Kinetic Study of the Dynamic Behavior of [M(C_6F_5)X($OPPy_nPh_{3-n}$)] (M = Pd, Pt; X = C_6F_5, Halide; *n* = 1−3): Activation Parameters for the Restricted Rotation about the M−Aryl Bond and for the Py Associative Exchange

Juan A. Casares, Pablo Espinet,* Jesús M. Martínez-Ilarduya, and Yong-Shou Lin

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain

Received October 10, 1996[⊗]

The behavior in $CDCl_3$ of complexes of the type [M(C_6F_5)X($OPPy_nPh_{3-n}$)] (M = Pd, Pt; X = C_6F_5; halide; *n* = 1−3) has been studied by ^{19}F and ^1H NMR spectroscopy. For the nonplanar N,N-chelating ligands with *n* = 2, 3, two processes have been observed and their activation parameters, $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$, have been determined, using magnetization transfer (MT) or line-shape analysis methods. The rotation of the C_6F_5 groups about the M−C_{ipso} bond occurs in the square-planar species without dissociation, and its rate depends on the size of the coordinated atom X, in the order C_6F_5 > Cl > Br > I. The rotation for the last three is very slow and is detected only by MT. With $OPPy_3$ the occurrence of associative exchange of free and coordinated Py groups is observed (studied only for X = C_6F_5, Cl), the rate depending on M and X in the order Pd > Pt and Cl > C_6F_5. Only for [Pd(C_6F_5)Cl($OPPy_3$)] is this rate faster than the C_6F_5 rotation, producing the effect of an apparent rotation with anomalously low activation parameters. The structures of two complexes, [Pd(C_6F_5)Br($OPPy_2Ph$)] and [Pd(C_6F_5)$_2$($OPPy_2Ph$)], have been studied by X-ray diffraction.

Introduction

The observation of restrictions to rotation about M−aryl bonds in square-planar complexes of Pd and Pt has been reported several times in the last few years.[1−6] Although the aryl complexes where this phenomenon is observed usually carry at least one ortho substituent (N=NPh, CH=NMe, Me, CH_2R, OMe), it has been shown that noticeable restriction leading to slow rotation can also occur in ortho-unsubstituted aryl rings flanked by bulky ligands in the coordination plane, as in [Pt(C_6H_3-3,5-Br_2)I(DIOP)].[5] A full kinetic study determining the activation parameters for the rotation, $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$, has been made only in the case of [Pt(Ar)$_2$(COD)] (Ar = 2-(CH_2OMe)-5-R-C_6H_3; R = H, Me),[1] whereas only $\Delta G^{\ddagger}$ at the coalescence temperature has been determined for [Pt(Ar)Cl(COD)],[1a] [Pd(C_6H_4-2-X)(η^5-C_5H_4R)L] (X = N=NPh, CH=NMe)[2] and for [Pd(C_6H_4-CH_2CH_2OH-*p*)Br(tmeda)].[4] In the latter case it was shown that the rotation (fast in CD_3OD but not detected in $CDCl_3$ at 200 MHz) involves Br dissociation; thus, it cannot be strictly considered as a rotation occurring in a square-planar complex.

Since the most stable conformation of a square-planar aryl derivative is that with the aryl ring or rings roughly normal to the coordination plane,[2] the aryl ligand can be used as an indicator of whether the coordination plane is or is not a mirror plane on the NMR time scale, provided that it is firmly established that its rotation has a sufficiently high energy barrier. Conversely, ancillary ligands that introduce a dissymmetry in the molecule, such that the coordination plane is not a mirror plane, should permit the study of the M−aryl rotational barriers.

Fluorinated aryls, such as C_6F_5 and C_6-3,5-Cl_2F_3, are particularly good for easy observation of the equivalence or nonequivalence of their halves because (i) ^{19}F NMR spectra are simple and free from other signals, compared to ^1H NMR spectra, (ii) their F_{ortho} signals appear well-separated from the rest and are easy to observe, (iii) the difference in chemical shift between two nonequivalent F_{ortho} signals in the same aryl ring is usually quite large (in Hz), certainly bigger than the usual differences between two nonequivalent H_{ortho} signals in ^1H spectroscopy, which makes the processes "slower" in ^{19}F than in ^1H NMR spectroscopy, and (iv) fluxional processes making the coordination plane a mirror plane on the NMR time scale are observed as an apparent rotation of the fluoroaryl group exchanging their two F_{ortho} atoms, i.e. a mathematically simple exchange between two equally populated sites.

The hindrance to rotation in fluoroaryl square-planar complexes was first observed in [PtRCl(dcy)] (R = C_6F_5,

* To whom correspondence should be addressed. E-mail: espinet@cpd.uva.es.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

(1) (a) Baumgärtner, R.; Brune, H. *J. Organomet. Chem.* **1988**, *350*, 115−127. (b) Debaerdemaeker, T.; Weisemann, C.; Brune, H. A. *J. Organomet. Chem.* **1988**, *350*, 91−99.

(2) Anderson, G. K.; Cross, R. J.; Manojlovic-Muir, L.; Muir, K. W.; Rocamora, M. *Organometallics* **1988**, *7*, 1520−1525.

(3) Rieger, A. L.; Carpenter, G. B.; Rieger, P. H. *Organometallics* **1993**, *12*, 842−847.

(4) Alsters, P. L.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1639−1647.

(5) Brown, J. M.; Pérez-Torrente, J. J.; Alcock, N. W.; Clase, H. J. *Organometallics* **1995**, *14*, 207−213.

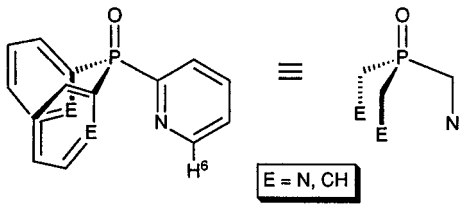
(6) (a) Brown, J. M.; Pérez-Torrente, J. J.; Alcock, N. W. *Organometallics* **1995**, *14*, 1195−1203. (b) Alcock, N. W.; Brown, J. M.; Pérez-Torrente, J. J. *Tetrahedron Lett.* **1992**, *3*, 389−392.

S0276-7333(96)00861-8 CCC: $14.00

p-MeOC$_6$F$_4$; dcy = dicyclopentadiene) and in [Pt(*p*-MeOC$_6$F$_4$)$_2$(dcy)] (apparently rigid at room temperature) and was attributed to the rotation involving unacceptably close H···F approaches (<1 Å).[7] The lack of rotation in [Pd(C$_6$F$_5$)$_2$(L-L)] and [Pd(C$_6$F$_5$)Br(L-L)] proved the lack of planarity in the coordinated 3,3′-dimethyl-2,2′-biindazole, in contrast to the planarity of their 5,5′- and 7,7′-isomers.[8] Nonequivalence of the two F$_{ortho}$ atoms at room temperature was also observed, for instance, in [{Pd(C$_6$F$_5$)(PPh$_3$)}$_2$(μ-OH)(μ-NHC$_6$H$_4$X-*p*)],[9] [{Pd(C$_6$F$_5$)(8-methylquinoline)}$_2$(μ-bpy)],[10] and [Pd$_3$(μ_3-SPPh$_2$)$_2$(C$_6$F$_5$)$_2$L(PPh$_3$)$_2$]ClO$_4$ (L = ortho-metalated ligand).[11] The use of spin magnetization transfer allows one to detect dynamic processes too slow for direct observation by variable-temperature NMR spectroscopy. Thus, a very detailed study of the complexes [Pd(C$_6$F$_5$)X(SPPy$_2$Ph-*N*,*S*)] (X = Cl, Br, I; Py = 2-pyridyl), which are apparently rigid in CDCl$_3$ although they show fast exchange in d_6-acetone, has proven that a very slow C$_6$F$_5$ rotation occurs with X dissociation to give a 14 e$^-$ intermediate.[12] This means that the barrier to a putative rotation in these tetracoordinated species should be higher than those found for the rotation with dissociation (for X = Cl: $\Delta H^{\ddagger} = 60.0$ kJ mol^{-1}; $\Delta S^{\ddagger} = -35.8$ J K^{-1} mol^{-1}; $\Delta G^{\ddagger} = 70.7$ kJ mol^{-1} at 298 K). These examples support the postulate that the rotation about the M−C$_{ipso}$ bond of an aryl ring fluorinated in the two ortho positions in a square-planar Pd or Pt complex can have a fairly high activation energy, so that in terms of direct observation by ^{19}F NMR it could be said that the groups do not rotate at room temperature in the cases mentioned.

On the other hand, many cases have been reported of Pd and Pt pentafluorophenyl derivatives showing temperature-dependent ^{19}F NMR spectra (equivalent to the effect of a rotation) due to the occurrence of fluxional processes not involving C$_6$F$_5$ rotation.[13] Finally, there are also many papers where free rotation of the C$_6$F$_5$ groups can be argued.[13b,e,14] Since a wrong assumption of free rotation in a square-planar coordination would hide the true dynamic process responsible for the equivalence observed, it seems convenient to have a closer estimation of the barriers to rotation in C$_6$F$_5$ and related Pd and Pt derivatives in order to assess when the assumption of easy rotation is plausible.

Chart 1



In this paper we study the behavior in CDCl$_3$ of complexes of the type [M(C$_6$F$_5$)X(OPPy$_n$Ph$_{3-n}$)] (M = Pd, Pt; X = C$_6$F$_5$, halide; n = 1−3) aiming to determine the activation parameters for the rotation of the C$_6$F$_5$ groups about the M−C$_{ipso}$ bond (M = Pd, Pt) in a square-planar coordination or, alternatively, the occurrence of ligand dissociative or associative processes. A sketch of the ligands and their simplified representation in Scheme 1 is depicted in Chart 1.

Experimental Section

General methods and NMR techniques, including magnetization transfer experiments, have been described in a previous paper.[12] [Pd(C$_6$F$_5$)Br(NCMe)$_2$], *cis*-[Pd(C$_6$F$_5$)$_2$(ether)$_2$], (NBu$_4$)$_2$[M$_2$(μ-Y)$_2$(C$_6$F$_5$)$_2$X$_2$] (M = Pd, X = Br, C$_6$F$_5$, Y = Br; n = 2, 3; M = Pt, X = C$_6$F$_5$, Y = Cl), and [M$_2$(μ-Cl)$_2$(C$_6$F$_5$)$_2$(tht)$_2$] (M = Pd, Pt; tht = tetrahydrothiophene) were prepared by reported methods.[15,18b] The ligands OPPy$_n$Ph$_{3-n}$ were also made by literature methods.[16]

Preparation of the Complexes. All the reactions were carried out under nitrogen atmosphere in deoxygenated solvents. The isolated products are stable in the air, but the syntheses give side products and lower yields when an inert atmosphere is not used.

[Pd(C$_6$F$_5$)Br(OPPyPh$_2$)] (1). To a solution of [Pd(C$_6$F$_5$)Br(NCMe)$_2$] (0.197 g, 0.453 mmol) in acetonitrile (20 mL) was added OPPyPh$_2$ (0.128 g, 0.458 mmol) in the same solvent (10 mL). The yellow solution was stirred for 10 min and evaporated to dryness. The resulting yellow oil was triturated in 10 mL of diethyl ether to give a yellow solid with metallic palladium impurity. The solid was extracted in acetone (10 mL) and filtered through charcoal, and 20 mL of *n*-hexane was added to precipitate yellow **1**. Yield: 0.16 g, 56%. Anal. Calcd: C, 43.67; N, 2.21; H, 2.23. Found: C, 43.58; N, 2.19; H, 2.52. IR (cm^{-1}): ν(P=O), 1134; X-sensitive C$_6$F$_5$, 777.

[Pd(C$_6$F$_5$)$_2$(OPPyPh$_2$)] (2). To a solution of *cis*-[Pd(C$_6$F$_5$)$_2$(ether)$_2$] (0.379 mmol) in acetonitrile (30 mL) was added OPPyPh$_2$ (0.105 g, 0.376 mmol). The colorless solution was

(7) Deacon, G. B.; Gatehouse, B. M.; Nelson-Reed, K. T. *J. Organomet. Chem.* **1989**, *359*, 267−283.
(8) Albéniz, A. C.; Cuevas, J. C.; Espinet, P.; de Mendoza, J.; Prados, P. *J. Organomet. Chem.* **1991**, *410*, 257−263.
(9) Ruiz, J.; Martínez, M. T.; Vicente, C.; García, G.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **1993**, *12*, 4321−4326.
(10) Forniés, J.; Navarro, R.; Sicilia, V.; Tomás, M. *Inorg. Chem.* **1993**, *32*, 3675−3681.
(11) Forniés, J.; Martínez, F.; Navarro, R.; Urrialobeitia, E. P.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1995**, 2805−2811.
(12) Casares, J. C.; Coco, S.; Espinet, P.; Lin, Y. S. *Organometallics* **1995**, *14*, 3058−3067.
(13) (a) Forniés, J.; Martínez, F.; Navarro, R.; Urrialobeitia, E. P. *Organometallics* **1996**, *15*, 1813−1819. (b) Ara, I.; Berenguer, J. R.; Forniés, J.; Lalinde, E.; Tomás, M. *Organometallics* **1996**, *15*, 1014−1022. (c) Forniés, J.; Gómez-Saso, M. A.; Lalinde, E.; Martínez, F.; Moreno, M. T. *Organometallics* **1992**, *11*, 2873−2883. (d) Casas, J. M.; Forniés, J.; Martín, A.; Menjón, B.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1995**, 2949−2954. (e) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martínez, F.; Urriolabeitia, E.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1994**, 1291−1299. (f) Abel, E. W.; Orrell, K. G.; Osborne, A. G.; Pain, H. M.; Sik, V.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1994**, 3341−3349. (g) Forniés, J.; Martínez, F.; Navarro, R.; Urriolabeitia, E.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2147−2152. (h) Amador, U.; Delgado, E.; Forniés, J.; Hernández, E.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **1995**, *34*, 5279−5284. (i) Coco, S.; Espinet, P. *J. Organomet. Chem.* **1994**, *484*, 113−118.
(14) (a) Falvello, L. R.; Forniés, J.; Navarro, R.; Rueda, A.; Urrialobeitia, E. P. *Organometallics* **1996**, *15*, 309−316. (b) Forniés, J.; Navarro, R.; Urrialobeitia, E. P. *J. Organomet. Chem.* **1993**, *452*, 241. (c) Forniés, J.; Menjón, B.; Gómez, N.; Tomás, M. *Organometallics* **1992**, *11*, 1187−1193. (d) López, G.; Ruiz, J.; Vicente, C.; Martí, J. M.; García, G.; Chaloner, P. A.; Hitchcock, P. B.; Harrison, R. M. *Organometallics* **1992**, *11*, 4090−4096. (e) Usón, J.; Forniés, J.; Tomás, M.; Menjón, B.; Welch, A. J. *Organometallics* **1988**, *7*, 1318−1323. (f) Casas, J. M.; Falvello, L. R.; Forniés, J.; Martín, A. *Inorg. Chem.* **1996**, *35*, 56−62. (g) Sánchez, G.; Ruiz, J.; Santana, M. D.; García, G.; López, G.; Hermoso, J. A.; Martínez Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1994**, 19−23. (h) López, G.; Ruiz, J.; García, G.; Vicente, C.; Rodríguez, V.; Sánchez, G.; Hermoso, J. A.; Martínez Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1992**, 1681−1686. (i) López, G.; Sánchez, G.; García, G.; García, J.; Martínez, A.; Hermoso, J. A.; Martínez Ripoll, M. *J. Organomet. Chem.* **1992**, *435*, 193−202.
(15) (a) Albéniz, A. C.; Espinet, P.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1990**, *9*, 1079−1085. (b) Usón, R.; Forniés, J.; Nalda, J. A.; Lozano, M. J.; Espinet, P.; Albéniz, A. C. *Inorg. Chim. Acta* **1989**, *156*, 251−256. (c) Usón, R.; Forniés, J. *Organomet. Synth.* **1986**, *3*, 161−185. (d) Usón, R.; Forniés, J.; Martínez, F.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1980**, 888−894. Usón, R.; Forniés, J.; Navarro, R.; García, M. P. *Inorg. Chim. Acta* **1979**, *33*, 69−75.
(16) Newcome, G.; Hagen, D. C. *J. Org. Chem.* **1978**, *43*, 947−949.

stirred for 10 min, whereupon a white precipitate of **2** appeared, which was filtered, washed with diethyl ether, and dried. Yield: 0.25 g, 92%. Anal. Calcd: C, 48.39; N, 3.39; H, 1.96. Found: C, 48.52; N, 3.36; H, 2.02. IR (cm^{-1}): ν(P═O), 1134; X-sensitive C_6F_5, 798, 789.

[Pd(C_6F_5)Cl($OPPy_2Ph$)] (3a). To a solution of [$Pd_2(\mu$-Cl)$_2$(C_6F_5)$_2$(tht)$_2$] (150 mg, 0.19 mmol) in 10 mL of Cl_2CH_2 was added the ligand $OPPy_2Ph$ (106 mg, 0.38 mmol). After 30 min the solution was concentrated to 5 mL; addition of ether afforded a yellow precipitate, which was filtered, washed with ether, and dried. Yield: 0.177 g, 79%. Anal. Calcd: C, 44.85; N, 4.75; H, 2.22. Found: C, 44.70; N, 4.63; H, 2.13. IR (cm^{-1}): ν(P═O), 1217; X-sensitive C_6F_5, 775; ν(Pd−Cl), 325.

[Pd(C_6F_5)Br($OPPy_2Ph$)] (3b). To a solution of (NBu_4)$_2$[$Pd_2(\mu$-Br)$_2$(C_6F_5)$_2$$Br_2$] (1.00 g, 0.740 mmol) in dichloromethane (30 mL) was added $OPPy_2Ph$ (0.456 g, 1.628 mmol). The yellow solution was stirred for 30 min and then concentrated to 10 mL. Addition of ethanol (30 mL) afforded a yellow precipitate, **3b**, which was filtered, washed with ethanol, and dried. Yield: 0.825 g, 88%. Anal. Calcd: C, 41.72; N, 4.42; H, 2.05. Found: C, 41.93; N, 4.35; H, 2.06. IR (cm^{-1}): ν(P═O), 1217; X-sensitive C_6F_5, 773.

[Pd(C_6F_5)I($OPPy_2Ph$)] (3c). To a solution of **3b** (0.215 g, 0.339 mmol) in acetone (50 mL) was added NaI (0.609 g, 0.34 mmol). The mixture was stirred for 1 h to give an orange solution, which was then evaporated to dryness. The residue was extracted in dichloromethane (30 mL), the extract was filtered, and the filtrate was concentrated to 10 mL. Addition of ethanol (15 mL) and further evaporation of the dichloromethane afforded orange needles of **3c**, which were filtered, washed with ethanol, and dried. Yield: 0.194 g, 84%. Anal. Calcd: C, 38.82; N, 4.11; H, 1.92. Found: C, 38.79; N, 4.01; H, 1.85. IR (cm^{-1}): ν(P═O), 1216; X-sensitive C_6F_5, 773.

[Pd(C_6F_5)$_2$($OPPy_2Ph$)] (4). To a suspension of (NBu_4)$_2$[$Pd_2(\mu$-Br)$_2$(C_6F_5)$_4$] (0.5 g, 0.327 mmol) in ethanol (25 mL) was added $OPPy_2Ph$ (0.196 g, 0.700 mmol). The mixture was stirred for 2 h and then concentrated to 10 mL. The resulting white precipitate, **4**, was filtered, washed with ethanol, and dried. Yield: 0.408 g, 85%. Anal. Calcd: C, 46.71; N, 3.89; H, 1.80. Found: C, 46.82; N, 3.75; H, 1.89. IR (cm^{-1}): ν(P═O), 1213; X-sensitive C_6F_5, 794, 776.

[Pt(C_6F_5)Cl($OPPy_2Ph$)] (5). To a suspension of [$Pt_2(\mu$-Cl)$_2$(C_6F_5)$_2$(tht)$_2$] (0.40 g, 0.412 mmol) in ethanol (30 mL) was added $OPPy_2Ph$ (0.253 g, 0.905 mmol). The mixture was refluxed for 1 h and then concentrated to 10 mL and cooled in the freezer at −20 °C. The resulting white crystals, **4**, were filtered, washed with ethanol, and dried (0.25 g). A second crop (0.21 g) was obtained upon addition of *n*-hexane to the mother liquors. Total yield: 0.46 g, 82%. Anal. Calcd: C, 38.98; N, 4.13; H, 1.93. Found: C, 39.19; N, 4.05; H, 2.11. IR (cm^{-1}): ν(P═O), 1202; X-sensitive C_6F_5, 771; ν(Pt−Cl), 339.

[Pt(C_6F_5)$_2$($OPPy_2Ph$)] (6). To a suspension of (NBu_4)$_2$[$Pt_2(\mu$-Cl)$_2$(C_6F_5)$_4$] (0.120 g, 0.074 mmol) in acetone (20 mL) was added $TlBF_4$ (0.043 g, 0.148 mmol) and $OPPy_2Ph$ (0.046 g, 0.16 mmol). The mixture was stirred for 2 h. The resulting precipitate (TlCl) was filtered off, and the filtrate was evaporated to dryness to give a colorless oil. Trituration with ethanol afforded a white precipitate precipitate, **6**, which was filtered, washed with ethanol, and dried. Yield: 0.085 g, 70%. Anal. Calcd: C, 41.54; N, 3.46; H, 1.62. Found: C, 41.43; N, 3.40; H, 1.56. IR (cm^{-1}): ν(P═O), 1210; X-sensitive C_6F_5, 805, 796.

[Pd(C_6F_5)Cl($OPPy_3$)] (7) was obtained as described for **3a**, using $OPPy_3$. Yield: 85%. Anal. Calcd: C, 42.74; N, 7.12; H, 2.05. Found: C, 43.08; N, 7.12; H, 2.16. IR (cm^{-1}): ν(P═O), 1220; X-sensitive C_6F_5, 777; ν(Pd−Cl), 329.

[Pd(C_6F_5)$_2$($OPPy_3$)] (8) was obtained as described for **4**, using $OPPy_3$. Yield: 67%. Anal. Calcd: C, 44.94; N, 5.48; H, 1.68. Found: C, 45.02; N, 5.33; H, 1.50. IR (cm^{-1}): ν(P═O), 1213; X-sensitive C_6F_5, 771, 782.

[Pt(C_6F_5)Cl($OPPy_3$)] (9) was obtained as described for **5**, using $OPPy_3$. Yield: 43%. Anal. Calcd: C, 37.12; N, 6.10; H, 1.83. Found: C, 37.16; N, 6.19; H, 2.18. IR (cm^{-1}): ν(P═O), 1221; X-sensitive C_6F_5, 806; ν(Pt−Cl), 334.

[Pt(C_6F_5)$_2$($OPPy_3$)] (10) was obtained as described for **6**, using $OPPy_3$. Yield: 45%. Anal. Calcd: C, 40.31; N, 5.15; H, 1.85. Found: C, 40.01; N, 5.18; H, 1.49. IR (cm^{-1}): ν(P═O), 1213; X-sensitive C_6F_5, 806, 796.

X-ray Structure Analysis of [Pd(C_6F_5)Br($OPPy_2Ph$)] (3b) and [Pd(C_6F_5)$_2$($OPPy_2Ph$)]·2$CHCl_3$ (4). Suitable crystals of [Pd(C_6F_5)Br(O═PPy_2Ph-*N*,*N*)] and [Pd(C_6F_5)$_2$(O═PPy_2Ph-*N*,*N*)]·2$CHCl_3$ for X-ray diffraction were grown by crystallization from their $CHCl_3$ solutions. The diffraction data were collected on a Rigaku AFC 5R diffractometer for [Pd(C_6F_5)Br(O═PPy_2Ph)] and an Enraf-Nonius CAD4 diffractometer for [Pd(C_6F_5)$_2$(O═PPy_2Ph)]·2$CHCl_3$, using graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). Crystal, collection, and refinement data are summarized in Table 1.

All data for both structures were corrected for Lorentz, polarization, and absorption (DIFABS). Anisotropic decay corrections were also applied for [Pd(C_6F_5)$_2$(O═PPy_2Ph)]·2$CHCl_3$. The structure of [Pd(C_6F_5)Br(O═PPy_2Ph)] was solved by the heavy-atom method and that of [Pd(C_6F_5)$_2$(O═PPy_2Ph)]·2$CHCl_3$ by direct methods; both were expanded using Fourier techniques and refined by full-matrix least-squares methods using the program of the Enraf-Nonius SDP package on a Micro Vax-II computer.[17] All non-hydrogen atoms in both molecules were refined with anisotropic thermal parameters; the hydrogen atoms were positioned by calculation and fixed during the refining.

Results

The following complexes were synthesized by reacting the corresponding $OPPy_nPh_{3-n}$ ligand with a convenient Pd or Pt precursor: [Pd(C_6F_5)Br($OPPyPh_2$)] (**1**); [Pd(C_6F_5)$_2$($OPPyPh_2$)] (**2**); [Pd(C_6F_5)X($OPPy_2Ph$)] (X = Cl (**3a**), Br (**3b**), I (**3c**)); [Pd(C_6F_5)$_2$($OPPy_2Ph$)] (**4**); [Pt(C_6F_5)Cl($OPPy_2Ph$)] (**5**); [Pt(C_6F_5)$_2$($OPPy_2Ph$)] (**6**); [Pd(C_6F_5)Cl($OPPy_3$)] (**7**); [Pd(C_6F_5)$_2$($OPPy_3$)] (**8**); [Pt(C_6F_5)Cl($OPPy_3$)] (**9**); [Pt(C_6F_5)$_2$($OPPy_3$)] (**10**). The methods are given in eqs 1−5.

$$[Pd(C_6F_5)Br(NCMe)_2] + OPPyPh_2 \rightarrow [Pd(C_6F_5)Br(OPPyPh_2)] + 2NCMe \quad (1)$$

$$cis\text{-}[Pd(C_6F_5)_2(OEt_2)_2] + OPPyPh_2 \rightarrow [Pd(C_6F_5)_2(OPPyPh_2)] + 2OEt_2 \quad (2)$$

$$(NBu_4)_2[M_2(\mu\text{-}Y)_2(C_6F_5)_2X_2] + 2OPPy_nPh_{3-n} \rightarrow 2[M(C_6F_5)X(OPPy_nPh_{3-n})] + 2(NBu_4)Y \quad (3)$$

M = Pd, X = Br, C_6F_5, Y = Br, n = 2, 3;
M = Pt, X = C_6F_5, Y = Cl, n = 2, 3

$$[M_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2] + 2OPPy_nPh_{3-n} \rightarrow 2[M(C_6F_5)Cl(OPPy_nPh_{3-n})] + 2\ tht \quad (4)$$

M = Pd, Pt, n = 2,3

$$[Pd(C_6F_5)Br(OPPy_2Ph)] + NaI \rightarrow [Pd(C_6F_5)I(OPPy_2Ph)] + NaBr \quad (5)$$

All the complexes are yellow solids, stable both in the solid state and in chloroform solution, except **1**, which

(17) Frenz, B. A. The Enraf-Nonius CAD 4 SDP-A Real-time System for Concurent X-Ray Data Collection and Crystal Structure Determination. In *Computing in Crystallography*; Schenk, H., Olthof-Hazelkamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 64−71.

Table 1. Crystallographic Data for [Pd(C$_6$F$_5$)Br(OPPy$_2$Ph)] (3b) and [Pd(C$_6$F$_5$)$_2$(OPPy$_2$Ph)]·2CHCl$_3$ (4)

compd	[Pd(C$_6$F$_5$)Br(OPPy$_2$Ph)]	[Pd(C$_6$F$_5$)$_2$(OPPy$_2$Ph)]·2CHCl$_3$
formula	$C_{22}H_{13}BrF_5N_2OPPd$	$C_{30}H_{15}Cl_6F_{10}N_2OPPd$
fw	633.64	959.54
temp, °C	22	23
cryst syst	monoclinic	triclinic
cryst size, mm^3	0.20 × 0.30 × 0.45	0.40 × 0.40 × 0.60
space group	$P2_1/n$	$P\bar{1}$
a, Å	8.757(2)	12.142(2)
b, Å	10.324(2)	17.217(4)
c, Å	23.675(4)	17.543(3)
α, deg		106.24(2)
β, deg	97.29(1)	95.07(1)
γ, deg		91.91(2)
V, Å^3	2123.1	3500.6
Z	4	4
d_{calcd}, g/cm^3	1.98	1.82
μ(Mo Kα), cm^{-1}	28.6	11.1
F(000)	1232	1880
scan mode	$\omega-2\theta$	$\omega-2\theta$
scan speed, deg/min	16 (in ω)	1−10 (in ω)
scan width, deg	1.15 + 0.300 tan θ	0.41 + 0.350 tan θ
$2\theta_{max}$, deg	52	50
no. of unique rflns	4450	12292
no. of rflns used	2925 ($I > 3\sigma(I)$	9535 ($I > 3\sigma(I)$)
no. of params refined	298	919
largest peak/hole, e/Å^3	0.50/-0.52	+0.82/−0.88
R^a	0.036	0.047
$R_w{}^b$	0.039	0.052

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma(F_o{}^2) + (0.010F_o)^2 + 1.000]$.

Table 2. ^{19}F NMR Spectra (CDCl$_3$, δ in ppm Referenced to CFCl$_3$)

compd (*T*/K)	F_o ($^3J_{Pt-F}$/Hz)	F_p	F_m
1, [Pd(C$_6$F$_5$)Br(OPPyPh$_2$)] (293)	−118.48,[a] −120.87[b]	−159.76,[a] −160.92[b]	−163.04[a], −164.37[b]
2, [Pd(C$_6$F$_5$)$_2$(OPPyPh$_2$)] (293)	−115.81, −117.57	−160.56, −161.58	−163.41, −164.41
3a, [Pd(C$_6$F$_5$)Cl(OPPy$_2$Ph)] (293)	−119.73, −122.60	−159.98	−162.71, −163.64
3b, [Pd(C$_6$F$_5$)Br(OPPy$_2$Ph)] (293)	−118.40, −121.77	−160.05	−162.79, 163.71
3c, [Pd(C$_6$F$_5$)I(OPPy$_2$Ph)] (293)	−115.40, −119.47	−160.00	−162.95, −163.75
4, Pd(C$_6$F$_5$)$_2$(OPPy$_2$Ph)] (210)	−115.36, −117.48	−159.85	−162.21, −162.96
5, [Pt(C$_6$F$_5$)Cl(OPPy$_2$Ph)] (293)	−120.67 (329.3), −123.68 (321.3)	−161.09	−163.85, −164.61
6, [Pt(C$_6$F$_5$)$_2$(OPPy$_2$Ph)] (210)	−118.33 (420.5), −120.52 (422.2)	−160.84	−163.21, −163.82
7, [Pd(C$_6$F$_5$)Cl(OPPy$_3$)] (202)	−120.97, −123.63	−158.93	−161.55, −162.55
8, [Pd(C$_6$F$_5$)$_2$(OPPy$_3$)] (210)	−115.97, −117.57	−159.73	−162.08, −162.94
9, [Pt(C$_6$F$_5$)Cl(OPPy$_3$)] (293)	−121.19 (324.8), −123.80 (322.8)	−160.97	−163.77, −164.42
10, [Pt(C$_6$F$_5$)$_2$(OPPy$_3$)] (210)	−118.84 (427.2), −120.59 (417.1)	−160.80	−163.17, −163.84

[a] Isomer with Py trans to C$_6$F$_5$. [b] Isomer with Py cis to C$_6$F$_5$.

Table 3. ^{1}H and ^{31}P NMR spectra (CDCl$_3$, δ in ppm Referenced to TMS or 85% H$_3$PO$_4$; *J* in Hz)

compd (*T*/K)	H(3)	H(4)	H(5)	H(6)	^{31}P ($^1J_{Pt-P}$)
1 (293)	*a*	*a*	*a*	9.54[b]	49.9,[b] 56.6[c]
2 (293)	7.53	7.95	a	7.99	49.8
3a (293)	8.70,[c] 8.54[b]	8.19,[b] 8.13[c]	7.73,[b] 7.40[c]	9.55,[b] 8.37[c]	20.7
3b (293)	8.70,[c] 8.54[b]	8.19,[b] 8.12[c]	7.73,[b] 7.42[c]	9.68,[b] 8.36[c]	20.8
3c (293)	8.69,[c] 8.55[b]	8.18,[b] 8.12[c]	7.69,[b] 7.45[c]	9.88,[b] 8.30[c]	21.0
4 (293)	8.69[c]	8.12[c]	7.53[c]	8.72[c]	20.7
5 (293)	8.64,[c] 8.58[b]	8.23,[b] 8.14[c]	7.80,[b] 7.31[c]	9.55,[b] 8.55[c]	21.7 (215.7)
6 (293)	8.71[c]	8.16[c]	7.50[c]	8.91[c]	22.3 (166.0)
7 (202)	8.70,[c] 8.61,[b] 7.91[d]	8.29,[b] 8.21,[c] 7.96[d]	7.89,[b] 7.69,[d] 7.55[c]	9.50,[b] 8.97,[d] 8.40[c]	14.6
8 (210)	8.68,[c] 7.74[d]	8.18,[c] 7.98[d]	7.68,[d] 7.60[c]	8.87,[d] 8.70[c]	16.2
9 (293)	8.66,[c] 8.64,[b] 7.81[d]	8.25,[b] 8.15,[c] 7.83[d]	7.80,[b] 7.55,[d] 7.34[c]	9.53,[b] 8.66,[d] 8.58[c]	15.5 (228.1)
10 (293)	8.72,[c] 7.70[d]	8.17,[c] 7.88[d]	7.58,[d] 7.52[c]	8.90,[c] 8.74[d]	17.4 (176.7)

[a] Overlapped with other aromatic signals. [b] Py coordinated cis to the halogen. [c] Py coordinated cis to the C$_6$F$_5$ group. [d] Noncoordinated Py group.

slowly decomposes in solution. Their relevant NMR data are collected in Tables 2 and 3. The solid-state IR spectra of the complexes show the expected number of "X-sensitive" C$_6$F$_5$ bands near 800 cm^{-1} (two for the complexes with two *cis* C$_6$F$_5$ groups, one for those with one C$_6$F$_5$ group);[18] **3a**, **5**, and **9** show ν(M—Cl) near 335 cm^{-1} (see Experimental Section). More interestingly, the complexes with OPPyPh$_2$ display a shift of ν(P═O) toward low wavenumbers compared to the free ligand, which is not observed for the complexes with OPPy$_2$Ph and OPPy$_3$. This suggests that OPPyPh$_2$ is acting as an O,N-chelate (using its only two coordinating atoms), whereas OPPy$_2$Ph and OPPy$_3$ behave as N,N-chelates. The coordination mode proposed for the OPPyPh$_2$ ligand is structurally similar to that found crystallographically for SPPy$_2$Ph in [Pd(C$_6$F$_5$)Br(SPPy$_2$Ph)],[12] although the

(18) (a) Maslowsky, E., Jr. *Vibrational Spectra of Organometallic Compounds*; Wiley: New York, 1977; p 437, and references therein. (b) Usón, R.; Forniés, J. *Adv. Organomet. Chem.* **1988**, *28*, 219−297 and references therein.

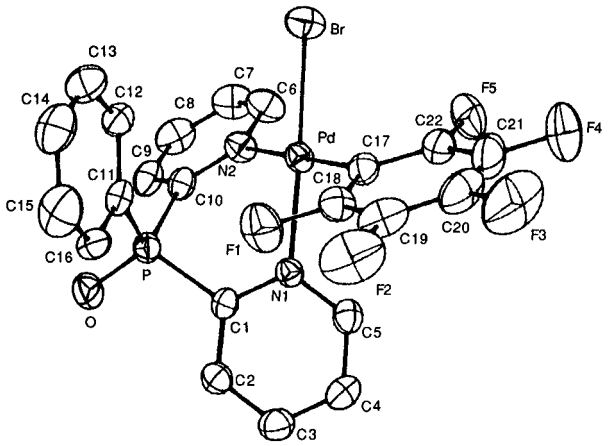


Figure 1. Molecular diagram of complex **3b**.

Table 4. Selected Bond Distances (Å) for 3b and 4

[Pd(C_6F_5)Br($OPPy_2Ph$)] (**3b**)		[Pd(C_6F_5)$_2$($OPPy_2Ph$)]·2$CHCl_3$ (**4**)	
Pd2−C51	2.015(4)	Pd1−C11	2.015(4)
Pd2−C61	2.007(4)	Pd1−C21	2.010(3)
Pd2−N81	2.111(3)	Pd1−N41	2.117(3)
Pd2−N82	2.118(3)	Pd1−N42	2.116(3)
P2−O2	1.480(2)	P1−O1	1.482(2)
P2−C71	1.780(4)	P1−C31	1.782(4)

lesser stability of the N,O-chelate is responsible for the instability of complex **1** and for the fact that this structure is found only for the monopyridyl ligands, whereas an N,N-chelating mode is preferred for the rest.

When the ligand has more than one pyridyl group, the N,N-chelation produces a boat conformation for the metallacycle. This kind of conformation has been found previously with related ligands such as polypyrazolyl and poly(2-pyridyl)borates, methanes, and silanes.[19−22] Two conformers, with either the oxygen or the aromatic free ring toward the metal, are possible. The NMR spectra of the complexes reveal only one conformer at low temperature. From the literature precedents, it is unlikely that a rapid interconversion of isomers is occurring at low temperature; most probably only one conformer is formed, but the preferred conformer cannot be unequivocally assigned. In order to firmly establish this point and other structural features, single-crystal X-ray analyses of **3b** (Figure 1) and **4** (Figure 2) were undertaken. The latter displayed two crystallographically independent molecules, shown in Figure 2, but they are very similar and only one will be discussed.

Molecular Structures of [Pd(C_6F_5)Br($OPPy_2Ph$)] (3b) and [Pd(C_6F_5)$_2$($OPPy_2Ph$)] (4). Selected bond lengths and angles of both structures are listed in Tables 4 and 5 and selected nonbonding distances in Table 6.

Table 5. Selected Bond Angles (deg) for 3b and 4

[Pd(C_6F_5)Br($OPPy_2Ph$)] (**3b**)		[Pd(C_6F_5)$_2$($OPPy_2Ph$)]·2$CHCl_3$ (**4**)	
C51−Pd2−C61	85.4(1)	C11−Pd1−C21	86.1(1)
C51−Pd2−N81	92.4(1)	C11−Pd1−N41	178.0(1)
C51−Pd2−N82	177.3(1)	C11−Pd1−N42	93.4(1)
C61−Pd2−N81	177.3(1)	C21−Pd1−N41	92.1(1)
C61−Pd2−N82	92.5(1)	C21−Pd1−N42	179.4(1)
N81−Pd2−N82	89.6(2)	N41−Pd1−N42	88.4(2)
C52−C51−C56	114.4(3)	C12−C11−C16	113.3(3)
C62−C61−C66	113.6(4)	C22−C21−C26	114.1(3)

Table 6. Selected Nonbonding Distances (Å) for 3b and 4

[Pd(C_6F_5)Br($OPPy_2Ph$)] (**3b**)		[Pd(C_6F_5)$_2$($OPPy_2Ph$)]·2$CHCl_3$ (**4**)	
Pd2−P2	3.34	Pd1−P1	3.39
Pd2−C11	3.39	Pd1−C31	3.55
Pd2−C14	5.13	Pd1−C43	5.38
Pd2−F1	3.11	Pd1−F12	3.20
Pd2−F5	3.19	Pd1−F16	3.18
C15−F1	3.42	Pd1−F22	3.21
C16−F1	3.13	Pd1−F26	3.16
Br1−F5	3.40	C32−F26	3.11
N1−F1	3.09	C33−F26	3.19
		C35−F12	3.01
		C36−F12	2.99
		F12−F26	2.82
		F16−F22	3.13

The palladium atom has an essentially square-planar geometry in both complexes. The Br−Pd−C1 and C21−Pd−C11 angles (88.4 and 86.1°) are almost identical with those found in the homologous bromo(diethyl malonato-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II) (88.60°) and bis(diethyl malonato-*C*)[2,2-bis(2-pyridyl)-1,3-dioxolane]palladium(II) (86.1°), whereas the N−Pd−N angles are about 5° more open in the pentafluorophenyl than in the diethyl malonato complexes.[22] The Pd−N bond lengths are also very similar to those found in the diethyl malonato complexes and reflect the high trans influence of the pentafluorophenyl ligand: two long distances are found in **4**, and the shortest bond length is found trans to the Br ligand in **3b**. The Pd−C distances are also normal. The Pd-C distance in **3b** (1.979 Å) is the same, within experimental error, as that found in [Pd(C_6F_5)Br($SPPy_2$Ph-*N*,*S*)] (1.978 Å), where the C_6F_5 group is also trans to a pyridyl group.[12] The Pd−C distances in **4** are somewhat longer (2.015 and 2.010 Å), but also in the range commonly found for other pentafluorophenyl Pd(II) or Pt(II) complexes.[13b,e,14a,d,18b,23] The internal angles at the ipso carbon atoms of the pentafluorophenyl ring are noticeably lower than 120°, as found in related complexes.[24] The Pd−Br distance is also normal.[12,22,25]

In both complexes the neutral ligand is acting as an N,N-chelate, as expected, and the six-membered chelate ring assumes a boat conformation. The coordinated pyridyl rings are inclined to the coordination plane, making angles of 45.07 and 50.44° in **3b** and 50.17 and 49.52° in **4**. The conformer found is that which places the phenyl ring above the coordination plane. This

(19) (a) Canty, A. J. ; Minchin, N. J.; Patrick, J. M.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1253−1259. (b) Canty, A. J.; Minchin, N. J.; Engelhart, L. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 645−650. (c) Brown, D. G.; Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 1231−1235. (d) Byers, P. K.; Canty, A. J.; Honeyman, R. T. *J. Organomet. Chem.* **1990**, *385*, 417−427. (e) Canty, A. J.; Jin, H.; Roberts, A. J.; Traill, P. R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995**, *489*, 153−159.

(20) Minghetti, G.; Cinellu, M. A.; Bandini, A. L.; Banditelli, G.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* **1986**, *315*, 387−399.

(21) Wright, M. E.; Lowe-Ma, C. K. *Organometallics* **1990**, *9*, 347−352.

(22) Newkome, G. R.; Gupta, V. K.; Taylor, H. C. R.; Fronczek, F. R. *Organometallics* **1984**, *3*, 1549−1554.

(23) Albéniz, A. C.; Espinet, P.; Jeannin, Y.; Philoche Levisalles, M.; Mann, B. E. *J. Am. Chem. Soc.* **1990**, *112*, 6594−6600.

(24) (a) Jones, P. G. *J. Organomet. Chem.* **1988**, *345*, 405−411. (b) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr., Sect. B* **1975**, *31*, 221.

(25) Giordano, T. J.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* **1978,** *17*, 1917−1922.

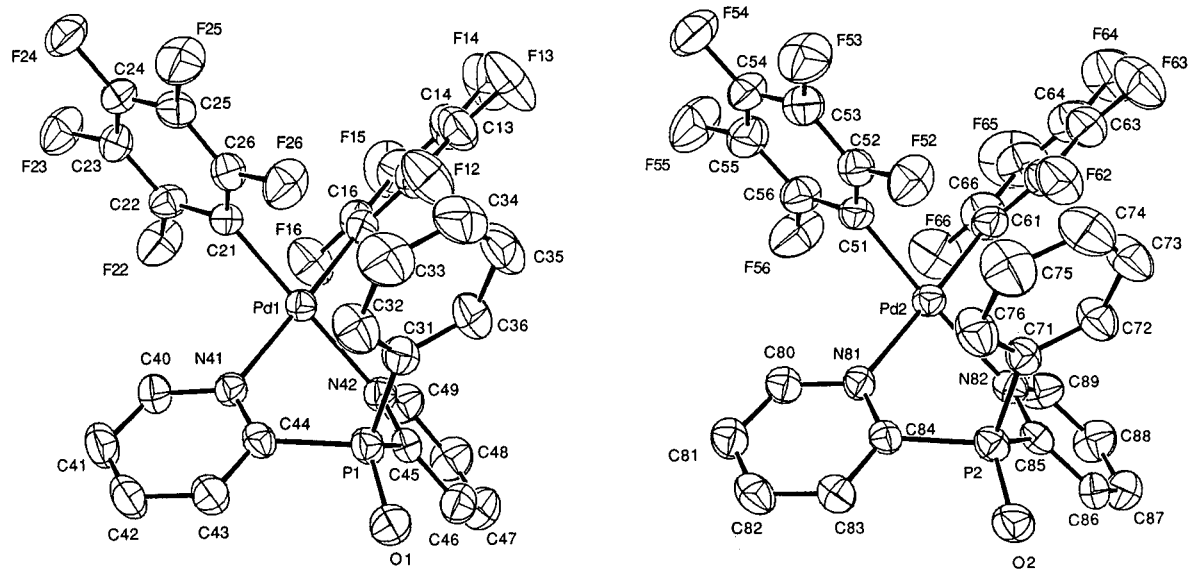


Figure 2. Molecular diagram of complex **4**. The two crystallographically independent molecules are shown.

produces a rather crowded situation with the bulky pentafluorophenyl ligands, which induces some important differences in the two complexes. In complex **3b** the pentafluorophenyl ring is inclined, making an angle of 65.30° to the coordination plane; this allows the phenyl ring to adopt also an inclination that causes one ortho carbon to approach the coordination plane (Pd···C16 = 3.42 Å; Pd···C12 = 4.28 Å; van der Waals distance 3.25 Å). The tilting of both rings is concerted, as shown by the short distances between the fluorine atoms and the phenyl ring (F1···C16 = 3.13 Å; F1···C11 = 3.31 Å), close to the sum of the van der Waals radii (3.15−3.30 Å). In contrast, in complex **4** the pentafluorophenyl rings are almost perpendicular to the coordination plane, making angles of 95.47 and 89.29°. It seems that their steric crowding with the phenyl ring cannot be reduced in this case by a concerted tilting, as observed for instance in [Pt(2,4,6-Me$_3$C$_6$H$_2$)$_2$bpy] or in [Pd{2,4,6-(CF$_3$)$_3$C$_6$H$_2$}$_2$bpy],[26,27] because the steric requirements of the pentafluorophenyl groups should favor an inclination of both groups to the same side, producing always a closer approximation of one ortho fluorine to the phenyl ring rather than a relief of interaction. Both halves of the phenyl ring are well separated from the coordination plane (Pd1···C36 = 3.91 Å; Pd1···C32 = 4.27 Å). The shortest distances between the fluorine atoms and the phenyl ring (F26···C32 = 3.11 Å; F26···C33 = 3.19 Å; F12···C36 = 2.99 Å; F12···C35 = 3.01 Å) again suggest van der Waals contacts.

The Pd···P distances in both complexes are similar (3.34 Å in **3b** and 3.39 Å in **4**; the van der Waals distance is 3.45 Å) but in complex **4** the *P*-phenyl moiety is forced to open away from the Pd atom by the repulsion of the two pentafluorophenyl rings (Pd···C14 = 5.13 Å in **3b**; Pd1···C34 = 5.38 Å in **4**). This reveals a flexibility in the boat conformation, which is further supported by the ^{19}F NMR spectra of the complexes [M(C$_6$F$_5$)$_2$(OPPy$_3$)] (**8** and **10**): a structure similar to that of **4** with an uncoordinated pyridyl group (as supported by the ^{1}H NMR spectra; see below) in place of the phenyl ring should render the two pentafluorophenyl groups inequivalent. The fact that they are seen as equivalent (only one F$_{para}$ signal) in **8** and **10**, even at low temperature, proves that the boat conformation seen in the solid state is flexible enough to allow for very fast rotation of the pyridyl (or phenyl) ring about the P−C bond.

NMR Spectra and Solution Behavior. The solution behavior of the complexes in CDCl$_3$ was studied by ^{31}P{^{1}H}, ^{1}H, and ^{19}F NMR spectroscopy at different temperatures. ^{31}P{^{1}H} NMR is useful in checking easily for the presence of possible isomers. NMR studies of ^{19}F and the H^6 hydrogen of the pyridyl groups give interesting information on the structures and about dynamic processes.[12]

For complexes **3**−**10** the ^{31}P{^{1}H} spectra displayed only one singlet at all temperatures. A boat-to-boat interconversion of conformers, very fast even at low temperature, seems quite unlikely in the absence of dissociation of at least one pyridyl group. ^{195}Pt satellites are seen for the platinum complexes, and exchange experiments showed that there is no exchange at an appreciable rate with free OPPy$_n$Ph$_{3-n}$ ligand. The dissociation of only one pyridyl group is also excluded by the results discussed below. Hence, we admit that inversion of the boat does not occur in solution, although if it was occurring very fast even at low temperature, this would be irrelevant for the rest of the discussion.

(1) In the complexes [Pd(C$_6$F$_5$)X(OPPyPh$_2$-*N*,*O*)] (X = Br, **1**; X = C$_6$F$_5$, **2**) the halves of each C$_6$F$_5$ group must be equivalent by symmetry even in a rigid molecule; thus, they cannot be used to study possible fluxional processes. Complex **1** showed the presence of the two possible isomers, with the Py group cis or trans to the C$_6$F$_5$ in the ratio 1:2.1 (the isomer with the Py cis to the bromine was assigned according to the chemical shift of H^6).[12,19c,d] The ^{19}F spectrum displayed two series of 2:1:2 signals, also in the ratio 1:2.1. For complex **2**, two F$_{para}$ signals revealed two different C$_6$F$_5$ rings, each with its halves equivalent (two series of 2:1:2 signals).

For the rest of the complexes the coordination plane is not a mirror plane, and the halves of each pentafluorophenyl ring are inequivalent in a static molecule, giving rise to five signals from each different C$_6$F$_5$ group.

(26) Klein, A.; Hansen, H.-D.; Kaim, W. J. *J. Organomet. Chem.* **1992**, *440*, 207−217.
(27) Bartolomé, C.; Espinet, P.; Villafañe, F.; Giesa, S.; Martín, A.; Orpen, A. G. *Organometallics* **1996**, *15*, 2019−2028.

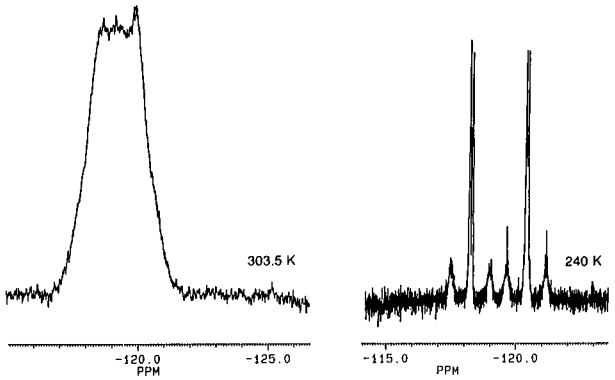


Figure 3. ^{19}F NMR spectra (only F_{ortho}) of complex **6** in $CDCl_3$ at 303.5 K (left) and 240 K (right).

Should equivalence be observed, it would indicate that a dynamic process is producing exchange of the halves of the C_6F_5 ring. Some dynamic processes were not evident from the spectra but were revealed by using magnetization transfer (MT) experiments.

(2) The complexes $[M(C_6F_5)X(OPPy_2Ph\text{-}N,N)]$ (M = Pd, X = Cl (**3a**), Br (**3b**), I (**3c**); M = Pt, X = Cl (**5**)) appeared as rigid both in the ^1H (two different Py groups) and in the ^{19}F (two F_{ortho} and the two F_{meta} signals) spectra in $CDCl_3$ up to 50 °C, but MT experiments on the F_{ortho} signals revealed that a very slow exchange of the two F_{ortho} (and the two F_{meta}) signals was occurring. Its rate was the same for Pd and Pt, varying with the halogen in the order Cl > Br > I. The F_{ortho} exchange process was not accelerated noticeably in acetone-d_6, CD_3CN, or DMSO-d_6, where five different signals were observed in each case. This behavior is different from that of $[Pd(C_6F_5)Br(SPPy_2Ph\text{-}N,S)]$, which appeared as rigid in $CDCl_3$; the exchange reaction was very much accelerated, however, in acetone-d_6, leading to equivalence of the F_{ortho} signals at room temperature; moreover, the rate of exchange for different halogens was I > Br > Cl.[12]

MT experiments on the H^6 signals of the Py groups showed that they do not exchange at an appreciable rate.

(3) The complexes $[M(C_6F_5)_2(OPPy_2Ph\text{-}N,N)]$ (M = Pd (**4**), Pt (**6**)) displayed broad signals for the F_{ortho} and the F_{meta} signals at room temperature that were resolved at −60 °C, coalesced at 30 °C, and were not completely sharpened at 45 °C (Figure 3).

(4) While in all the previous complexes the behaviors of Pd and Pt are similar, for the complexes $[M(C_6F_5)Cl(OPPy_3\text{-}N,N)]$ (M = Pd (**7**), Pt (**9**)) they are dramatically different. The palladium complex **7** displayed one signal for the two F_{ortho} atoms at room temperature, which was split in two at low temperature. The ^1H NMR spectra (H^6 signals) revealed that the exchange of the halves of the C_6F_5 was associated with the exchange of only two Py groups: that trans to the C_6F_5 ligand and the free Py group. This exchange was much faster than that observed for $[Pd(C_6F_5)_2(OPPy_3\text{-}N,N)]$ (**8**; see below) and was the only appreciable one at low to room temperature (Figure 4). Above 25 °C the involvement in the exchange of the Py group cis to the C_6F_5 ligand began to be detectable.

In contrast, the platinum complex **9** appeared as rigid both in the ^1H (three different Py groups) and in the ^{19}F (two F_{ortho} signals) spectra in $CDCl_3$ up to 50 °C. MT experiments on the F_{ortho} signals revealed a very slow exchange of the two F_{ortho} signals at 50 °C, while there is no exchange of the free and coordinated Py groups, as observed by MT experiments on H^6.

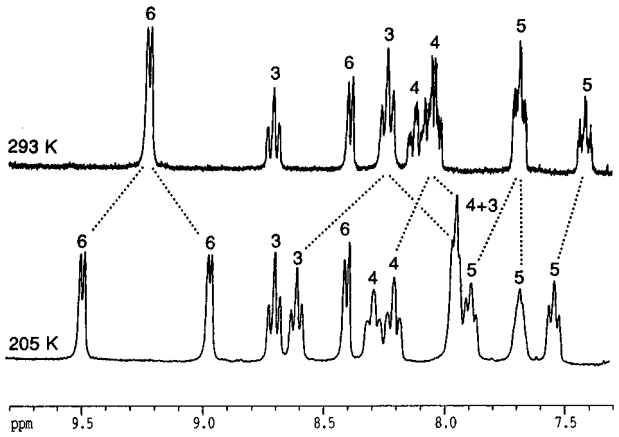


Figure 4. ^1H NMR spectra of complex **7** in $CDCl_3$ at 205 and 293 K showing the exchange of two Py groups. The numbers refer to the H position in the ring. The assignments are given in Table 3.

Putative atropisomers due to a slow rotation of the noncoordinated Py group could not be observed within the range of temperatures used (from 200 K above).

(5) In the complexes $[M(C_6F_5)_2(OPPy_3\text{-}N,N)]$ (M = Pd (**8**), Pt (**10**)) the two C_6F_5 groups are seen as equivalent (only one F_{para} signal) even at low temperature, proving that the boat conformation seen in the solid state is flexible enough to allow for free rotation of the noncoordinated Py ring around the P−C bond. The F_{ortho} atoms appear as two broad signals at room temperature that were resolved at −60 °C. For the platinum complex **10** satellites are observed for the ortho fluorines with $^3J(^{19}F-^{195}Pt)$ values of 426.3 and 428.9 Hz at −50 °C.

The ^1H NMR spectra give additional information: for the platinum complex the signals of the coordinated Py groups (showing coupling of H^6 to ^{195}Pt of about 30 Hz) are distinguished from the uncoordinated Py (which does not show ^{195}Pt satellites); on heating, exchange of the coordinated and the free Py groups does not occur at a rate detectable by MT. In contrast, for the palladium complex **9** there is exchange between the free and the coordinated Py groups, and the rate of this exchange (measured by line shape analysis) is comparable to that found for the exchange of the F_{ortho} atoms.

Kinetic studies were undertaken for all the complexes using magnetization transfer experiments on the F_{ortho} signals at different temperatures (see Eyring plots in Figure 5), or line shape analysis. The activation parameters obtained are given in Table 7.

Discussion

The possible mechanisms that need to be considered as possible sources of F_{ortho} exchange are discussed below: (1) inversion of the chelating ligand, (2) C_6F_5 rotation in a three-coordinate intermediate, and (3) C_6F_5 rotation in the square-planar complex.

Inversion of the Chelating Ligand. For inversion of the chelating ligand we mean the type of process represented in Scheme 1. A simple boat inversion (or envelope shift) movement does not exchange the two sides of the coordination plane.

Table 7. Activation Parameters for F_{ortho} Exchange and Py Exchange (Standard Deviations in Parentheses)[a]

	F_{ortho} exchange			Py exchange		
compd	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta G^{\ddagger}_{298}$ (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta G^{\ddagger}_{298}$ (kJ mol^{-1})
3a	58.6(8)	−39.2(3)	70.3(9)			
3b	64.8(1.6)	−35.3(4)	75.3(4)			
3c[b]	72.1	−35.3	82.6			
4	52.7(4)	−18.2(1)	58.2(4)			
5	57.9(8)	−39.8(2)	69.8(9)			
6	51.8(8)	−18.8(3)	57.3(9)			
7	48.0(1.2)	9.4(1.5)	45.2(1.6)	45.6(9)	−0.3(7)	45.7(1.0)
8	57.0(4)	−4.0(2)	58.2(5)	61.6(2)	2.8(1)	60.8(2)
9	59.1(3)	−35.0(7)	69.6(5)	76.5(1.3)	−0.3(3)	76.6(1.4)
10	53.4(5)	−19.5(2)	59.2(6)		exchange not observed	

[a] F_{ortho} exchange parameters were obtained by magnetization transfer experiments; for **7** line shape analysis was also used and gave the same values within experimental error. Py exchange rates were obtained by line shape analysis (DNMR 6). [b] At 298 K the process is too slow for direct measurement. The values given were estimated from the measurement of k_{rot} at 330.7 K.[32] At this temperature k_{obs} = 0.40 s^{-1}, and $\Delta G^{\ddagger}_{330.7}$ = 83.8 kJ mol^{-1}.

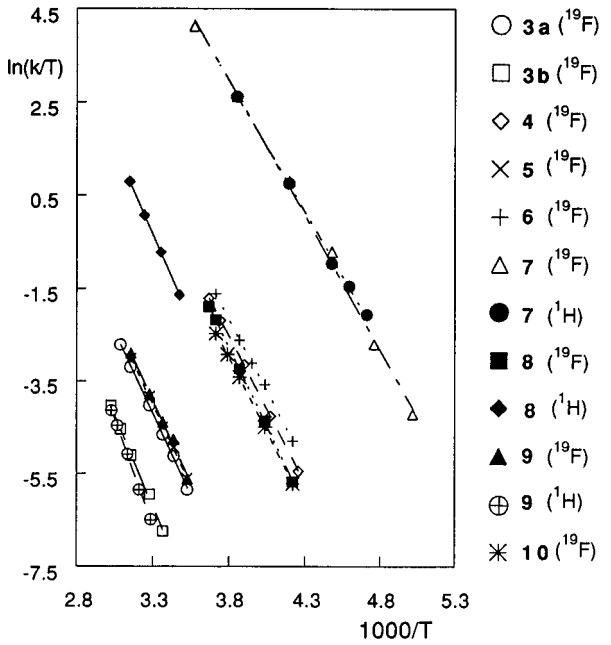
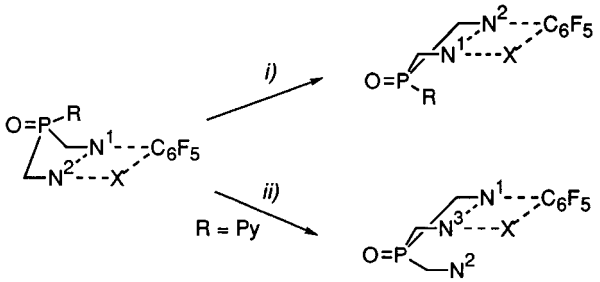


Figure 5. Eyring plots for the two types of processes studied. For each symbol the number of the complex and the nucleus observed are given.

The dissociative process (i) involves decoordination of at least one Py group, followed by topomerization of the remaining coordinated group and recoordination. This process can be discounted, because it should produce at the same rate the equivalence of all the Py groups in complexes **3**, **5**, and **7**−**10**, which is not observed (equivalence is in fact observed for complex **7**, but the mechanism is different, as discussed below). Moreover, one could expect exchange with free ligand, which is also not observed.

The associative process (ii) can occur only in the OPPy$_3$ derivatives and should produce exchange of at least two Py groups for the mono(pentafluorophenyl) derivatives (one free and one coordinated) and the three Py groups for the bis(pentafluorophenyl) complexes. Such exchange is in fact observed for three of the four complexes, but for **8** and **9** it is slower than the fluorine exchange; hence, in these two complexes the Py exchange is not determining the activation parameters of the fluorine exchange. For complex **7** the result is very different: the fluorine exchange and the Py exchange occur at the same rate, this rate being noticeably faster than for the related complexes **3**, **5**, and **9**. We conclude

Scheme 1



that in complex **7** fast associative substitution of the Py group trans to the C$_6$F$_5$ group is occurring, rendering the coordination plane a mirror plane on the NMR time scale. Thus, the parameters measured for the fluorine exchange in **7** do not correspond to a rotation of C$_6$F$_5$.

Complex **7** is the only case where a clear associative substitution of Py groups is seen. It is well-known that usually the rate of ligand substitution is noticeably faster for Pd(II) than for Pt(II). Although only in a few cases can Pd and Pt complexes be compared directly, it has been found that $k_{Pd} \approx 10^5 k_{Pt}$ for the substitution of Cl$^-$ for py in [MClR(PR′$_3$)$_2$][28] and $k_{Pd} = (1.4 \times 10^6) k_{Pt}$ for the exchange of water in [M(H$_2$O)$_4$]$^{2+}$,[29] although the rates of substitution for both metals can become comparable for good π-acceptor entering ligands.[30] The faster substitution in Pd complexes is attributed to the better energetic accessibility of a five-coordinate intermediate in the associatively activated process. In this respect complex **7** has also less steric hindrance than **8** for the coordination of the third Py group, as shown by the structures of the homologous **3b** and **4** (probably in **8** the coordination of the third Py group needs to be concerted with the rotation of a C$_6$F$_5$ group). Support for an associative substitution also in **8** and **9** comes from the fact that for a dissociative exchange one should expect (i) not very different parameters for Pd and Pt, whereas they are very different for **8** and **10**, and (ii) faster exchange for **10** than for **9** (the presence of two R groups favors dissociation),[31] whereas the opposite is observed.

(28) Basolo, F.; Chatt, J.; Gray, H. B.; Pearson, R. G.; Shaw, B. L. *J. Chem. Soc.* **1961**,2207−2207.
(29) Helm, L.; Elding, L. I.; Merbach, A. E. *Inorg. Chem.* **1985**, *24*, 1719−1721.
(30) Olsson, A.; Kofod, P. *Inorg. Chem.* **1992,** *31*, 183−186 and references therein.
(31) Frey, U.; Helm, L.; Merbach, A. E.; Romeo, R. *J. Am. Chem. Soc.* **1989**, *111*, 8161−8165 and references therein.

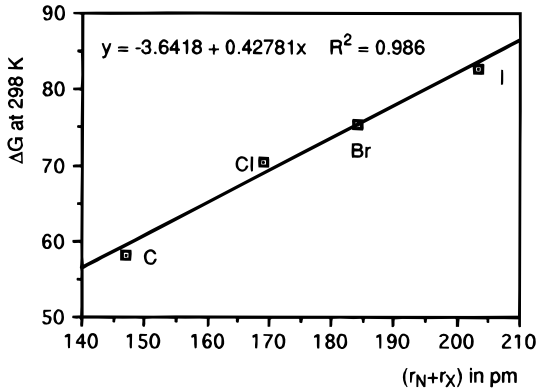


Figure 6. Variation of $\Delta G^{\ddagger}$ for C_6F_5 rotation with the size of the flanking atoms.

C_6F_5 Rotation in a Three-Coordinate Intermediate. The steric hindrance to C_6F_5 rotation can be very much diminished by dissociation of a ligand cis to it. In such a case the barrier for rotation should be related to the ease of dissociation. For the reasons just discussed we discount dissociation of a Py group. Thus, the formation of a three-coordinate intermediate should require halide dissociation (as observed in [Pd(C_6F_5)X(SPPy$_2$Ph-*N*,*S*)]; X = Cl, Br, I)[12] or, in the case of the bis(pentafluorophenyl) derivatives, C_6F_5 dissociation; the order of dissociation energies ($C_6F_5 \gg$ Cl > Br > I)[12] is not the order of difficulty for rotation observed, but exactly the opposite. Thus, a three-coordinate intermediate has to be discounted for the complexes considered in this work.

C_6F_5 Rotation in the Square-Planar Complex. This leaves the rotation in the square-planar complex as the mechanism giving rise to fluorine exchange in complexes **3**−**10**, with the exception of **7**. By comparison of the $\Delta G^{\ddagger}$ values or the k_{rot} values at 298 K it can be seen that for the whole series studied [M(C_6F_5)X(OPPy$_n$Ph$_{3-n}$)] (M = Pd, Pt; X = C_6F_5, Cl, Br, I) there is no noticeable influence of the metal (the same values are found for Pd and Pt) and there is a large influence of the size of the donor atom of the second ligand, X, flanking the rotating C_6F_5 group (one group is always a Py group). k_{rot} varies in the order C_6F_5 > Cl > Br > I according to the variation in size C < Cl < Br < I.

As we have already mentioned, the free Ph or Py ring hanging over the coordination plane is rotating very fast even at low temperature, due to the flexibility of the boat. This means also that its contribution to hindrance of the C_6F_5 rotation must be negligible and the parameters observed must be correlated exclusively to the hindrance produced by the two ligands cis to the rotating group. Obviously for X = Cl, Br, I this is determined by the size of these ligands. For X = C_6F_5 it is mainly the C_{ipso} atom which produces the hindrance to rotation of the second group. For a pyridine ligand it would be the size of the N atom, but since these Py groups are somewhat inclined, it is likely that there is some contribution of the CH[6] group. In other words, an inclined Py group is somewhat "bulkier" for the rotation of a cis C_6F_5 than a perpendicular py ligand but less "bulky" than a Py group in a coplanar 2,2′-bpy, or a NR_2 fragment, a PR_2 fragment, etc.

A plot of $\Delta G^{\ddagger}$ at 298 K (mean values when there are several compounds of the same type) versus the sum of covalent radii of the donor atoms of the two ligands flanking the rotating C_6F_5 (i.e. $r_N + r_X$) gives a linear correlation (Figure 6) that is surprisingly good, considering the naive approximation used, and allows us to make some crude estimations of other barriers to rotation imposed only by the two coordinated atoms flanking the C_6F_5 group.[32,33] Thus, combinations such as C/Cl, C/P, C/Br, C/S, Cl/Cl, S/S, S/Br, and P/P give values ranging from 70 to 100 kJ mol^{-1}, all noticeably greater that the value found for complex **3a**. Even if these values are somehow overestimated (because the hindrance of the inclined Py group is probably greater than that of a N atom), it seems reasonably safe to expect for these combinations of ligands a spectrum corresponding to a nonrotating C_6F_5 group at room temperature, as found for **3a**. A dynamic spectrum should be an alert for a careful study of the system, even more in cases where the donor atoms have substituents protruding toward the C_6F_5 position and making their actual hindrance to C_6F_5 rotation greater. Of course this is a very crude and general rule, and the possibility of geometrical variations in the coordination plane (see below) has to be taken into account, as well as the fact that the coalescence temperatures depend not only on $\Delta G^{\ddagger}$ but also on the chemical shift difference of the exchanging nuclei, so small chemical shift differences might happen to produce dynamic situations at room temperature even for quite hindered systems.[34]

Some cases in the literature can be reviewed in light of these results. For instance, it is very unlikely that the C_6F_5 rings are "freely rotating" in the square-planar anion [Ni$_2$(C_6F_5)$_4$(μ-SR)$_2$]$^{2-}$,[14g] since the hindrance to rotation has to be even greater for the smaller Ni than for the Pd or Pt derivatives. Obviously the mirror plane for this dimer on the NMR time scale must be produced by the well-known low-energy pyramidal inversion of the sulfur atoms, as proposed for instance for the closely related [Cp$_2$Ti(μ-SR)$_2$M(C_6F_5)$_2$] (M = Pd, Pt)[13h] and other cases.[13i] Free rotation is also not to be expected in [Ni(C_6F_5)$_2$(pyt-*N*,*S*)],[14i] pyt =pyridine-2-thiolate), and the invoked rotation is unnecessary, since the coordination plane is a mirror plane in this case. The same holds true for the complexes [(C_6F_5)$_2$M(μ-X)$_2$M′(COD)] (X = Cl, Br, I; M, M′ = Pd, Pt).[14e]

The proposal of C_6F_5 rotation in the complexes *cis*-[M(C_6F_5)$_2$(PH$_2$PCHRPPh$_2$)] (M = Pd, Pt; R = Me, Et, PPh$_2$),[14a,b] seems to be correct. Although the assumption that the chelated ring MP$_2$CHMe "behaves as a rigid body in solution" is not exact,[35] the fact that P exchange is not observed for R = PPh$_2$ allows us to conclude that any dissociative or associative ligand

(32) The value of $\Delta G^{\ddagger}_{298}$ for [Pd(C_6F_5)I(OPPy$_2$Ph)] **(3c)** was estimated as follows: From the experimental value of k_{rot} at 330.7 K (k_{obs} = 0.40 s^{-1}) $\Delta G^{\ddagger}_{330.7}$ was calculated (83.8 kJ mol^{-1}). Assuming a $\Delta S^{\ddagger}$ value of −35.3 J K^{-1} mol^{-1} (as found for **3b**), $\Delta H^{\ddagger}$ was estimated (72.1 kJ mol^{-1}) and used to calculate $\Delta G^{\ddagger}_{298}$. The result is 82.6 kJ mol^{-1}. A representation of $\Delta G^{\ddagger}_{298}$ versus the radii for the three halogens only gives a perfect linear correlation.

(33) Covalent radii taken from: Emsley, J. *The Elements*, 2nd ed.; Clarendon Press: Oxford, Great Britain, 1991.

(34) According to the Eyring equation for the exchange of two equally populated sites, for the coalescence $\Delta G^{\ddagger}_c = 4.57T_c\{9.97 + \log(T_c/\Delta\nu)\}$. See for instance: Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH: Deerfield Beach, FL, 1985; p 5.

(35) For instance, it has been shown that *cis*-[M(C_6F_5)$_2$(PH$_2$PCH$_2$PPh$_2$)] (M = Pd, Pd) undergo exchange with free PH$_2$PCH$_2$PPh$_2$ through the formation of *cis*-[M(C_6F_5)$_2$(PH$_2$PCH$_2$PPh$_2$)$_2$], but this process is very slow: Uson, R.; Forniés, J.; Espinet, P.; Navarro, R.; Fortuño, C. *J. Chem. Soc., Dalton Trans.* **1987**, 2077−2081.

inversion mechanism is much slower than the observed fluorine exchange. This fast rotation at room temperature of C_6F_5 groups flanked by the pair C/PPh_2 might seem in contradiction with the generalizations we made above and with the observation of "rigid" behavior in apparently less hindered systems. In fact, it is an excellent example of a second factor to be considered, namely that severe distortions in the assumed square-planar geometry affect dramatically the hindrance to rotation. In effect, the P−M−P angle in these complexes is only 74°,[14a] and this takes the PPh_2 groups away from the C_6F_5 groups, decreasing the barrier to rotation. Thus, the observation of an unexpectedly easy rotation, as in this case, might also alert us on possible distortions from an ideal square-planar coordination.

Acknowledgment. Financial support by the Dirección General de Investigación Científica y Técnica (Project PB93-0222) and the European Community (Contract CHRX-CT93-0147; DG 12 DSCS) is very gratefully acknowledged. J.A.C. and Y.-S.L. acknowledge studentships from the Ministerio de Educación y Ciencia.

Supporting Information Available: Tables of observed rate constants for the C_6F_5 rotation and/or the Py exchange for complexes **3**−**10** and tables of atomic coordinates, bond distances and angles, least-squares planes, and anisotropic thermal parameters for **3b** and **4** (55 pages). Ordering information is given on any current masthead page.

OM960861+