$P(CH_2CH_2Py)_nPh_{3-n}$ (Py = 2-Pyridyl; n = 1, 2, 3) as Chelating and as Binucleating Ligands for Palladium

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Several neutral palladium(II) complexes of the type $[PdRCl(PN_n)]$ with the ligands $P(CH_2CH_2Py)Ph_2$ (PN), $P(CH_2CH_2Py)_2Ph$ (PN_2), and $P(CH_2CH_2Py)_3$ (PN_3) have been prepared by reacting the corresponding phosphines with $[Pd_2(\mu\text{-}Cl)_2R_2(tht)_2]$ (R = $C_6Cl_2F_3$, C_6F_5; tht = tetrahydrothiophene). In all these complexes, the ligands act as bidentate P,N-chelating ligands. Abstraction of the chloride with $AgBF_4$ leads to the formation of the dimeric compounds $[Pd_2R_2(PN_2)_2](BF_4)_2$ and $[Pd_2R_2(PN_3)_2](BF_4)_2$, in which the PN_n ligands act as P,N-chelating and P,N-bridging ligands. The bridges are labile, and exchange experiments on mixtures of the complexes with different R groups show the equilibrium in solution between the dimeric "pure" complexes and the mixed complexes $[Pd_2(C_6F_5)(C_6Cl_2F_3)(PN_n)_2]^{2+}$. The structure of the complex $[Pd_2(C_6Cl_2F_3)_2\{P(CH_2CH_2Py)_2Ph\}_2](BF_4)_2$ has been studied by X-ray diffraction.

Introduction

Metal complexes with ligands containing donor atoms with different donor characteristics are of interest for their ability to act as "hemilabile" ligands. Thus, the combination of P and O or P and N donor atoms on a soft metal center can afford labile M−O or M−N bonds and more inert M−P bonds.[1] In this context, pyridylphosphines, and particularly 2-pyridyl mono- and diphosphines, have received attention in view of their structural features, reactivity, and catalytic applications.[2] They usually behave as bridging ligands,[3] but their less favored behavior as chelating ligands forming a four-membered ring has also been described.[4] 2-Pyridyl monophosphines with the P atom separated from the Py group by one or two methylene links, capable of forming five- and six-membered rings by chelation, have been much less studied.

As a part of our research on complexes with pyridylphosphines and derivatives,[3a,5] we have synthesized a group of neutral and cationic complexes of palladium(II) with the ligands $P(CH_2CH_2Py)Ph_2$ (PN), $P(CH_2CH_2Py)_2Ph$ (PN_2), and $P(CH_2CH_2Py)_3$ (PN_3) (Py = 2-pyridyl), in order to study the behavior of these multidentate ligands. The coordination properties of PN have been previously tested with a variety of metal centers: Mo,[6] Ir,[7] Ru,[8] Os,[9] Cu, Ag, and Au.[10] The synthesis of the complexes $[PdCl_2(PN)]$ and $[Pd(PN)_2](ClO_4)_2$ has also been reported,[11] as well as the use of related secondary and primary phosphines $PH(CH_2CH_2Py)Ph$ and $PH_2(CH_2CH_2Py)$.[12] Surprisingly little attention has been paid to the synthesis of compounds with PN_2 and PN_3 ligands, although tri- or tetradentate phosphines, as well as tri- or tetradentate amines, are very often used in the stabilization of metal complexes.[13] Both ligands can potentially act as polydentate ligands on the same metal center or as bridging ligands. Some of their possibilities are depicted in Chart 1.

Results and Discussion

1. Neutral Complexes. The base-catalyzed addition of P−H bonds to 2-vinylpyridine provides an easy route to prepare (2-

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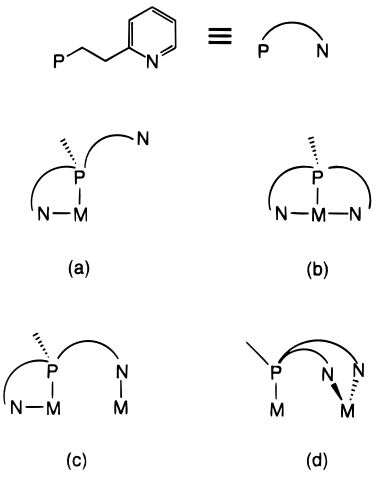
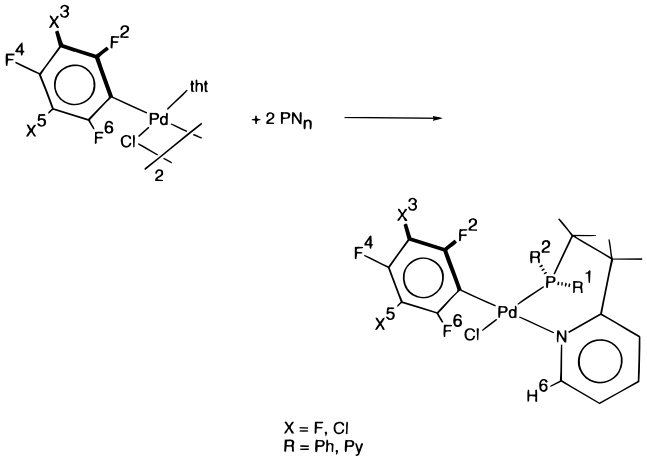
Chart 1



Scheme 1



pyridylethyl)phosphines PN_n, which react with the dimers $[Pd_2(\mu\text{-}Cl)_2(R)_2(tht)_2]$ (R: C_6F_5, $C_6Cl_2F_3$) to generate the neutral complexes $[PdCl(R)(PN_n)]$ (Scheme 1). Their NMR parameters are given in the Experimental Section (^{1}H) or in Table 1 (^{19}F and ^{31}P).

In complexes **1**−**6**, the phosphorus is coordinated "cis" to the fluoroaryl ring and one Py group is coordinated "cis" to the chloride, as evidenced by the deshielding of H^6.[5a,14] This preference of the soft phosphorus to coordinate "cis" to the Pd−C bond obeys the antisymbiotic effect commonly observed for Pd[15] and has been found for other palladium complexes with P,N ligands.[16] The ^{31}P NMR spectra of all these complexes show a triplet due to coupling with the *ortho*-fluorine atoms from the fluoroaryl group.

For complexes **1** and **2**, the ^{19}F NMR spectra show the equivalence of the two *ortho*-fluorine atoms from the fluoroaryl rings, even at −60 °C. Since the rotation of these groups is expected to have a high $\Delta G^{\ddagger}$ value,[5b] this suggests that the equivalence is attained by means of conformational inversion of the six-membered metallacycle formed by the chelating P,N ligand, which is plane-averaged on the NMR time scale. This conformational change has a very low energetic barrier, in contrast to the case of other P,N chelating ligands.[16] This mechanism of equivalence is further supported by the fact that the two H atoms on each methylene group of the phosphine also become equivalent; rotation of the aryl group would not produce this equivalence. The question of whether the conformational inversion occurs with or without N decoordination is answered by the fact that it is clearly faster than the exchange of Py groups discussed below for **3** and **4**. Hence the conformational inversion does not involve N decoordination.

Complexes **3** and **4** show exchange between the coordinated and free Py groups (Scheme 2) with preservation of the $^4J_{P-F}$ coupling. In the static limit, the two F_{ortho} signals, as well as the H^6 signals for the free and coordinated Py groups, should be inequivalent. This is the situation observed at −30 °C. At room temperature, the H^6 signals in the ^{1}H NMR spectrum and the F_{ortho} signals in the ^{19}F NMR spectrum are broad but have not yet reached coalescence. T_c for both compounds in the ^{1}H NMR spectrum is approximately 40 °C. At T_c, the exchange rates (estimated as $k = \pi\Delta\nu/\sqrt{2}$) are 560 s^{-1} for **3** and 572 s^{-1} for **4**. These rates are much slower than the Py exchange rates observed for other analogous complexes such as $[PdCl(C_6F_5)(OPPy_3\text{-}N,N)]$ (for which k = 17 500 s^{-1} at 6.7 °C).[5b] The activation parameters for the exchange have been obtained by NMR line shape analysis[17] and are given in Table 2.

As expected, the $\Delta G^{\ddagger}_{298}$ values obtained are higher than that observed for $[PdCl(C_6F_5)(OPPy_3\text{-}N,N)]$, and it can be seen that the difference arises from higher $\Delta S^{\ddagger}$ values for the complexes described in this paper, although the $\Delta H^{\ddagger}$ values are similar for both kinds of complexes. Since we have previously proved that the exchange in $[PdCl(C_6F_5)(OPPy_3\text{-}N,N)]$ is associative, we assume that the exchange is also associative for **3** and **4**. Although the interpretation of activation entropies is always difficult, the main difference between compounds **3** and **4** and $[PdCl(C_6F_5)(OPPy_3\text{-}N,N)]$ is that in the latter the Py group is connected to a very rigid boatlike metallacycle in which an associative exchange of Py groups does not produce a great change in the geometry, while in **3** and **4** the simultaneous coordination of both Py groups leads to a much more ordered situation compared to that of the ground state. Thus, it is not unreasonable that the activation entropies are more negative for the latter.

The same fluxional behavior is observed for the compounds with the PN_3 ligand, **5** and **6**. In these compounds, the exchange has no effect on the ^{19}F NMR, since the F_{ortho} atoms are not diastereotopic even in a rigid situation, but the exchange of uncoordinated and coordinated Py groups can be observed in ^{1}H NMR. The exchange observed is slightly faster than for PN_2 (the presence of two uncoordinated Py groups in the PN_3 complexes makes higher the "concentration" of the entering Py ligand). The activation parameters obtained, given in Table 2, are very close to those of **3** and **4**.

2. Cationic Complexes. Halide abstraction by thallium(I) in complexes **3**−**6** gives the cationic complexes **7**−**10**, in which the position previously occupied by the halide must be filled by the second Py group. The NMR data for **7** and **8** are not in agreement with a simple intramolecular substitution to give the bischelated complex (Scheme 3). First of all, the two coordinated Py groups are inequivalent at room temperature in the ^{1}H NMR. Although a different rigid conformation in the two six-membered metallacycles formed could explain this fact, such behavior is in disagreement with the fast conformational inversion observed for **1** and **2**. The second point is that there is a through-space coupling of only one F_{ortho} atom to the H^6 atom of only one of the two coordinated Py groups. Selective ^{19}F decouplings at the frequency of this F_{ortho} signal (**7**, δ =

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Table 1. ^{19}F NMR and ^{31}P NMR Data (δ, ppm; J, Hz)[a]

no.	compound	T, K	F_o	F_p	F_m	^{31}P ($4J_{P-F}$)
1	$[Pd(C_6Cl_2F_3)Cl\{P(C_2H_4Py)Ph_2\}]$[b]	293	−91.35	−120.50		31.72 (10.5)
2	$[Pd(C_6F_5)Cl\{P(C_2H_4Py)Ph_2\}]$[b]	293	−117.75	−161.92	−163.66	31.89 (10.6)
3	$[Pd(C_6Cl_2F_3)Cl\{P(C_2H_4Py)_2Ph\}]$[b]	213	−90.52, −92.03	−118.6		28.38 (10.2)
4	$[Pd(C_6F_5)Cl\{P(C_2H_4Py)_2Ph\}]$[b]	243	−116.72, −118.08	−159.96	−162.08, −162.54	28.80 (9.2)
5	$[Pd(C_6Cl_2F_3)ClP(C_2H_4Py)_3]$[b]	293	−90.02	−118.13		31.64 (8.3)
6	$[Pd(C_6F_5)ClP(C_2H_4Py)_3]$[b]	293	−116.65	−159.99	−162.39	32.29 (8.5)
7	$[Pd_2(C_6Cl_2F_3)_2\{P(C_2H_4Py)_2Ph\}_2][(BF_4)_2$[c]	293	−88.73, −89.52	−117.03		27.93 (7.6)
8	$[Pd_2(C_6F_5)_2\{P(C_2H_4Py)_2Ph\}_2](BF_4)_2$[c]	293	−111.92, −116.60	−158.93	−159.61, −164.45	28.11
9	$[Pd_2(C_6Cl_2F_3)_2\{P(C_2H_4Py)_3\}_2](BF_4)_2$[d]	243	−88.86, −88.95	−116.93		34.64 (6.0)
10	$[Pd_2(C_6F_5)_2\{P(C_2H_4Py)_3\}_2](BF_4)_2$[d]	263	−111.23, −116.18	−159.21	−158.96, −161.19	34.46 (5.8)

[a] Reference $CFCl_3$ or 85% H_3PO4. [b] Solvent $CDCl_3$. [c] Solvent acetone-d_6. [d] Solvent CD_3CN.

Scheme 2

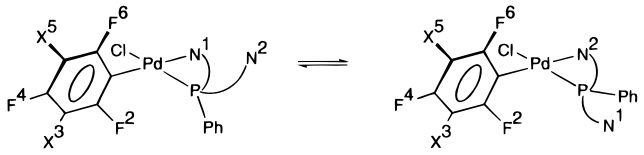
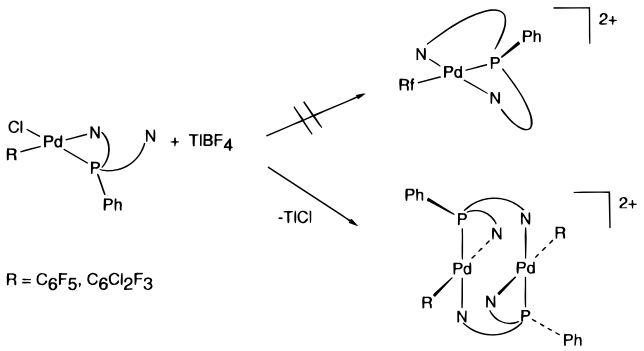


Table 2. Activation Parameters for the Exchange between Py Groups

compound	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta G_{298}^{\ddagger}$, kJ mol^{-1}
3	47.9(0.9)	−39.0(3.0)	59.5(2)
4	47.7(1.0)	−39.9(3.4)	59.6(2)
5	52.2(1.0)	−20.6(3.6)	58.3(2)
6	47.7(0.9)	−35.1(3.1)	58.1(2)
$[Pd(C_6F_5)Cl(OPPy_3)]$[a]	45.6(9)	−0.3(7)	45.7(1.0)
$[Pd(C_6F_5)_2(OPPy_3)]$[a]	61.6(2)	2.8(1)	60.8(2)

[a] Data from ref 5b.

Scheme 3



−89.52; **8**, $\delta = -116.60$) simplify the signal of the corresponding H^6 (**7**, $\delta = 8.45$; **8**, $\delta = 8.35$) from an apparent triplet to a doublet. This kind of $^{19}F-^{1}H$ coupling is often observed in complexes with fluorinated aryls, provided that the F and H atoms are in close proximity in a rigid structure.[18] Although these data suggest an intramolecular coordination of the second Py group, the structure of **7** was determined by X-ray diffraction methods to obtain unambiguous and detailed information about the geometry of the compounds.

3. Molecular Structure of $[Pd(C_6Cl_2F_3)\{\mu\text{-}PPh(C_2H_4Py)_2\text{-}P,N,\mu\text{-}N'\}]_2(BF_4)_2\cdot CH_3CN$ (7). The crystal structure of complex **7** contains centrosymmetric dimeric dications $[Pd(C_6Cl_2F_3)\{\mu\text{-}PPh(C_2H_4Py)_2\text{-}P,N,\mu\text{-}N'\}]_2$ together with disordered BF_4 anions and solvent acetonitrile molecules. A displacement ellipsoid diagram is shown in Figure 1. The orientation of the metal centers is mutually "transoid". Each palladium atom is in a square planar environment. The metal is coordinated to a $C_6Cl_2F_3$ group *trans* to a pyridyl group of the $PPh(C_2H_4Py)_2$ ligand. This group forms a six-membered chelate ring with the phenylphosphine function of the ligand. The remaining arm of the ligand bridges the second palladium with the pyridyl group occupying the remaining coordination site at palladium, *trans* to the phosphine. A highly puckered, 12-membered ring is created in which the two palladium coordination planes are exactly parallel and *trans*-bridged by $P(C_2H_4Py)$ moieties. The Pd···Pd nonbonding distance is 5.261(2) Å.

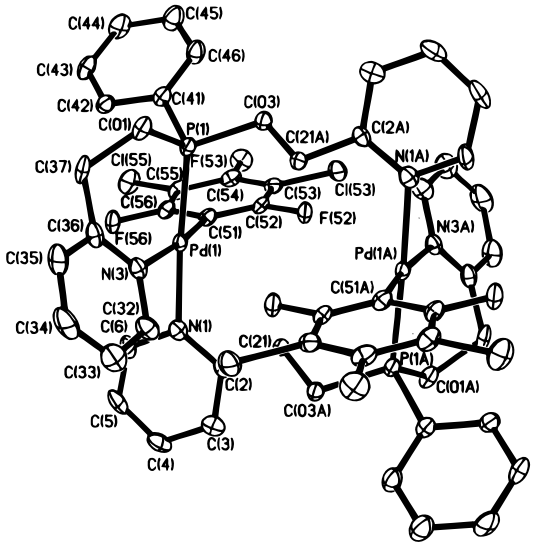


Figure 1. Molecular structure of complex **7** showing the labeling scheme. All hydrogens have been omitted for clarity. Atoms are shown as displacement ellipsoids enclosing 30% probability density.

The Pd−C distance (2.018(8) Å) is within the range commonly found for other pentahalophenyl Pd(II) or Pt(II) complexes.[19] The internal angles at the *ipso* carbon atoms of the pentahalophenyl ring are noticeably lower than 120°, as found in related complexes.[20] Other selected distances and angles are listed in Table 3.

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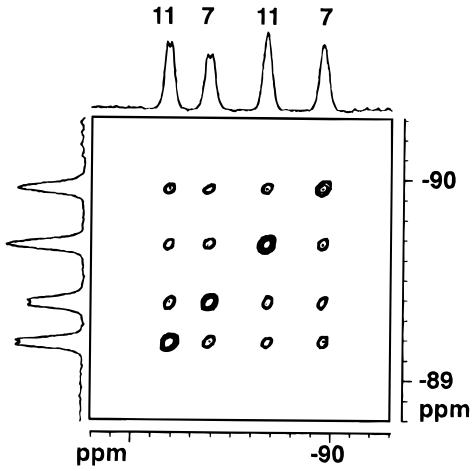

Figure 2. Phase-sensitive NOESY spectrum (F_{ortho} region only, CD_3CN, 273 K) showing the equilibrium between complexes **7** and **11** and the exchange between both F_{ortho} of each $C_6Cl_2F_3$ group.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Pd(C_6Cl_2F_3)\{P(C_2H_4Py)2Ph\text{-}P,N\text{-}\mu\text{-}N'\}]_2(BF_4)_2\cdot CH_3CN$ (**7**)

Pd(1)−C(51)	2.018(8)	Pd(1)−N(3)	2.144(6)
Pd(1)−N(1)	2.140(7)	Pd(1)−P(1)	2.237(2)
C(51)−Pd(1)−N(1)	90.0(3)	C(51)−Pd(1)−P(1)	85.9(2)
C(51)−Pd(1)−N(3)	172.9(3)	N(1)−Pd(1)−P(1)	175.6(2)
N(1)−Pd(1)−P(3)	90.7(3)	N(3)−Pd(1)−P(1)	93.6(2)

The bridging Py group is nearly perpendicular to the coordination plane of the metal (dihedral angle 86.3(2)°) whereas the chelating Py group is more nearly parallel to it (dihedral angle of 34.3(2)°). In spite of the very different coordination geometries for the bridging and chelating Py groups and the different groups *trans* to them, the Pd−N bond lengths are very similar. The H^6 atom of the bridging pyridyl group is only 2.62(7) Å from the nearest fluorine atom, consistent with the presence of through-space F−H coupling in the NMR spectra noted above.

The dimeric nature of the cationic compounds raises the question of the stability of the bridge. Although **7** and **8** show apparently static NMR spectra at room temperature, the complexes with PN_3, **9** and **10**, show very broad signals. It must be noted that it is not possible to exchange the uncoordinated Py with the chelated one unless the bridging Py also decoordinates, thus allowing a 120° rotation of the phosphine around the P−Pd bond. The involvement of the bridging Py group is confirmed by the fact that **7** and **8** also show exchange, although at a somewhat higher temperature. The bridge splitting is definitely proved by exchange experiments: A 1:1 mixture of **7** and **8** gives within minutes a statistical 1:1:2 mixture of **7**, **8**, and the mixed complex $[Pd_2(C_6F_5)(C_6Cl_2F_3)(PN_2)_2]^{2+}$ (**11**), which can be identified by ^{19}F NMR spectroscopy. The exchange between **7** and **11** can be clearly seen in the phase-sensitive NOESY shown in Figure 2, in which cross peaks are observed correlating (a) the two inequivalent F_{ortho} atoms on each $C_6Cl_2F_3$ ring (exchanging as discussed before) and (b) each F_{ortho} atom of **7** with the two F_{ortho} atoms of **11**. Thus, the spectrum confirms that there is an intermolecular equilibrium between complexes **7** and **11**, where obviously **8** must be involved. Similarly, a 1:1 mixture of **9** and **10** gives a statistical 1:1:2 mixture of **9**, **10**, and the mixed complex $[Pd_2(C_6F_5)(C_6Cl_2F_3)(PN_3)_2]^{2+}$ (**12**).

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Experimental Section

General Methods and NMR Techniques. Commercial 2-vinylpyridine, phenylphosphine, diphenyl phosphine, diethylphosphonate, and potassium *tert*-butoxide were used without further purification. Solvents were distilled and degassed using standard methods. $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$ was prepared as reported in the literature,[21] and $[Pd_2(\mu\text{-}Cl)_2(C_6Cl_2F_3)_2(tht)_2]$ was prepared similarly using 1,3,5-$C_6Cl_3F_3$ instead of BrC_6F_5.[22] $PH_2(CH_2CH_2Py)$, $P(O)(CH_2CH_2Py)(OEt)_2$, and 2-$PyCH_2CH_2Cl$ were prepared by published methods.[23−25]

^1H NMR (300.16 MHz), ^{19}F NMR (282.4 MHz) and ^{31}P NMR (121.4 MHz), spectra were recorded on a Bruker ARX 300 instrument equipped with a VT-100 variable-temperature probe. Chemical shifts are reported in ppm from tetramethylsilane (^1H), CCl_3F (^{19}F), or H_3PO_4 (85%) (^{31}P), with positive shifts downfield, and at ambient probe temperature unless otherwise stated. ^{19}F EXSY experiments were carried out with a standard NOESY program operating in the phase-sensitive mode, with a 5% random variation of the evolution time to avoid COSY cross-peaks. Combustion CHN analyses were made on a Perkin-Elmer 2400 CHN microanalyzer. All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. The phosphines prepared have varying sensitivities to oxygen, forming the corresponding phosphine oxides. The isolated metal complexes are air stable.

Synthesis of the Ligands. The ligand $P(CH_2CH_2Py)Ph_2$ (PN), first prepared by Uhlig and Maaser,[26] was synthesized according to the general method described for the preparation of polytertiary phosphines by King *et al.*[27] and was purified according to Wang *et al.*[7a] Vinylpyridine (10 mmol, 1.05 g), KBu^tO (0.6 mmol, 0.067 g), and $PHPh_2$ (10 mmol, 1.862 g) were dissolved in THF (30 mL) in a three-necked flask, and the mixture was refluxed for 4 h. Evaporation of the solvent gave the crude phosphine as a thick yellow oil. The product was purified by passing it through a silica gel column, using diethyl ether as eluant, and crystallized from ether. Yield: 1.6 g (55%).

The ligand $P(CH_2CH_2Py)_2Ph$ (PN_2), previously synthesized in a different way by Du Bois *et al.*,[28] was prepared by the same method used for (PN). Vinylpyridine (175 mmol, 18.96 mL), KBu^tO (11 mmol, 1.270 g), and PH_2Ph (86 mmol, 9.466 g) were dissolved in THF (200 mL) in a three-necked flask, and the mixture was refluxed for 4 h. Evaporation of the solvent gave a yellow oil which was dissolved in diethyl ether, washed with water, and dried over $MgSO_4$. The solvent was evaporated, and the product was purified by passing it through a silica gel column, using as eluant *n*-hexane (only vinylpyridine is removed) and then diethyl ether. The compound was obtained as a colorless oil. Yield: 20.57 g (75%).

The ligand $P(CH_2CH_2Py)_3$ (PN_3) was prepared similarly. To a solution of $PH_2(CH_2CH_2Py)$ 4.870 g (35 mmol) in 40 mL of THF were added 8.10 mL (75.0 mmol) of vinylpyridine and 0.53 g (4.7 mmol) of KBu^tO. The mixture was refluxed until completion of the reaction (about 30 h, monitored by $^{31}P\{^1H\}$ NMR of aliquots of the crude mixture in acetone-d_6). The solvent was evaporated, and the excess vinylpyridine was removed by heating under vacuum at 80 °C. Yield: 9.137 g (74%). Anal. Calcd: C, 72.19; N, 12.08; H, 6.87. Found: C, 72.22; N, 12.31; H, 6.92. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −26.4 (s). ^1H NMR (acetone-d_6): δ 8.49 (m, 1H), 7.66 (m, 1H), 7.28 (m, 1H), 7.14 (m, 1H), 2.91 (m, 2H), 1.92 (m, 2H).

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Synthesis of the Complexes. [PdCl($C_6Cl_2F_3$)(PN)] (1). To a stirred solution of $[Pd_2(\mu\text{-}Cl)_2(C_6Cl_2F_3)_2(tht)_2]$ (106.6 mg, 0.134 mmol) in CH_2Cl_2 (20 mL) was added PN (78 mg, 0.268 mmol) in 10 mL of CH_2Cl_2. After 30 min, the pale yellow solution was filtered, 15 mL of ethanol was added, and the solution was concentrated to 10 mL. After the concentrate was allowed to stand overnight at −20 °C, **1** crystallized as a white product, which was filtered off and dried in vacuum. Yield: 129 mg (76%). Anal. Calcd: C, 47.42; N, 2.21; H, 2.86. Found: C, 46.85; N, 2.00; H, 3.05. ^{1}H NMR ($CDCl_3$): δ 9.25 (d, 1H), 7.76 (td, 1H), 7.30 (m, 12H), 3.71 (m, 2H), 2.60 (m, 2H).

[Pd(C_6F_5)Cl(PN)] (2). To a stirred solution of $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$ (100 mg, 0.126 mmol) in CH_2Cl_2 (20 mL) was added PN (74 mg, 0.254 mmol) in 10 mL of CH_2Cl_2. After 30 min, the solution was filtered and evaporated to dryness. The resulting oil was washed twice with 10 mL of *n*-hexane to remove the remaining tht, and the product **2** was crystallized from CH_2Cl_2/ethanol. Yield: 131 mg (87%). Anal. Calcd: C, 50.05; N, 2.33; H, 3.00. Found: C, 50.12; N, 2.41; H, 2.88. ^{1}H NMR ($CDCl_3$): δ 9.22 (d, 1H), 7.65 (td, 1H), 7.3 (m, 12H), 3.67 (m, 2H), 2.52 (m, 2H).

[Pd($C_6Cl_2F_3$)Cl(PN_2)] (3). This compound was prepared as described for **1**, but using PN_2 (85.8 mg, 0.268 mmol) instead of PN. Yield: 142 mg (81%). Anal. Calcd: C, 47.16; N, 4.23; H, 3.20. Found: C, 47.02; N, 4.11; H, 3.31. ^{1}H NMR ($CDCl_3$ at 213 K): δ 9.28 (d, coord Py, 1H), 8.48 (d, free Py, 1H), 7.83 (m, 1H) 7.63 (m, 1H), 7.28−7.60 (m, 7H), 7.17 (dd, 1H), 6.99 (d, 1H), 3.60 (broad m, 2H), 2.95 (broad m, 1H), 2.45 (broad m, 2H), 2.27 (broad m, 3H).

[Pd(C_6F_5)Cl(PN_2)] (4). This compound was prepared as described for **2**, but using PN_2 (81.4 mg, 0.254 mmol) instead of PN. Yield: 105 mg (66%). Anal. Calcd: C, 47.71; N, 4.45; H, 3.33. Found: C, 47.68; N, 4.35; H, 3.41. ^{1}H NMR ($CDCl_3$ at 213 K): δ 9.29 (d, coord Py, 1H), 8.45 (free Py, 1H), 7.83 (m, 1H), 7.62 (m, 1H), 7.49 (dd, 2H), 7.36 (m, 5H), 7.17 (dd, 1H), 7.00 (d, 1H), 3.58 (broad m, 2H), 2.97 (broad m, 1H), 2.40 (broad m, 3H), 2.25 (broad m, 2H).

[Pd($C_6Cl_2F_3$)Cl(PN_3)]·0.5 CH_2Cl_2 (5). This compound was prepared as described for **1**, but using PN_3 (93.6 mg, 0.268 mmol) instead of PN. Yield: 149 mg (81%). Anal. Calcd: C, 45.15; N, 5.74; H, 3.42. Found: C, 45.23; N, 5.80; H, 3.52. ^{1}H NMR ($CDCl_3$ at −60 °C): δ 9.32 (coord Py, 1H), 8.43 (free Py, 2H), 7.78 (m, 1H), 7.62 (m, 2H), 7.2−7.4 (m, 2H), 7.11 (m, 4H), 3.35 (broad m, 2H), 3.22 (broad m, 2H), 2.68 (broad m, 2H), 2.09 (broad m, 2H), 1.65 (broad m, 4H).

[Pd(C_6F_5)Cl(PN_3)] (6). This compound was prepared as described for **1**, but using PN_3 (88.7 mg, 0.254 mmol) instead of PN. Yield: 125 mg (75%). Anal. Calcd: C, 49.28; N, 6.41; H, 3.65. Found: C, 49.14; N, 6.33; H, 3.47. ^{1}H NMR (−213 K, $CDCl_3$): δ 9.40 (dd, coord Py, 1H), 8.43 (dd, free Py, 2H), 7.87 (t, coord Py, 1H), 7.63 (t, free Py, 2H), 7.38 (m, coord Py, 2H), 7.15 (m, free Py, 4H), 3.28 (broad m, free CH_2CH_2Py, 4H), 2.71 (broad m, coord CH_2CH_2Py, 2H), 2.12 (broad m, coord CH_2CH_2Py, 2H), 1.89 (broad m, free CH_2CH_2Py, 4H).

[$Pd_2(C_6Cl_2F_3)_2(PN_2)_2$]($BF_4$)$_2$ (7). To a stirred solution of **3** (111.2 mg, 0.168 mmol) in acetone (30 mL) was added $AgBF_4$ (33 mg, 0.168 mmol). After 30 min, the AgCl formed was removed by filtration. Addition of ethanol (15 mL) and evaporation gave a white precipitate, which was filtered off and dried in vacuum. Yield: 97 mg (81%). Anal. Calcd: C, 43.76; N, 3.93; H, 2.97. Found: C, 43.63; N, 3.75; H, 3.07. ^{1}H (acetone-d_6): 8.8 (broad d, coord Py, 1H), 8.4 (t, bridging Py, J_{F-H} = 4.8 Hz, 1H), 8.19 (td, 1H), 8.08 (td, 1H), 7.83 (ddd, 2H), 7.74 (dd, 2H), 7.52 (m, 3H), 7.38 (m, 2H), 5.41 (broad m, 1H), 3.98 (broad m, 3H), 3.48 (m, 1H), 3.30 (m, 1H), 2.63 (m, 2H).

[$Pd_2(C_6F_5)_2(PN_2)_2$](BF_4)$_2$ (8). This compound was prepared as described for **7**, but starting from **4** (106 mg, 0.168 mmol) instead of **3**. Yield: 80 mg (70%). Anal. Calcd: C, 45.88; N, 4.16; H, 2.79. Found: C, 45.59; N, 4.06; H, 2.58. ^{1}H (acetone-d_6): 8.92 (broad d, coord Py, 1H), 8.35 (t, bridging Py, J_{F-H} = 4.1 Hz, 1H), 8.21 (td, 1H), 8.11 (td, 1H), 7.80 (ddd, 2H), 7.70 (dd, 2H), 7.49 (m, 3H), 7.35 (m, 2H), 5.40 (broad m, 1H), 3.90 (broad m, 3H), 3.47 (m, 1H), 3.30 (m, 1H), 2.58 (m, 2H).

[$Pd_2(C_6Cl_2F_3)_2(PN_3)_2$]($BF_4$)$_2$ (9). This compound was prepared as described for **7**, but starting from **5** (110 mg, 0.168 mmol) instead of **3**. Yield: 73 mg (61%). Anal. Calcd: C, 44.77; N, 5.80; H, 3.31. Found: C, 44.63; N, 5.74; H, 3.45. ^{1}H NMR (243 K, CD_3CN): δ 8.45 (d, 1H), 8.36 (dd, 1H), 7.96 (t, 1H), 7.93 (t, 1H), 7.82 (t, 1H), 7.65 (m, 2H), 7.55 (d, 1H), 7.31 (m, 2H), 7.17 (m, 2H), 4.99 (broad m, 1H), 3.50 (broad m, 4H), 3.37 (m, 2H), 2.60 (m, 2H), 2.58 (m, 3H).

[$Pd_2(C_6F_5)_2(PN_3)_2$](BF_4)$_2$ (10). This compound was prepared as described for **8**, but starting from **6** (110 mg, 0.18 mmol) instead of **4**. Yield: 95 mg (78%). Anal. Calcd: C, 45.71; N, 5.95; H, 3.38. Found: C, 45.82; N, 6.01; H, 3.49. ^{1}H NMR (243 K, CD_3CN): δ 8.53 (d, 1H), 8.38 (dd, 1H), 7.95 (m, 2H), 7.82 (t, 1H), 7.65 (m, 3H), 7.35 (t, 1H), 7.24 (t, 1H), 7.17 (m, 2H), 4.94 (broad m, 1H), 3.60−3.1 (broad m, 5H), 2.65 (m, 2H), 2.48 (m, 1H), 2.07 (m, 3H).

Equilibrium between 7 and 8. Complexes **7** (10.4 mg, 0.0073 mmol) and **8** (9.9 mg, 0.0073 mmol) were dissolved in 0.5 mL of CD_3CN in an NMR tube. The ^{19}F NMR spectrum at room temperature showed the signals of the complex $[Pd_2(C_6F_5)(C_6Cl_2F_3)(PN_2)_2](BF_4)_2$ (**11**). ^{19}F NMR (acetone-d_6): δ($C_6F_3Cl_2$ group), −88.85 (d, $^3J_{F-P}$ = 8 Hz, 1F), −89.1 (t, 1F), −117.45 (s, 1F); δ(C_6F_5 group) −112.02 (m, 1F), −116.71 (m, 1F), −159.50 (t, 1F), −159.85 (m, 1F), −162.32 (m, 1F).

Equilibrium between 9 and 10. Complexes **9** (17.4 mg, 0.0117 mmol) and **10** (16.6 mg, 0.0117 mmol) were dissolved in 0.6 mL of CD_3CN in an NMR tube. The ^{19}F NMR spectrum at 243 K showed signals (1:1:2 ratio) for complexes **9** and **10** and for $[Pd_2(C_6F_5)(C_6Cl_2F_3)(PN_3)_2](BF_4)_2$ (**12**). ^{19}F NMR (CD_3CN) for **12**: δ($C_6F_3Cl_2$ group) −88.41 (broad, 1F), −88.53 (broad d, 1F), −117.12 (s, 1F); δ(C_6F_5 group) −111.40 (m, 1F), −116.49 (m, 1F), −158.7 (m, 1F), −159.18 (m, 1F), −161.21 (m, 1F).

X-ray Structure of [$Pd_2(C_6Cl_2F_3)_2$\{μ-PPh(C_2H_4Py)$_2$-*P,N,*μ-*N*′\}$_2$](BF_4)$_2$·CH_3CN (7). Crystal data and other details of the structure analysis are presented in Table 4. Colorless crystals of **7** were recrystallized from an acetonitrile/2-propanol/ether solution and showed a regular blocklike habit. The mother liquors, as well as the crystals, showed signs of decomposition, yielding metallic palladium. The crystals showed signs of partial decomposition of the crystal, reflected in broad diffraction peaks and high-background scattered radiation. After checking a number of crystals, we selected one with approximate dimensions of 0.4 × 0.37 × 0.60 mm for study and mounted it on a glass fiber with vacuum grease.

All diffraction measurements were made at −100 °C with a Siemens three-circle SMART[29] area detector diffractometer using graphite-monochromated Mo Kα radiation. Unit cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω), each at 10 s exposure. A full hemisphere of reciprocal space (1321 frames in total, 10 s exposure per frame) was scanned by 0.3° ω

Table 4. Crystal Data and Structure Refinement Details for $[Pd(C_6Cl_2F_3)\{\mu\text{-}P(C_2H_4Py)_2PhP,N,\mu\text{-}N'\}]_2(BF_4)_2$·$CH_3CN$ (**7**)

empirical formula	$C_{58}H_{45}B_2Cl_4F_{14}N_5P_2Pd_2$
fw	1516.2
crystal size, mm	0.4 × 0.37 × 0.60
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	10.972(2)
b, Å	11.113(2)
c, Å	12.898(3)
α, deg	70.55(1)
β, deg	88.39(1)
γ, deg	75.13(1)
V, Å^3	1430.4(5)
Z	1
ρ(calcd), Mg m^{-3}	1.76
μ, mm^{-1}	0.960
θ range, deg	2.39−25.09
no. of collcd reflecns	6844
no. of reflecns for calcns	4858 [*R*(int) = 0.0973]
final R1, wR2[a]	0.0775, 0.1857
goodness-of-fit, *S*[a]	1.088
max peak in final diff map, e Å^{-3}	2.33

[a] Residuals calculated for reflections with $I > 2\sigma(I)$; wR2 = $[\sum w\Delta^2/\sum wF_o^4]^{0.5}$; $S = [\sum w\Delta^2/(N - NV)]^{0.5}$; R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; $\Delta = F_o^2 - F_c^2$.

(29) SMART Siemens Molecular Analysis Research Tool V4.014, Siemens Analytical X-ray Instruments, Madison, WI.

steps at $\phi = 0$, 88, and 180° with the area detector center held at $2\theta = -27°$. A final set of 50 frames collected repeated the first 50 in order to check for signs of decay over the period of data collection. The reflections were integrated using the SAINT[30] program. No further crystal decay over the period of data collection was observed. A total of 6884 diffracted intensities were measured, and 4858 unique observations remained after averaging of duplicate and equivalent measurements ($R_{int} = 0.097$) and deletion of the systematic absences; of these, 3987 had $I > 2\sigma(I)$. An absorption correction was applied; transmission coefficients were in the range 0.837−0.584. Lorentz and polarization corrections were applied.

The structure was solved by direct and Fourier methods and refined using full-matrix least-squares calculations on F^2 with the SHELXL-93 program[31] and a Silicon Graphics IRIS computer. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. The anion shows signs of disorder, and the fluorine atoms F(91) and F(92) are disordered over two sites (in the ratio 0.74(2):0.26(2)); the acetonitrile is disordered about the inversion center. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} values of their attached carbons for the aromatic hydrogens. The displacement parameters of the disordered fluorine atoms were restrained to be nearly isotropic. Hydrogen atoms of the CH_3CN were not located or geometrically imposed due to the disorder of the molecule.

Refinement of the 407 least-squares variables converged to the residuals given in Table 4. Weights, w, were set equal to $1/[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$ and $a = 0.1190$ and $b = 7.64$ were varied to minimize the variation in S as a function of $|F_o|$. Final difference electron density maps showed features in the range +2.32 to −1.93 e Å^{-3}, the largest being within 1 Å of the palladium atoms. The poor residual indices and high difference electronic density features are presumably related to the crystal quality problems noted above and consequent difficulties with accurate integration of the intensity data. Complex neutral-atom scattering factors were taken from ref 32.

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Supporting Information Available: Listings of observed rate constants for the Py exchange in complexes **3**−**6** and, for the crystal structure of **7**, tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions and isotropic thermal parameters (8 pages). Ordering information is given on any current masthead page.

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(30) SAINT (Siemens Area detector INTegration) program, Siemens Analytical X-ray Instruments, Madison, WI.
(31) SHELXTL Rev. 5.0, Siemens Analytical X-ray Instruments, Madison, WI.
(32) *International Tables for Crystallography;* Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.