheme 1 for numbering scheme. Unless specified, the signals are singlets. bd = broad doublet. [b]The values in square brackets correspond to signals overlapping with those of complexes **7** and **8**.

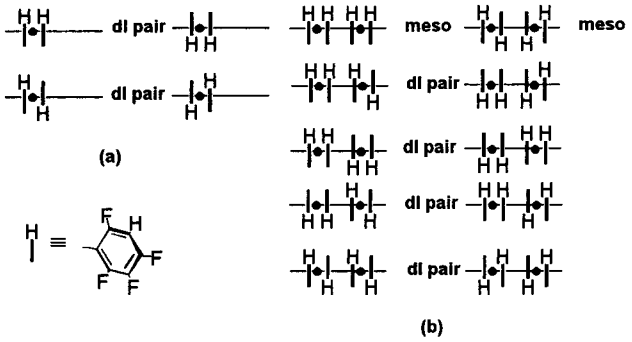
The symmetrical binuclear complexes **3**, **4**, and **7** show a symmetrical pattern with one set of signals for the pyrazole protons and carbons and for the pyrimidine C_4 and C_6. In contrast, the asymmetrical mononuclear complexes **1**, **2**, **5**, and **6** and the binuclear complex **9** show two sets of signals for each of the above nuclei. Compound **8,** although it bears four identical ligands, is not strictly symmetrical owing to the presence of several atropoisomers (see later on), but the effect on the resonances, even that associated with C_2 and $C_{3'}$, is too small to observe any splitting of these signals (Tables 1 and 2).

The ^1H and ^{13}C NMR resonances of the coordinated pyrazole and pyrimidine rings are generally shifted to higher frequency as a consequence of their coordination to the palladium center. However, in complexes with bispolyfluorophenyl fragments (**5**−**9**) the pyrazole and especially the pyrimidine protons adjacent to the coordinated nitrogens ($H_{3'}$ of pyrazole and H_2 of pyrimidine) are shifted to lower frequency with respect to the free ligands as a consequence of the ring current anisotropy of the polyfluorophenyl groups,[62] as has been found in several complexes with other aromatic rings.[63,64] This strong effect (up to −2 ppm) produces the inversion of the signals corresponding to H_2 and H_5.

We have observed for these complexes that, although asymmetric allylic groups are expected, the H_{anti}, H_{syn} protons and the terminal allylic carbons appear as unique signals in each case at room temperature. These observations point to a fluxional behavior similar to that observed for other allylpalladium complexes with N-donor ligands.[49,65]

The ^{19}F NMR spectra (see Experimental Section) of **5** and **7** clearly show the existence of two different C_6F_5− groups (cis to pyrazole or pyrimidine) with the two F_{ortho} or F_{meta} atoms equivalent in each ring. This may be indicative of free rotation of the C_6F_5 groups, but taking into account the plane of symmetry existing in the (bpzpm)Pd moiety, a static and perpendicular disposition of these rings could also account for the ^{19}F NMR observations. The first possibility is less likely considering the steric hindrance in the coordination environment of the Pd center.[66−72]

Scheme 2. Schematic View of the Possible Rotamers for Complexes **6** (a) and **8** (b) Considering an Averaged Perpendicular Orientation of the C_6HF_4 Groups



To distinguish between these two alternatives, the analogous derivatives **6** and **8** were synthesized, and these contain the nonsymmetrically substituted tetrafluorophenyl groups (the H atom is in one of the meta positions). If the phenyl rings were freely rotating, two types of tetrafluoro groups would also be observed for each complex. However, in an averaged perpendicular situation with restricted rotation several atropoisomers[66] would be expected depending on the relative orientation of the C_6HF_4 groups. This situation is represented in Scheme 2, where H represents the orientation of this atom of the phenyl ring with respect to the molecular plane. For complex **6** two dl pairs (syn-H,H and anti-H,H) are expected, whereas for **8**, with two Pd-$(C_6HF_4)_2$ fragments, up to four dl pairs and two meso forms could be formed. ^{19}F NMR spectroscopy has been useful for studying this problem, and the assignment of the different fluorine resonances has been made on the basis of $^{19}F-^{19}F$

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correlation spectroscopy (COSY) experiments and the expected chemical shifts according to literature.[66] The resonances that most effectively indicate the presence of atropoisomers are those of F_4. Four different doublets in a 1:1:1:1 ratio are observed for this fluorine in the spectrum of complex **6**, which indicates the existence of the four different C_6HF_4 groups expected for the two dl pairs of **6** (1:1 ratio). Although in some casual coincidence of chemical shifts, the appearance of three doublets (2:1:1 ratio) for F_2 and two complex signals (3:1 ratio) for F_6 are in accordance with the restricted rotation of the two polyfluorophenyl groups. F_3 only gives rise to two multiplets with identical integrals. The ^{1}H and ^{13}C NMR spectroscopies are not able to show the existence of atropoisomers in this compound probably because of very small differences in chemical shifts. The C_6HF_4 signal is very broad and complex, and in the C_6HF_4 (*C*H) resonance, although several lines are observed, the existence of C−F coupling constants prevents an unequivocal elucidation of the signal. For complex **8**, although it is not possible to observe separately the 16 signals theoretically expected for the whole set of isomers, at least 6 resonances are seen for F_4. (Probably only the local symmetry has a noticeable effect on the chemical shifts.) This is also in accordance with the existence of several atropoisomers considering that only two signals would be expected if the fluorophenyl rings were in a fast rotation regime. The rest of the fluorine atoms F_2, F_3, and F_6 also show patterns more complicated than those expected for a nonrestricted rotation of the fluorophenyl rings. Besides, in the ^{1}H NMR spectrum a set of three broad signals in a 2:1:1 ratio is observed for C_6HF_4 while two signals would be expected if the polyfluorophenyl groups were freely rotating. Therefore, we can conclude that in complexes **6** and **8**, and by extrapolation also in **5** and **7**, there is a restricted rotation of the polyfluorophenyl groups and they are situated in an averaged perpendicular position with respect to the coordination plane. Neither close nor distant interannular $F_{ortho}-F_{ortho}$ couplings were observed in the COSY experiment for **8**, a situation that is in contrast with the observation of other authors[66] for this type of through-space contact in comparable polyfluorophenyl groups with restricted rotation.

For complex **9**, a situation similar to that previously described for **6** would be expected, but unfortunately, **9** is always in a thermodynamic mixture with **7** and **8**, which precludes a clear identification of its ^{19}F resonances. Only the signals unambiguously discerned have been indicated in the Experimental Section, and unfortunately, the existence of atropoisomerism cannot be conclusively stated, although the presence of three different resonances for F_{para} of the C_6F_5 groups could be estimated as a valuable indication.

Cross Reaction Experiments. Several cross reaction experiments were envisaged to confirm the ease of mobility of the Pd organometallic fragments on the R−bpzpm ligands and to show the role of the free coordination position of the ligand in the case of the mononuclear complexes.

In the first experiment equimolecular amounts of **1** and the free ligand Me−bpzpm in acetone-d_6 solution were mixed. A fast reaction led to a statistical distribution of ligands with formation of compound **2** and free bpzpm according to the equilibrium

$$\mathbf{1} + \text{Me}-\text{bpzpm} \rightleftharpoons \mathbf{2} + \text{bpzpm} \qquad (2)$$

In a different experiment, equimolecular amounts of complexes **1** and **2** were dissolved in acetone-d_6, and separated allyl resonances for each compound were observed at room temperature. As the temperature was increased, the two H_{syn} resonances of both complexes coalesced, and the same phenomenon was observed for the H_{anti} signals. This is clearly a consequence of the exchange of the allyl−Pd fragments between the two ligands. The $\Delta G_c^{\ddagger}$ values at the coalescence temperatures were calculated: $\Delta G_c^{\ddagger}{}_{303} = 63.4$ and $\Delta G_c^{\ddagger}{}_{307} = 65.7$ kJ mol^{-1} for H_{anti} and H_{syn}, respectively.

A similar experiment was carried out for the dinuclear complexes **3** and **4** (which have the second coordination position blocked by an allylpalladium unit), and these compounds showed an unchanged spectrum over the temperature range studied (183−323 K). According to these data, the allylpalladium fragment must be weakly coordinated in complexes **1**−**4**, but contrary to the relative residual charge of the complexes, the barrier for the exchange of these Pd groups is higher (in fact, unattainable in our experiment) in the dinuclear complexes **3** and **4** than in the mononuclear derivatives **1** and **2**. This result points to the participation of the second coordination position in the process of interchange. This hypothesis is in accordance with the results of the study of the fluxional behavior of complex **1** (see below).

A mixture of equimolecular amounts of the mononuclear complexes **5** and **6** showed no changes over the temperature range studied (183−323 K), and this is consistent with the polyfluorophenylpalladium groups being more strongly bonded to the ligands.

The reaction of **7** with **8** at room temperature and monitored by NMR led to the progressive formation of **9**. Finally, a statistical distribution of the polyfluorophenyl groups with the establishment of the equilibrium ratio **7**/**8**/**9** = 1:1:2 took place. The corresponding resonances are separated in the NMR spectrum over the temperature range studied (183−323 K), and no coalescences were observed. The equilibrium **7** + **8** ⇌ **9** must be established by thermodynamic control, but the energy barrier for the exchange is too high to observe the process by means of NMR coalescences.

From the results described in this section it can be concluded that the exchange between the polyfluorophenylpalladium fragments must occur at higher energies than with allylpalladium groups, but in any case, the dissociation of the metallic moieties from the N-donor ligands is possible. The exchange is favored by the existence of a free coordination position in the ligand.

Fluxional Behavior of Complexes 1 and 3. (a) Complex 3. In the ^{1}H NMR spectra, the methyl, H_{syn}, and H_{anti} signals of the allyl groups are single at room temperature while they are split at 183 K (see Table 1). Assignment of H_{syn} and H_{anti} resonances was performed by nuclear Overhauser effect (NOE) experiments and H,H correlations. (For example, irradiation at the frequency of H_2 of the pyrimidine ring shows an NOE in the H_{syn} and H_{anti} close to this ring; see $H_{s'}$ and $H_{a'}$ in Table 1, and see also Scheme 1.) Some coalescences have been measured and the corresponding free activation energies at the coalescence temperature ($\Delta G_c^{\ddagger}$) calculated (see Table 3).

All these data correspond to the existence of two interconverting compounds: a meso form and a dl pair of enantiomers (see Scheme 3), similar to what we have found for complexes with related ligands.[49] The molecular structure of the meso form has been determined by an X-ray diffraction study (see below).

The existence at room temperature of a unique signal for the H_{syn} and the H_{anti} protons implies that at this temperature not

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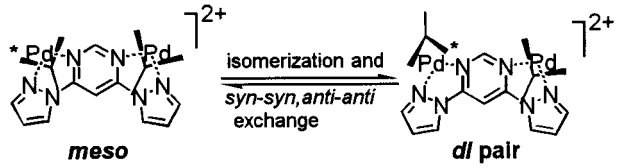
Table 3. Observed Coalescences and Calculated Free Activation Energies from the Variable Temperature ^{1}H NMR Spectra of **1** and **3** in Acetone-d_6 Solution[a]

complex	coalescence[b]	T_c (K)[c]	$\Delta G_c^{\ddagger}$ (kJ/mol)[d]
3	$H_a + H_a$	209	46.3
	$H_{s'} + H_{s'}$	214	45.8
	$(H_a + H_a) + H_{a'}$	233	50.0
	$(H_{s'} + H_{s'}) + H_s$	240	49.1
1	$H_s + H_{s'}$	255	53.9
	$H_a + H_{a'}$	263	54.2

[a] See Figures 1 and 2a. [b] See Scheme 1 for assignment. [c] Coalescence temperatures. [d] Free activation energies at the coalescence temperatures calculated by $\Delta G_c^{\ddagger} = aT[9.972 + \log(T/\delta\nu)]$ ($a = 1.914 \times 10^{-2}$).

Scheme 3



only does an isomer interconversion take place but also a syn−syn, anti−anti interchange in each allylic group. For a similar complex with a central triazine ring,[49] we have found that the apparent allyl rotation implying Pd−N bond rupture[65,73−81] is the origin of both types of interconversion. For a more detailed explanation about the mechanism, see refs 49 and 65.

(b) Complex 1. Low-Temperature Study. The ^{1}H NMR spectrum of **1** at room temperature in acetone-d_6 solution exhibits the signals for H_{syn} and H_{anti} of the allyl group as one singlet each. Because both H_{syn} and H_{anti} protons are situated in different environments, this equivalence could be indicative of an apparent allyl rotation similar to that observed for complex **3**.

At 183 K two signals for both H_{syn} (4.57 and 4.64) and H_{anti} (3.39 and 3.48) are observed. The assignment of these protons was performed by NOE experiments similar to those carried out for complex **3**. When the temperature is increased, coalescence of H_{syn} ($T_c = 255$ K) and H_{anti} ($T_c = 263$ K) is achieved (see Figure 2a). The calculated free activation energies ($\Delta G_c^{\ddagger}$) are given in Table 3, and they are comparable to the corresponding values for the same process in **3**.

(c) Complex 1. High-Temperature Study. Increasing the temperature to 323 K leads to a clear broadening of the pyrazole signals, although the boiling point of the solvent prevents the determination of the coalescence temperatures. These coalescences have been clearly observed using 1,1,2,2-tetrachloroethane-d_2 as solvent (see Figure 2b). Because of the lack of a nitrogen atom in the 5-position of the central ring to assist the palladium fragment in its migration between the two coordination sites of the ligand, the equivalence of the pyrazole nucleus should be explained by an intermolecular exchange of the allylpalladium group. Such an intermolecular process could also explain the equivalence of the two halves of the allyl group.

To determine if an intermolecular process induces the equivalence of the two pyrazolyl rings and if this process is also the origin of the syn−syn, anti−anti allylic interconversion, we decided to determine the coalescence temperatures of the allyl and pyrazolyl protons at different concentrations using 1,1,2,2-tetrachloroethane-d_2 as the solvent. In Table 4 the coalescence temperatures and the calculated free energies of activation for H_{syn}, H_{anti}, and also H_3, H_4, and H_5 of pyrazol at various concentrations are given, and Figure 3 represents the variation of $\Delta G_c^{\ddagger}$ as a function of the coalescence temperature for each proton and concentration.

From Table 4 and Figure 3 the following is evident. (i) The free activation energy for the interchange of the pyrazolyl protons is always markedly higher than for the interchange of the allyl protons, indicating the existence of two different processes. (ii) There is a clear tendency in the variation of the free activation energy with concentration in the pyrazolyl protons with $\Delta G_c^{\ddagger}$ values that increase when the concentration decreases, and this corresponds to an intermolecular process. This effect is negligible in the allyl protons, since this corresponds to an intramolecular mechanism. (iii) A negative activation entropy has been found for the process that interchanges the two pyrazolyl fragments, and this would be expected for an associative process. Although the sign of the activation entropy cannot be unequivocally deduced for the syn−syn, anti−anti allyl interchange, the values obtained for $\Delta G_c^{\ddagger}$ point to a positive sign for this parameter. (iv) The free activation energy values found for the allyl interchange in acetone are smaller than those determined in the less coordinating solvent 1,1,2,2-tetrachloroethane-d_2, a phenomenon that could be due to the participation of the solvent molecules in the process.

From the data reported, we propose that two different mechanisms are operating in complex **1**. The process of palladium coordination site exchange that interconverts the two pyrazolyl groups must be associative in nature, possibly with the participation of the free coordination site of another molecule of the ligand, as shown in Scheme 4. This is in accordance with the different barriers observed in the cross reaction experiments between mononuclear and dinuclear allylic derivatives. An apparent allyl rotation with a smaller energy barrier must also be operating in the complex. Because of the negligible effect of the concentration and the possible positive activation entropy, we propose a dissociative mechanism as the most likely alternative. Stabilization of the three-coordinate intermediate could be achieved by the coordination of the acetone molecules or even the counterion.

X-ray Structure of 3. To support our studies, we determined the molecular structure of **3** (meso form) by X-ray diffraction. The crystal structure consists of a dinuclear Pd cation and two triflate counterions, one of which is disordered. An ORTEP plot of the cation is shown in Figure 4, and a selected list of bond lengths and angles is given in Table 6.

The cation lies on a crystallographic mirror plane perpendicular to the molecular plane, which contains the atoms C(10) and C(8), so that only half of the molecule is crystallographically independent. The geometry around the Pd(1) atom is approximately square planar, and the five-membered chelate ring, including the Pd atom, shows only very small deviations from planarity. The dihedral angle between the pyrazole and the pyrimidine fragments is only 6.0(1)°. The Pd(1)−N(2) and Pd(1)−N(9) bonds form the basis of the five-membered chelate ring, and the distances are only slightly different [Pd(1)−N(2),

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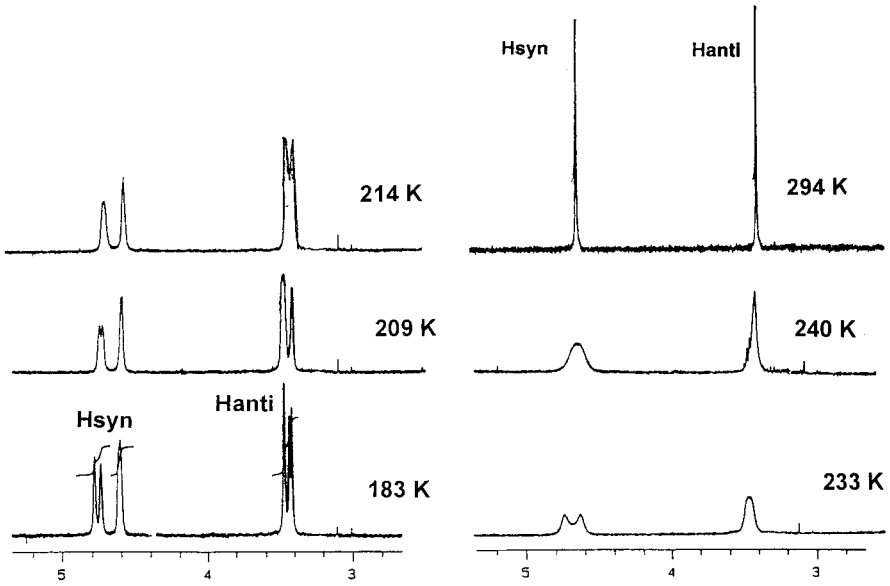


Figure 1. Variable-temperature ^{1}H NMR study (acetone-d_6) of complex **3** in the allylic region. See Table 1 for assignments. A simultaneous syn−syn, anti−anti, and meso = dl isomer exchange of these two isomers is observed (see Scheme 3).

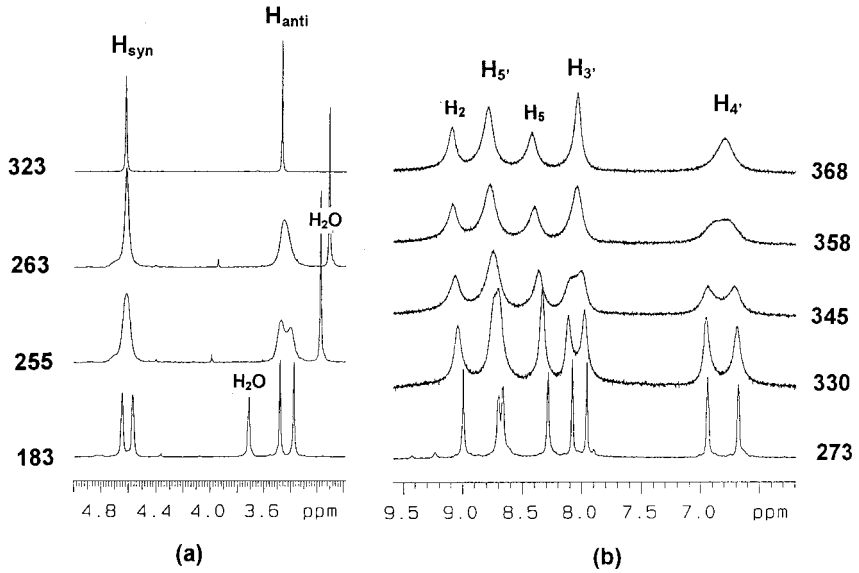


Figure 2. Variable-temperature ^{1}H NMR study of complex **1** in the allylic (a) (acetone-d_6) and the aromatic (b) (1,1,2,2-tetrachloroethane-d_2, 2.87 × 10^{-2} mol/L) regions. Temperatures are in kelvin. In the allylic region an apparent rotation of the allyl unit is observed. In the aromatic region the coordination site exchange of the allyl−Pd group on the ligand is observed.

Table 4. Observed Coalescences and Calculated Free Activation Energies from the Variable Temperature ^{1}H NMR Spectra at Different Concentrations of **1** in 1,1,2,2-Tetrachloroethane-d_2 Solution[a]

[**1**][b] (mol/L)	coalescence	T_c (K)[c]	$\Delta G_c^{\ddagger}$ (kJ/mol)[d]	[**1**][b] (mol/L)	coalescence	T_c (K)[c]	$\Delta G_c^{\ddagger}$ (kJ/mol)[d]
2.87×10^{-2}	$H_a + H_a'$	279	58.9	1.21×10^{-2}	$H_a + H_a'$	280	59.3
	$H_s + H_s'$	270	59.7		$H_s + H_s'$	272	60.2
	$H_4' + H_4''$	355	72.1		$H_4' + H_4''$	371	75.4
	$H_3' + H_3''$	345	71.7		$H_3' + H_3''$	360	74.9
	$H_5 + H_{5_1}''$	330	71.0		$H_5' + H_5''$	339.3	73.4
1.76×10^{-2}	$H_a + H_a$	279	58.9	9.56×10^{-3}	$H_a + H_a'$	280	59.1
	$H_s + H_s'$	271	59.7		$H_s + H_s'$	273	60.3
	$H_4' + H_4''$	362	73.6		$H_4' + H_4''$	371	77.1
	$H_3' + H_3''$	350	72.7		$H_3' + H_3''$	360	75.5
	$H_5' + H_5''$	334	72.4		$H_5' + H_5''$	339	74.0

[a] See Figure 2b. [b] Concentration of **1**. [c] Coalescence temperatures. [d] Free activation energies at the coalescence temperatures calculated by $\Delta G_c^{\ddagger} = aT[9.972 + \log(T/\delta\nu)]$ ($a = 1.914 \times 10^{-2}$).

2.089(4) Å; Pd(1)−N(9), 2.132(4) Å] in accordance with the expected difference in basicity of the respective heterocycles. The Pd−η^3-allyl distances are as follows: Pd(1)−C(11) = 2.100(6) Å; Pd(1)−C(12) = 2.141(5) Å; Pd(1)−C(13) = 2.119(6) Å. These latter values are in the range expected for a Pd(II)−allyl bond with nitrogen ligands in trans positions. The

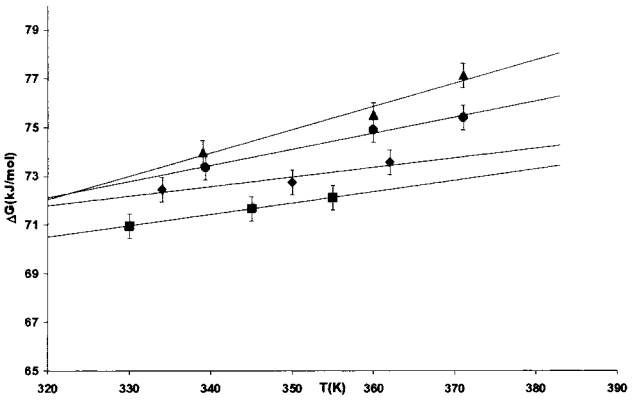


Figure 3. Linear plot of $\Delta G_c^{\ddagger}$ (kJ/mol) versus T_c (K) for complex **1** (see Table 4): (■) 2.87×10^{-2} mol/L; (◆) 1.76×10^{-2} mol/L; (●) 1.21×10^{-2} mol/L; (▲) 9.56×10^{-3} mol/L.

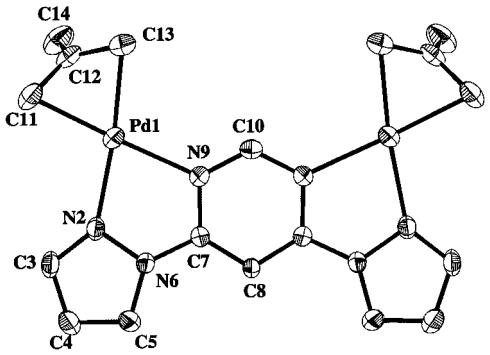
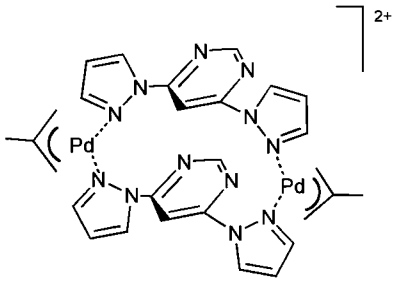


Figure 4. ORTEP view with atomic numbering of the cation of **3** (meso form) (30% probability ellipsoids).

Scheme 4



coordination plane defined by the Pd(1)−N(2)−N(9) atoms is approximately perpendicular to the allyl ligand plane (defined by the C(11)−C(12)−C(13) atoms) with a dihedral angle of 116.4(4)°. In the allyl ligand the C(12)−CH_3 vector points away from the metal. C(14) is 0.306(8) Å away from the allylic plane.

X-ray Structure of 6. An ORTEP plot of the structure of complex **6** is shown in Figure 5, and a selected list of bond lengths and angles is given in Table 6. The palladium atom is in an approximately square plane geometry with the bpzpm ligand coordinated in a bidentate fashion with distances Pd(1)−N(1) of 2.101(6) and Pd(1)−N(6) of 2.062(6) Å. As in complex **3**, the difference found in the Pd−N distances is in accordance with the basicities of the respective heterocycles. Two tetrafluorophenyl groups complete the coordination sphere around the metal. The bpzm ligand is approximately planar. The dihedral angle between the coordinated pyrazolyl and the pyrimidine ring is 5.4(3)°, and that formed between pyrimidine and the free pyrazolyl group is 5.1(3)°. The five-membered metallacycle (Pd(1), N(6), N(5), C(4), N(1)) is also nearly planar. The two tetrafluorophenyl groups are bound to the square-planar unit (C21, N6, N1, C11, Pd1) with dihedral angles of 78.3(2)° and 105.9(3)°, the dihedral angle between the two rings being 93.8(3)°. In each unit cell a dl pair is present, with the two enantiomers being related by an inversion center. Because the

Table 5. Crystallographic Data for **3** and **6**

	3	**6**
empirical formula	$C_{20}H_{22}F_6N_6O_6Pd_2S_2$	$C_{22}H_{10}F_8N_6Pd$
fw	833.36	616.76
space group	*I*2/*m*	$P\bar{1}$
a, Å	9.368(2)	8.845(6)
b, Å	16.191(3)	12.6609(9)
c, Å	20.228(6)	12.826(3)
α, deg	90	88.45(2)
β, deg	101.26(3)	74.36(3)
γ, deg	90	89.32(2)
V, Å^3	3009.1(12)	1382.6(10)
Z	4	2
T, °C	25	25
λ, Å	0.710 70	0.710 70
ρ_{calcd}, g/cm^3	1.840	1.481
μ, cm^{-1}	14.16	7.45
R_1 [$I > 2\sigma(I)$][a]	0.0361	0.0631
wR2 [$I > 2\sigma(I)$][b]	0.0875	0.2061

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Table 6. Crystal Data and Structure Refinement for **6** and **3**

bond length (Å)		bond angle (deg)	
		6	
Pd(1)−C(11)	1.984(8)	C(11)−Pd(1)−C(21)	85.9(3)
Pd(1)−C(21)	1.999(7)	C(11)−Pd(1)−N(6)	175.5(3)
Pd(1)−N(6)	2.062(6)	C(21)−Pd(1)−N(6)	98.7(3)
Pd(1)−N(1)	2.101(6)	C(11)−Pd(1)−N(1)	97.7(3)
N(1)−C(4)	1.326(9)	C(21)−Pd(1)−N(1)	175.5(3)
N(3)−C(2)	1.387(9)	N(6)−Pd(1)−N(1)	77.8(2)
N(5)−N(6)	1.374(7)	C(4)−N(1)−Pd(1)	115.2(5)
N(5)−C(4)	1.411(8)	N(6)−N(5)−C(4)	117.2(5)
		N(5)−N(6)−Pd(1)	113.9(4)
		3	
Pd(1)−N(2)	2.089(4)	N(2)−Pd(1)−C(11)	105.7(2)
Pd(1)−C(11)	2.100(5)	N(2)−Pd(1)−C(13)	172.8(2)
Pd(1)−C(13)	2.119(5)	C(11)−Pd(1)−C(13)	68.2(2)
Pd(1)−N(9)	2.132(4)	N(2)−Pd(1)−N(9)	76.80(14)
Pd(1)−C(12)	2.141(4)	C(11)−Pd(1)−N(9)	175.6(2)
N(2)−N(6)	1.371(5)	C(13)−Pd(1)−N(9)	109.1(2)
N(6)−C(7)	1.379(5)	N(2)−Pd(1)−C(12)	138.1(2)
C(7)−N(9)	1.361(5)	N(6)−N(2)−Pd(1)	114.0(3)
C(7)−C(8)	1.370(5)	N(2)−N(6)−C(7)	119.1(3)
N(9)−C(10)	1.329(4)	N(9)−C(7)−N(6)	115.0(3)
		C(7)−N(9)−Pd(1)	115.1(3)
		C(13)−C(12)−C(11)	115.2(5)
		C(13)−C(12)−C(14)	122.3(6)
		C(11)−C(12)−C(14)	121.0(6)

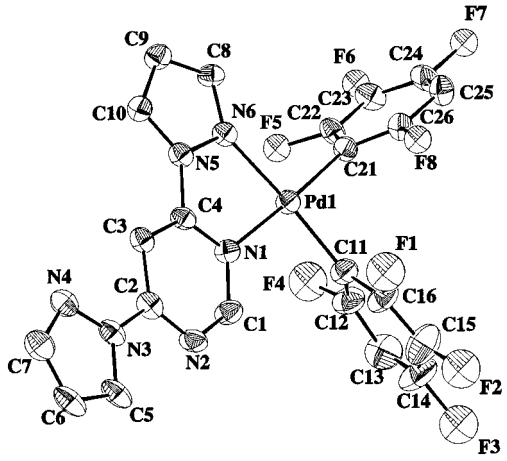


Figure 5. ORTEP view with atomic numbering of **6** (30% probability ellipsoids).

F(2) atom is disordered over the two meta positions (occupancy factors of 0.5), the two dl pairs are present along the crystal. These occupancy factors are in accordance with the presence of the two atropoisomers in a 1:1 ratio, as has been deduced by NMR.

Conclusions

We have described and characterized new mono- and dinuclear palladium complexes with the bpzpm and Me−bpzpm ligands. Coordination of the first metallic center induces the bonding in the second position in a kind of chemical symbiosis driven by the ligand rather than the metal center, as is usually the case. This behavior can also be considered as an expression of molecular recognition, the ligand being a ditopic receptor. The study of the exchange of the metallic fragments allows the conclusion to be drawn that the strength of the Pd−N bonds depends on the ancillary ligands and, in dinuclear complexes, on the presence of identical or very similar metallic fragments. The polyfluorophenyl groups have a restricted rotation around the Pd−C bond and are situated on average in a perpendicular orientation with respect to the coordination plane. Several atropoisomers for the complexes **6** and **8**, with *m*-C_6HF_4, have been detected.

The fluxional behavior of complexes **1** and **3** has been studied, and the free energies of activation have been calculated from the coalescence temperatures determined by NMR spectroscopy. Two processes have been detected in complex **1**: an intramolecular apparent allyl rotation and an intermolecular process of interconversion of the two pyrazolyl groups, with negative activation entropy, for which an associative mechanism is proposed. The existence of this latter process indicates that the presence of a nitrogen atom is not necessary in the 5-position of the central heterocycle of the ligands in order for an interconversion of the two pyrazolyl groups to take place. However, participation of a nitrogen atom in the 5-position cannot be excluded when it is present.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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