Monoarylated Fluoromesitylpalladium Complexes

Camino Bartolomé,[a] Pablo Espinet,*[a] Jose M. Martín-Alvarez,[a] and Fernando Villafañe[a]

Keywords: Palladium / Fluorinated ligands / Ligand substitution / Bulky ligands / Steric hindrance

Monoarylated complexes [PdCl(Fmes)(L-L)] [Fmes = 2,4,6-tris(trifluoromethyl)phenyl or fluoromesityl] and *trans*-[PdCl(Fmes)L_2] have been obtained by arylation of [$PdCl_2$(L-L)] (L-L = tmeda) or *trans*-[$PdCl_2L_2$] (L = SMe_2), by splitting the bridging chloro ligands in [Pd(μ-Cl)(Fmes)(NCMe)]$_2$ {L-L = 4,4′-Me_2bipy, biquinolyl (2,2′-biquinoline), OPPhPy$_2$-*N*,*N*′, (OH)(CH_3)CPy$_2$-*N*,*N*′, dppe, pte [1,2-bis(phenylthio)ethane]; L = 4-pic}, or by substitution of the diolefin in [PdCl(Fmes)(COD)] (L = *t*BuNC). A 1:1 ratio of [Pd(μ-Cl)(Fmes)(NCMe)]$_2$ and monodentate ligands affords [PdCl(Fmes)(NCMe)L] (L = 2,6-lut, 3,5-lut, PPh_3), whereas a 1:1 mixture of [{PdCl(Fmes)(NCMe)}$_2$(μ-dppe)] and [PdCl(Fmes)(dppe)] is obtained with dppe under mild conditions. The precursor [Pd(μ-Cl)(Fmes)(NCMe)]$_2$ is generated by boiling under reflux [PdCl(Fmes)(COD)] in MeCN, and has been used to obtain various binuclear monoarylated complexes [Pd(Fmes)(μ-X)L]$_2$ [X = Br, L = MeCN, P(*o*-Tol)$_3$; X = Cl, L = CO, 4-pic, 3,5-lut, P(*o*-Tol)$_3$]. Other [Pd(Fmes)(μ-X)L]$_2$ complexes have been obtained from *trans*-[PdCl(Fmes)(SMe_2)$_2$] (X = Cl, L = tht, SMe_2, PPh_3) and from K[Pd_4(Fmes)$_4I_5$] [X = I, L = P(*o*-Tol)$_3$]. Despite the steric hindrance imposed by the Fmes ligand (*ortho* effect), the ligand-substitution reactions are suggestive of associative mechanisms.

Introduction

The high steric demand of the 2,4,6-tris(trifluoromethyl)phenyl (nonafluoromesityl or Fmes) group, an interesting ligand for main-group[1,2] and transition metals,[3] hinders rotation around the M−Fmes bonds, restricts rotation of other ancillary ligands on the same metal center, and shows a high degree of axial protection in square-planar complexes (*ortho* effect).[4]

Like other such ligands Fmes can stabilize species that are otherwise difficult to obtain. Thus, its coordination to palladium has resulted in an unprecedented self-assembled pyramidal tetrametallic complex with a halide apex in the [$Pd_4(Fmes)_4X_5$]$^-$ (X = Cl, Br, I), and has lead to the formation of neutral aquo complexes, and to a new halocarbon ligand that acts as a chelate.[5] Weak M···F interactions, invoked in many other complexes,[1−3] are deemed absent in our fluoromesitylpalladium(II) complexes based on analysis of a number of solid-state structures.[4,5]

The Fmes group's bulk makes its coordination by arylation difficult. In fact, our initial results on the coordination of Fmes in palladium(II) complexes indicate that arylation depends greatly on the size of the ancillary ligands in the parent complex.[4] Therefore, ligand substitution of monoarylated complexes accessible by arylation may widen the range of monoarylated species available. Here we describe the synthesis and characterization of several monoarylated Fmes palladium(II) complexes, with monodentate or bidentate ligands, as well as binuclear monoarylated complexes.

Results and Discussion

The synthesis and structural characterization of the parent complex [Pd(μ-Cl)(Fmes)(NCMe)]$_2$ is described first, followed by discussion of the four types of complexes prepared, i.e. [PdCl(Fmes)(L-L)], [PdCl(Fmes)L_2], [PdCl(Fmes)(NCMe)L], and [Pd(Fmes)(μ-X)L]$_2$.

Synthesis and Characterization of [Pd(μ-Cl)(Fmes)(NCMe)]$_2$

Refluxing [PdCl(Fmes)(COD)][4] in MeCN the dimeric complex [Pd(μ-Cl)(Fmes)(NCMe)]$_2$ (**1a**) was formed, which could be isolated as a yellow solid [Equation (1)].

$$2\,[\mathrm{PdCl(Fmes)(COD)}] \xrightarrow[\curvearrowright\ 2\,\mathrm{COD}]{2\,\mathrm{MeCN}} \underset{\mathbf{1a}}{[\mathrm{Pd}(\mu\text{-Cl})(\mathrm{Fmes})(\mathrm{NCMe})]_2} \qquad (1)$$

The ^1H and ^{19}F NMR spectra of **1a** show the presence of *cis* and *trans* isomers in solution (Scheme 1). The ^{19}F NMR spectrum in $CDCl_3$ at room temperature has two singlets (ca. 75:25 ratio) corresponding to the *para*-CF_3 groups of each isomer. The *ortho*-CF_3 groups' signals in $CDCl_3$ are coincident, and only one singlet is observed, but two sing-

---

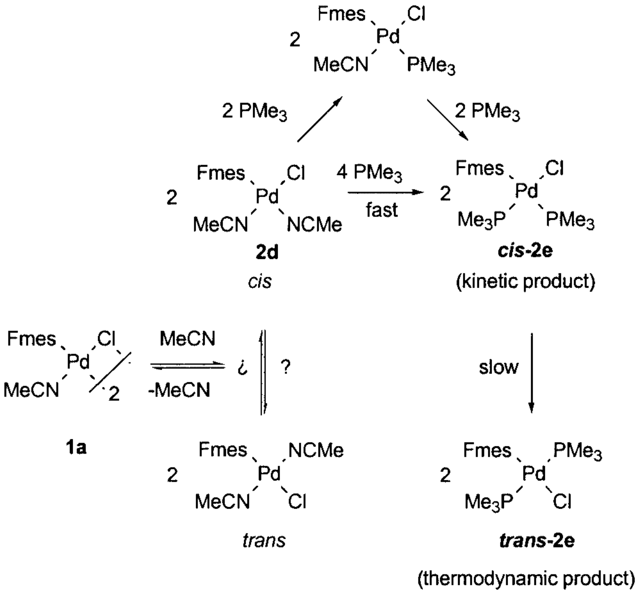
[a] Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid,
47005 Valladolid, Spain
E-mail: espinet@qi.uva.es

DOI: 10.1002/ejic.200300229

lets are clearly distinguished in the spectrum recorded in [D$_6$]acetone. Addition of acetone to a solution of **1a** in CDCl$_3$ produces a progressive increase of the less intense resonance, indicating that it corresponds to the polar *cis* isomer, which is expected to be favored in more polar solvents.[6]

Scheme 1. The *trans* and *cis* isomers of complexes [Pd(μ-Cl)(Fmes)L]$_2$ (**1**)

When **1a** was dissolved in MeCN the initial yellow solution became nearly colorless and only one singlet for the *ortho*-CF$_3$ and one singlet for the *para*-CF$_3$ were detected by ^{19}F NMR spectroscopy. This indicates that MeCN has split the chloro bridges, giving rise to only one isomer (either *cis* or *trans*), or to a fast exchange between the two possible isomers (Scheme 2). The solid monomer could not be isolated due to its marked tendency to regenerate **1a**, releasing the MeCN ligand *trans* to the Fmes group,[7] which has a high *trans* influence.[8] The ^{19}F NMR spectrum of **1a** in CDCl$_3$ is hardly affected by the addition of MeCN (**1a**/MeCN, 1:2), and the monomer concentration is high only in the presence of a high excess of acetonitrile in solution.

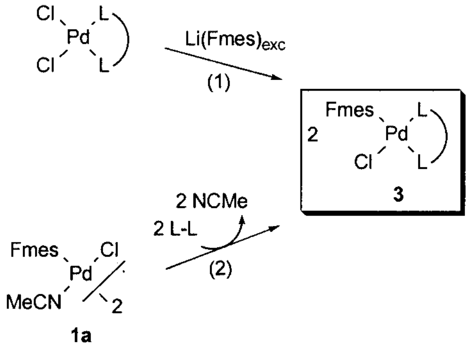


Scheme 2. Complexes detected in solutions of **1a** with MeCN and PMe$_3$

To understand the reaction behavior of the monomer, PMe$_3$ was added to a solution of **1a** in MeCN. Instantaneous formation of *cis*-[PdCl(Fmes)(PMe$_3$)$_2$] (*cis*-**2e**) was observed when two equivalents of PMe$_3$ per palladium were added, suggesting an associative substitution on *cis*-**2d** promoted by the high *trans* effect of the Fmes ligand.[9] The solution of *cis*-**2e** then isomerizes to the thermodynamic product *trans*-**2e**, according to the general antisymbiotic effect,[10] or to a high *transphobia* between the phosphane and the Fmes group.[11] The geometry of *cis*- or *trans*-**2e** is readily deduced by looking for P−F coupling between the coordinated phosphorus atom and the *ortho*-CF$_3$ groups. As reported for [PdCl(Fmes)(PPh$_3$)$_2$],[4] P−F coupling is observed when Fmes and a phosphane are coordinated *cis*, but not when these groups are coordinated *trans*.

Synthesis of [PdCl(Fmes)(L-L)]

Complexes [PdCl(Fmes)(L-L)] (**3**) were synthesized by two methods (Scheme 3): (1) arylation of the dichloro complex with Li(Fmes); or (2) bridge splitting and concomitant substitution of MeCN in **1a** by a bidentate ligand as chelate. The first method successfully furnished [PdCl(Fmes)(tmeda)] (**3a**), as we have reported for other monoarylated complexes containing bidentate chelating ligands.[4] Different neutral bidentate ligands L-L cleaved the chloro bridges and replaced MeCN from **1a** to give [PdCl(Fmes)(L-L)] (L-L= 4,4′-Me$_2$bipy, **3b**; biquinolyl, **3c**; OPPhPy$_2$-*N,N*′, **3d**; (OH)(CH$_3$)CPy$_2$-*N,N*′, **3e**; pte, **3f**; dppe, **3g**). All processes were carried out at room temperature, but to obtain [PdCl(Fmes)(dppe)] (**3g**), refluxing in toluene was needed, as milder conditions lead to a mixture of **3g** and [(μ-dppe){PdCl(Fmes)(NCMe)}$_2$] (**4d**).

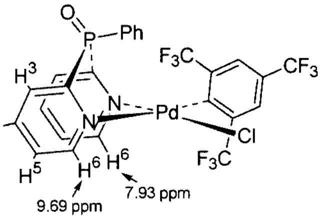


Scheme 3. Synthesis of [PdCl(Fmes)(L-L)] complexes **3**; (1) tmeda, **3a**. (2) 4,4′-Me$_2$bipy, **3b**; biquinolyl (2,2′-biquinoline), **3c**; OPPhPy$_2$-*N,N*′, **3d**; (OH)(CH$_3$)CPy$_2$-*N,N*′, **3e**; pte [1,2-bis(phenylthio)ethane], **3f**; dppe, **3g**

The ^{19}F NMR spectrum of **3g** in CDCl$_3$ shows one doublet for the *ortho*-CF$_3$ due to coupling with the phosphorus atom *cis* to the Fmes ($J_{P,F}$ = 5.5 Hz). The ^{31}P{^{1}H} NMR spectrum displays two signals, a doublet of septuplets for the phosphorus atom *cis* to the Fmes group, and a doublet for the phosphorus atoms *trans* to Fmes ($J_{P,P}$ = 23.2 Hz). Coupling between the hydrogen atoms of the Fmes group and the phosphorus atom *trans* to the Fmes ($^4J_{P,H}$ = 1 Hz) is observed in the ^{1}H NMR spectrum.

The ^{1}H NMR spectra of complexes **3** show the nonequivalence of the two halves of the bidentate ligands, confirming their coordination as a chelate with two different ligands in the other positions of the square plane. The chemical shifts detected for the H^6 of the pyridyl groups in **3b**, **3c**, **3d** and **3e** are very sensitive to the ligand coordinated *cis*. Thus, those *cis* to the chloro ligand appear at lower field than for the free ligand,[12] whereas anisotropic shielding produces an upfield shift of the H^6 signals *cis* to the Fmes ring.

Two conformers may be proposed for **3d**, depending on whether the oxygen atom (*endo*-O) or the phenyl group (*endo*-Ph) of the $OPPhPy_2$ ligand takes the *endo* position in the boat-like metallacycle described by the chelating ligand. An *endo*-Ph conformation (Scheme 4) has been found for solid $[Pd(C_6F_5)Br(OPPhPy_2\text{-}N,N')]$,[13] which is consistent with the clear upfield chemical shift here of one of the *ortho*-CF_3 groups in the ^{19}F NMR spectrum.



Scheme 4. Proposed conformation for $[PdCl(Fmes)(OPPhPy_2\text{-}N,N')]$ (**3d**)

Two similar conformers, (*endo*-OH) or (*endo*-Me), are possible for **3e**. A single-crystal X-ray analysis of **3e** was therefore undertaken to establish this point and other structural features. A perspective view of the molecular structure of **3e** is given in Figure 1, and selected bond lengths and angles are listed in Table 1. The square-planar geometry of Pd is distorted towards tetrahedral to some extent, as the N(1) atom is 0.196(7) Å above the plane described by the C(21), Pd(1) and Cl(1) atoms, and N(2) is 0.307(7) Å below this plane. The C−C−C angle at the *ipso* carbon is significantly less than 120° [ca. 114.4(6)°], due to the electronic effects of the electropositive metal and electronegative CF_3 substituents at these positions.[14] The fluoromesityl ligand adopts the expected coordination, essentially perpendicular to the coordination plane. The Pd···F_3C-*ortho* distances in **3e** [the shortest, Pd(1)···F(291), is 2.914(11) Å] are longer than those found in bisarylated "$Pd(Fmes)_2$" complexes. Bonding M···F interactions can be discounted in a coordinatively saturated metallic center because such contacts should involve a high energy orbital of the palladium atom as an acceptor of electronic density. Therefore, the crowding in **3e** is deemed responsible for the short nonbonding Pd···F contacts, as in other cases previously analyzed.[4]

The conformer found has the methyl group of the $(OH)(CH_3)CPy_2$ ligand oriented toward the axial position of the coordination plane (Figure 1). The hydrogen atom of the alcohol group was located in a difference Fourier map and refined;[15] it is involved in O−H···Cl intermolecular contacts. The O(1F)−Cl(1A) and H(6F)−Cl(1A) distances are 3.251(9) and 2.306(9) Å respectively, whereas the O(1F)−H(6F)−Cl(1A) angle is 165.4(8)°. The H−Cl distance is within the usual range for H−Cl hydrogen bonds,[16] suggesting that the conformation of the chelating ligand in **3e** helps to stabilize this conformer in the solid state. In solution the intermolecular hydrogen contacts probably break down and the spectroscopic evidence available does not allow us to ascertain whether the conformation of the chelating ligand found in the solid state is retained in the solution.

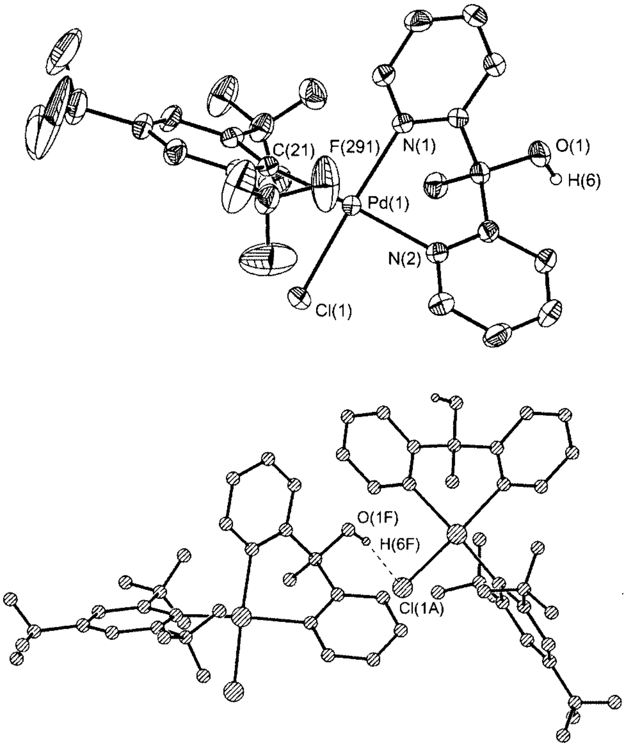


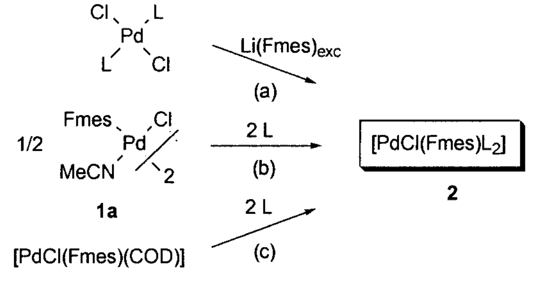
Figure 1. Top: Molecular structure of **3e** showing the atom numbering scheme. The ellipsoids are drawn at the 30% probability level. Bottom: Intermolecular H···Cl hydrogen bonds observed in **3e**

Table 1. Selected bond lengths [Å] and angles [°] for **3e**

Pd(1)−C(21)	1.988(7)	C(21)−Pd(1)−Cl(1)	86.4(2)
Pd(1)−Cl(1)	2.296(2)	N(2)−Pd(1)−Cl(1)	90.92(17)
Pd(1)−N(1)	2.068(6)	C(21)−Pd(1)−N(2)	171.2(3)
Pd(1)−N(2)	2.095(6)	N(1)−Pd(1)−Cl(1)	173.56(17)
C(21)−Pd(1)−N(1)	96.9(3)	C(26)−C(21)−C(22)	114.3(6)
N(1)−Pd(1)−N(2)	86.6(2)		

Synthesis of $[PdCl(Fmes)L_2]$

Scheme 5 shows three different ways to synthesize $[PdCl(Fmes)L_2]$ complexes: (1) by arylation of $[PdCl_2L_2]$ with Li(Fmes); (2) by bridge splitting and substitution of MeCN in **1a** by two equivalents of monodentate ligand; and (3) by substitution of the COD ligand in [PdCl(Fmes)(COD)].[4]



Scheme 5. Synthesis of $[PdCl(Fmes)L_2]$ (**2**). (a) L = SMe_2, **2a**. (b) L = 4-pic, **2b**. (c) L = *t*BuNC, **2c**

The complex *trans*-[PdCl(Fmes)(SMe_2)$_2$] (**2a**) was obtained by the same procedure previously described for *trans*-[PdCl(Fmes)(tht)$_2$] (tht = tetrahydrothiophene),[4] i.e. arylation of *trans*-[$PdCl_2$(SMe_2)$_2$] with Li(Fmes), which also gave [Pd(μ-Cl)(Fmes)(SMe_2)]$_2$ (**1h**) and *trans*-[Pd(Fmes)$_2$(SMe_2)$_2$] as by-products. The latter can be synthesized selectively by the method reported for *trans*-[Pd(Fmes)$_2$(tht)$_2$].[4]

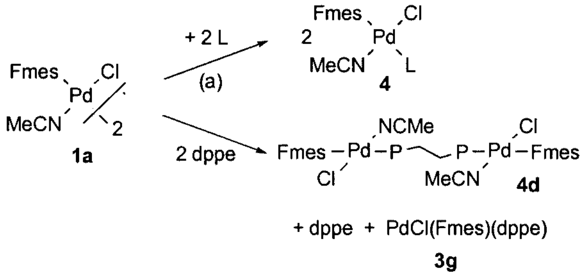
Treatment of **1a** with 4-pic leads to *cis*-[PdCl(Fmes)(4-pic)$_2$] (**2b**), as shown by the nonequivalence of both 4-pic ligands in the ^{1}H NMR spectrum. The solid must be isolated rapidly from its solution, otherwise a mixture with the *trans* isomer and [Pd(μ-Cl)(Fmes)(4-pic)]$_2$ (**1d**) is obtained.

The reaction of [PdCl(Fmes)(COD)] with two equivalents of *t*BuNC per palladium in refluxing acetone lead to *trans*-[PdCl(Fmes)(CN*t*Bu)$_2$] (**2c**), as evidenced by the equivalence of the two CN*t*Bu ligands in the ^{1}H NMR spectrum. Under milder conditions a mixture of the *cis* and *trans* isomers is obtained. All attempts to isolate the pure *cis* isomer were unsuccessful.

These results suggest that the *cis* isomers are the kinetic products formed initially by associative substitution of acetonitrile or COD, the reactions being controlled by the higher *trans* effect of Fmes. Whenever a *cis*-[PdCl(Fmes)L$_2$] is isolated (**2b**) or detected (*cis*-**2c**, or *cis*-**2e**) it readily isomerizes in solution to the thermodynamic product, i.e. the corresponding *trans* isomer, since Fmes is the ligand with the higher *trans* influence.[10] The *cis* to *trans* isomerization seems more favored for *cis*-**2c** than for **2b**. In fact, the isomerization of *cis*-**2c** occurs even in the solid state, because the CN*t*Bu (C-donor ligand) *trans* to Fmes is more destabilized than 4-pic (N-donor ligand). Details for these isomerizations are provided in the Exp. Sect.

Synthesis of [PdCl(Fmes)(NCMe)L]

Complexes [PdCl(Fmes)(NCMe)L] (**4**) were obtained from **1a** (Scheme 6).



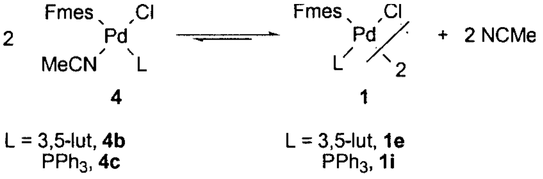
Scheme 6. Synthesis of [PdCl(Fmes)(NCMe)L] (**4**): a) L = 2,6-lut, **4a**; 3,5-lut, **4b**; PPh_3, **4c**

Treatment of **1a** with N- or P-donor ligands (1:1 ratio) in dichloromethane at room temperature leads to [PdCl(Fmes)(NCMe)L] (L = 2,6-lut, **4a**; 3,5-lut, **4b**; PPh_3, **4c**). The reaction with dppe (1:1 ratio) affords a mixture of [(μ-dppe){PdCl(Fmes)(NCMe)}$_2$] (**4d**), [PdCl(Fmes)(dppe)] (**3g**), and free dppe. The dimetallic complex **4d** is scarcely soluble in dichloromethane, which allows its separation from **3g**, which in turn can be isolated pure after free dppe is extracted with Et_2O. The formation of the kinetic product **4d** is a plausible result of the high *trans* effect of Fmes. Nevertheless, under thermodynamic conditions (in refluxing toluene), only **3g** is formed (Scheme 3).

The *trans* to Fmes coordination of the incoming ligand was confirmed by NMR spectroscopic data of the complexes containing phosphanes **4c** and **4d**, since the signals corresponding to the *ortho*-CF_3 and to the phosphorus atoms are singlets. The same geometry is expected for the complexes containing N-donor ligands, but NMR spectroscopic data do not give unequivocal support in this case. The solid IR spectra of all these complexes fit well a relative *cis* arrangement of the Fmes and chloro ligands, since the Pd−Cl stretching wavenumbers are consistently higher than those for unambiguously *trans*-[PdCl(Fmes)L$_2$] complexes.

Halogenoaryl complexes containing two different neutral ligands coordinated to the metal center, such as **4**, are not common and their disproportionation to two symmetric molecules seems to be favored [Equation (2)].[17] Although such disproportionation has not been observed for our complexes **4**, they are not indefinitely stable in solution and slowly lose MeCN to yield [Pd(Fmes)(μ-X)L]$_2$ (**1**) (Scheme 7). Details for the formation of complexes **4** in solution are provided in the Exp. Sect.

$$2\,\mathrm{MRXLL'} \rightleftharpoons \mathrm{MRXL_2} + \mathrm{MRXL'_2} \qquad (2)$$

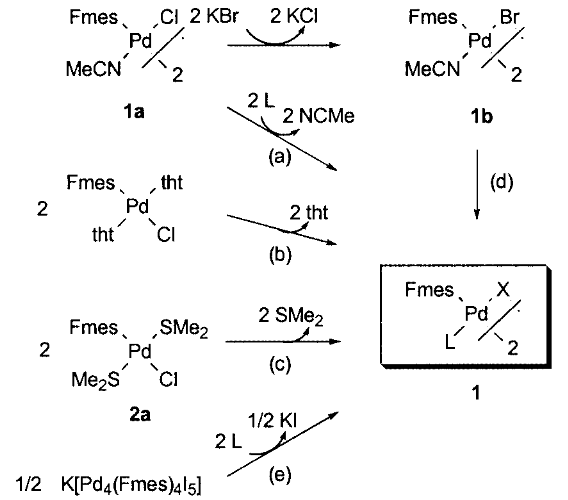


Scheme 7. Evolution of **4b** and **4c** in $CDCl_3$ solution

The destabilizing effect associated with the high "*transphobia*" between the phosphane and the Fmes group may help in the evolution of **4c** to **1i**.[11] Moreover, the process is entropically favored. The behavior of the complexes with N-donor ligands is remarkable: While **4a** is stable in solution, the $CDCl_3$ solutions of **4b** at room temperature are always in equilibrium with **1e**, revealing a lower tendency to give the dimer than for phosphanes. Solid **4b** is assumed to be pure, since the ^{19}F NMR spectrum of a sample dissolved at −60 °C in $CDCl_3$ showed no signals of **1e**. The different behavior of **4a** and **4b** in solution is explained upon considering that the *cis* disposition of the two bulky groups Fmes and 2,6-lut (both with *ortho* substituents) needed to form the corresponding dimer is highly destabilized.

Synthesis of [Pd(Fmes)(μ-X)L]$_2$

The syntheses of [Pd(Fmes)(μ-X)L]$_2$ (**1**) are depicted in Scheme 8. The main route to [Pd(Fmes)(μ-Cl)L]$_2$ [L = CO, **1c**; 4-pic, **1d**; 3,5-lut, **1e**; P(*o*-Tol)$_3$, **1f**] was the addition of neutral monodentate ligands L (Pd/L, 1:1) to solutions of **1a**. For **1c**, carbon monoxide was bubbled through the solution until a white solid precipitated. Boiling under reflux in toluene was needed to obtain **1d** and **1e**, otherwise the monometallic complexes *cis*-[PdCl(Fmes)(4-pic)$_2$] (**2b**) and [PdCl(Fmes)(NCMe)(3,5-lut)] (**4b**) were obtained as shown.



Scheme 8. Synthesis of [Pd(Fmes)(μ-X)L]$_2$ (**1**); (a) L = CO, **1c**; 4-pic, **1d**; 3,5-lut, **1e**, P(*o*-Tol)$_3$, **1f**. (b) L = tht, **1g**. (c) L = SMe$_2$, **1h**; PPh$_3$, **1i**. (d) L = P(*o*-Tol)$_3$, **1j**. (e) L = P(*o*-Tol)$_3$, **1k**

Conversely, boiling under reflux **2a** or [PdCl(Fmes)(tht)$_2$] in toluene affords [Pd(μ-Cl)(Fmes)(SMe$_2$)]$_2$ (**1h**) or [Pd(μ-Cl)(Fmes)(tht)]$_2$ (**1g**) respectively. With PPh$_3$, [Pd(μ-Cl)(Fmes)(PPh$_3$)]$_2$ (**1i**) was obtained. The latter was not selectively obtained using **1a** as starting material, as this process gives a mixture of **1i** and **4c**.

Bromo-bridged dimers can be obtained from **1a**. For instance, reaction of **1a** with KBr in MeCN yields [Pd(μ-Br)(Fmes)(NCMe)]$_2$ (**1b**), which reacts with P(*o*-Tol)$_3$ in toluene to give [Pd(μ-Br)(Fmes){P(*o*-Tol)$_3$}]$_2$ (**1j**). The similar iodo-bridged dimer [Pd(Fmes)(μ-I){P(*o*-Tol)$_3$}]$_2$ (**1k**) has been obtained by treating K[Pd$_4$(Fmes)$_4$I$_5$] with P(*o*-Tol)$_3$.[5a]

As described above for **1a**, two isomers are present in the solutions of these binuclear complexes (Scheme 1). The *trans* isomer is always the major one, but the exact *cis*:*trans* ratio in the solutions of complexes **1** seems to depend on the size of the monodentate ligand coordinated to the metal center: The bulkier the ligand, the higher the *trans*:*cis* ratio (for example, 95:5 for **1i**, L = PPh$_3$; 72:28 for **1c**, L = CO). Spectroscopic details are provided in the Exp. Sect.

All the spectroscopic and analytical data of complexes **1** confirm the geometry proposed, except for binuclear complexes with P(*o*-Tol)$_3$ (**1f**, **1j**, **1k**), where broad signals in their NMR spectra and the lack of P−F coupling prevented an unambiguous assignment. Therefore, an X-ray crystal structure analysis was carried out, revealing that the disposition of the phosphanes is *trans*. A perspective view of the molecular structure of **1j** is given in Figure 2 and selected distances and angles are listed in Table 2.

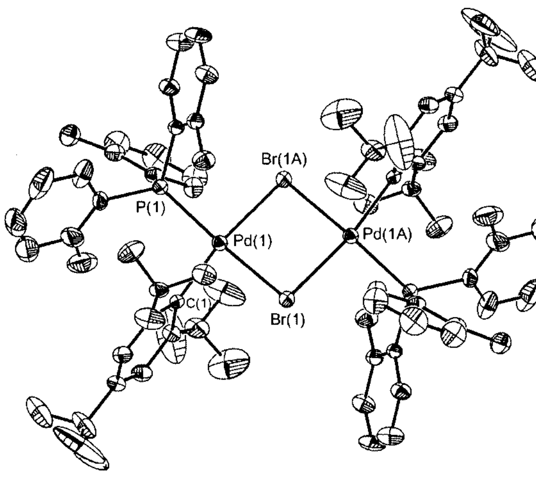


Figure 2. Molecular structure of **1j** showing the atom numbering scheme; the ellipsoids are drawn at 30% probability level

Table 2. Selected bond lengths [Å] and angles [°] for **1j**

Pd(1)−C(1)	2.036(8)	Pd(1)−P(1)	2.328(3)
C(1)−Pd(1)−P(1)	97.8(2)	P(1)−Pd(1)−Br(1)	176.48(7)
C(1)−Pd(1)−Br(1)	85.2(2)	C(1)−Pd(1)−Br(1A)	170.3(2)
Pd(1)−Br(1)	2.5119(13)	Pd(1)−Br(1A)	2.5438(13)
P(1)−Pd(1)−Br(1A)	90.51(7)	Pd(1)−Br(1)−Pd(1A)	93.35(5)
Br(1)−Pd(1)−Br(1A)	86.65(5)	C(2)−C(1)−C(6)	114.9(7)

The two palladium atoms are essentially square planar with minor distortions. Although the fluoromesityl ligand deviates by only 5.7° with respect to the perpendicular to the coordination plane, this keeps them away from the bulky phosphane, thus diminishing the steric hindrance. As usual, the C−C−C angle at the *ipso* carbon atom is less than 120° [ca. 115.0(7)°].[14] The Pd(1)−Br(1) distance at 2.5116(13) Å is smaller than Pd(1)−Br(1A) [2.5437(12) Å], and suggests a higher *trans* influence of the fluoromesityl group compared to the phosphane, as found for other aryl or alkyl phosphane complexes with bromo[18] or chloro bridges.[19]

The shortest Pd···F$_3$C-*ortho* distance found in **1j** [2.807(14) Å] is slightly longer than those found in bisarylated "Pd(Fmes)$_2$" complexes, but shorter than that in **3e**. Again this suggests that this distance is related to the degree of crowding in the fluoromesitylpalladium complexes, rather to bonding interactions.[4]

P(*o*-Tol)$_3$ has an *exo*$_2$ conformation in which an *o*-methyl group is oriented away from the metal. This reduces the rotation of the M−P−C$_{ipso}$ plane, thus also reducing the phosphane cone angle by ca. 35°.[20]

The P(1)−Pd(1)−C(1) angle is 97.8(2)°, instead of the ideal 90°, presumably due to steric constraints. The absence of a P−F coupling in the spectra of **1j** might be related to of this angle. In fact, $J_{\text{P-F}}$ is 4.6 Hz in **1i** (X = Cl, L = PPh$_3$). The involvement of increasingly bulky ligands in the sequence **1i** < **1j** would consistently open the X−Pd−P angle and decrease the P−F coupling.[21]

The broad signals in the NMR spectra of **1f**, **1j** and **1k** may be due to three different dynamic processes:[18,22] (1) *cis*−*trans* exchange, similar to that of the other binuclear complexes synthesized here (Scheme 1); (2) slow rotation of the Pd−P bond; (3) the so-called "two-flip mechanism" consisting of a slow rotation of the P-C_{ipso} bond which exchanges the exo_2 and exo_3 conformers.[23] The ^{19}F NMR spectra of **1f**, **1j** and **1k** show broad signals corresponding to the *ortho*-CF_3 groups. When X = Cl (**1f**) the two *ortho*-CF_3 give rise to only one broad signal at room temperature, whereas two broad signals are displayed by the *ortho*-CF_3 when X is Br (**1j**) or I (**1k**), showing their nonequivalence at room temperature. At lower temperatures many species are observed, since the three possible dynamic processes are restricted, and different conformations of the possible isomers become discernible. The main species for each complex might be assigned to the stable conformer found in the solid state structure of **1j**, but the minor species cannot be assigned only from the spectroscopic data because of the many possible rotamers.

Conclusion

Various $[PdXRL_2]$ complexes with the bulky Fmes group can be obtained, many via ligand substitution processes under mild conditions. This suggests that a single Fmes group does not give a high degree of axial protection, probably because the group can tilt, making associative ligand substitutions kinetically accessible. The results of the ligand-substitution reactions are consistent with a high *trans* effect of the Fmes group. Thus, the kinetic product (where the incoming ligand coordinates *trans* to the Fmes) is first formed. Subsequent isomerization or evolution to the expected thermodynamic product (if only electronic factors were considered) does not always take place. In fact the stability of both isomers depends on electronic (antisymbiotic effect), steric, and entropic factors. Complexes containing two bulky ligands with *ortho* substituents mutually *cis* seem much disfavored, while mutually *trans* substituents can be tolerated.

Experimental Section

General Remarks: All reactions were carried out under dry N_2. Solvents were purified according to standard procedures.[24] 1,3,5-$C_6H_3(CF_3)_3$ (FmesH) was purchased from Fluorochem and used as received. Li(Fmes) was prepared as described in the literature,[25] and used immediately in situ without further purification. The compounds *trans*-$[PdCl_2(tht)_2]$, *trans*-$[PdCl_2(SMe_2)_2]$,[26] $[PdCl_2(tmeda)]$,[27] $OPPhPy_2$,[28] and $(OH)(CH_3)CPy_2$,[29] were prepared according to literature procedures.

Infrared spectra were recorded with a Perkin−Elmer 883 apparatus as Nujol mulls between polyethylene films from 4000 to 200 cm^{-1}. NMR spectra were recorded with Bruker AC-300 or ARX-300 instruments and are referred to TMS, 85% H_3PO_4, or $CFCl_3$. Elemental analyses were performed with a Perkin−Elmer 2400B microanalyzer.

$[Pd(\mu\text{-}Cl)(Fmes)(NCMe)]_2$ (1a): [PdCl(Fmes)(COD)][4] (1.090 g, 2 mmol) was boiled under reflux in acetonitrile and monitored by ^{19}F NMR until the starting material disappeared (24 h). The yellow solution thus obtained was filtered through dry Celite, the solvents were pumped off and a yellow solid obtained that was washed with *n*-hexane and vacuum dried to yield 0.850 g (89%) of product. IR: $\tilde{\nu}$ = 2335 m, 2309 w, 1618 s, 1574 m, 1308 vs, 1286 vs, 1265 vs, 1189 vs, 913 vs, 1088 s, 1021 s, 914 s, 955 m, 836 m, 584 vw (br), 574 w, 438 w, 373 vw, 334 vw (sh), 323 w, 302 vw, 277 w cm^{-1}. ^1H NMR: δ = 7.79 [s, $C_6H_2(CF_3)_3$, 2 H, *trans*], 7.69 [s, $C_6H_2(CF_3)_3$, 2 H, *cis*], 2.17 (s, $NCCH_3$, 3 H, *cis*), 2.13 (s, $NCCH_3$, 3 H, *trans*), (*trans*/*cis*, 77:23) ppm. ^{19}F NMR: δ = −58.65 (s, *ortho*-CF_3, 6 F, *cis* and *trans*), −63.15 (s, *para*-CF_3, 3 F, *trans*), −63.29 (s, *para*-CF_3, 3 F, *cis*), (*trans*/*cis*, 77:23) ppm. $C_{22}H_{10}Cl_2F_{18}N_2Pd_2$ (928.0): calcd. C 28.47, H 1.09, N 3.02; found C 28.26, H 1.15, N 2.81.

$[Pd(\mu\text{-}Br)(Fmes)(NCMe)]_2$ (1b): KBr (0.173 g, 1.45 mmol) was added to a solution of **1a** (0.135 g, 0.145 mmol) in acetonitrile (30 mL) and stirred for 1 h at room temperature. Then the solvent was removed in vacuo and the resultant yellow residue extracted with dichloromethane (30 mL), filtered, washed with *n*-hexane (3 × 10 mL) and dried to yield 0.128 g (87%) of **1b**. IR: $\tilde{\nu}$ = 2335 m, 2309 w, 1836 vw, 1646 vw, 1619 s, 1575 m, 1300 vs, 1283 vs, 1231 m, 1191 vs, 1122 vs, 1084 s, 1025 s, 954 vw, 913 s, 854 m, 835 s, 683 s, 667 w, 581 vw, 564 vw, 472 w, 438 m, 305 w, 227 w, 218 w cm^{-1}. ^1H NMR: δ = 7.81 [s, $C_6H_2(CF_3)_3$, 2 H, *cis*], 7.73 [s, $C_6H_2(CF_3)_3$, 2 H, *trans*], 2.18 (s, $NCCH_3$, 3 H, *trans*), 2.14 (s, $NCCH_3$, 3 H, *cis*), (*cis*/*trans*, 72:28) ppm.In the presence of MeCN, **1b** undergoes a process similar to that depicted for **1a** in Scheme 2, giving rise to different NMR signals. ^{19}F NMR: δ = −58.30 (s, *ortho*-CF_3, 6 F, *cis*), −58.31 (s, *ortho*-CF_3, 6 F, *trans*), −62.12 (s, *para*-CF_3, 3 F, *cis*), −63.26 (s, *para*-CF_3, 3 F, *trans*), (*cis*/*trans*, 72:28) ppm. ^{19}F NMR (CH_3CN/$[D_6]Me_2CO$): δ = −57.18 (s, *ortho*-CF_3, 6 F), −62.14 (s, *para*-CF_3, 3 F) ppm. $C_{22}H_{10}Br_2F_{18}N_2Pd_2$ (1016.9): calcd. C 25.98, H 0.99, N 2.76; found C 26.19, H 1.06, N 2.89.

$[Pd(\mu\text{-}Cl)(Fmes)(CO)]_2$ (1c): Carbon monoxide was bubbled through a solution of **1a** (0.696 g, 0.75 mmol) in toluene (30 mL) at room temperature for 10 h with stirring. The resultant white solid was decanted and washed with toluene (3 × 5 mL), yielding 0.498 g (74%) of **1c**. IR: $\tilde{\nu}$ = 2149 vs, 2102 w, 1622 s, 1583 m, 1301 vs, 1283 vs, 1269 vs, 1208 vs, 1190 vs, 1130 s, 1091 s, 1023 s, 919 s, 855 m, 839 m, 749 s, 695 m, 683 m, 672 w, 585 vw, 477 m, 436 w, 395 vw, 369 vw, 301 w, 282 m cm^{-1}. ^1H NMR: δ = 8.00 [s, $C_6H_2(CF_3)_3$, 2 H, *trans*], 7.90 [s, $C_6H_2(CF_3)_3$, 2 H, *cis*], (*trans*/*cis*, 72:28) ppm. ^{19}F NMR: δ = −59.31 (s, *ortho*-CF_3, 6 F, *trans*), −59.35 (s, *ortho*-CF_3, 6 F, *cis*), −63.39 (s, *para*-CF_3, 3 F, *trans*), −63.53 (s, *para*-CF_3, 3 F, *cis*), (*trans*/*cis*, 72:28) ppm. $C_{20}H_4Cl_2F_{18}O_2Pd_2$ (901.9): calcd. C 26.63, H 0.45; found C 26.57, H 0.69.

$[Pd(\mu\text{-}Cl)(Fmes)(4\text{-}pic)]_2$ (1d): 4-Pic (10 μL, 0.096 mg, 0.1 mmol) was added to a yellow solution of **1a** (0.046 g, 0.05 mmol) in acetone (10 mL) and boiled under reflux for 3 h. The volatiles were then pumped off and the resultant yellow solid was dissolved in dichloromethane; *n*-hexane was then added and the mixture was concentrated and cooled to −20 °C. The yellow crystals thus obtained were decanted, washed with *n*-hexane (3 × 5 mL) and vacuum dried to yield 0.041 g (79%) of product. IR: $\tilde{\nu}$ = 2343 vw (br), 2019 vw (br), 1618 m, 1572 w, 1507 w, 1298 s, 1281 vs, 1191 vs, 1126 vs, 1085 m, 1070 m, 1027 m, 911 m, 854 w, 835 w, 572 w, 696 w, 685 m, 564 vw (br), 498 w, 438 w cm^{-1}. ^{1}H NMR: δ = 8.23 [d, J = 6.5 Hz, $NC_5H_4(CH_3)$, 2 H, *cis*], 8.19 [d, J = 6.5 Hz, $NC_5H_4(CH_3)$, 2 H, *trans*], 7.78 [s, $C_6H_2(CF_3)_3$, 2 H, *trans*], 7.71 [s, $C_6H_2(CF_3)_3$, 2 H, *cis*], 7.03 [d partially hidden, J = 6.0 Hz, $NC_5H_4(CH_3)$, 2 H, *cis*], 7.00 (d, J = 6.0 Hz, NC_5H_4, 2 H, *trans*), 2.32 [s, $NC_5H_4(CH_3)$, 3 H, *cis*], 2.29 [s, $NC_5H_4(CH_3)$, 3 H, *trans*], (*trans*/*cis*, 78:22) ppm. ^{19}F NMR: δ = −58.29 (s, *ortho*-CF$_3$, 6 F, *trans*), −58.35 (s, *ortho*-CF$_3$, 6 F, *cis*), −63.21 (s, *para*-CF$_3$, 3 F, *trans*), −63.31 (s, *para*-CF$_3$, 3 F, *cis*), (*trans*/*cis*, 78:22) ppm. $C_{30}H_{18}Cl_2F_{18}N_2Pd_2$ (1032.2): calcd. C 34.91, H 1.76, N 2.71; found C 34.71, H 1.79, N 2.67.

[Pd(μ-Cl)(Fmes)(3,5-lut)]$_2$ (1e): 3,5-Lut (12.5 μL, 0.012 mg, 0.11 mmol) was added to a yellow solution of **1a** (0.046 g, 0.05 mmol) in acetone (10 mL) and boiled under reflux for 3 h. The volatiles were then pumped off and the resultant yellow solid dissolved in dichloromethane; *n*-hexane was then added and the solution concentrated and cooled to −20 °C. The yellow crystals obtained were decanted, washed with *n*-hexane (3 × 5 mL) and vacuum dried to yield 0.040 g (75%) of **1e**. IR: $\tilde{\nu}$ = 2342 w, 2020 vw, 1899 vw (br), 1819 vw (br), 1617 m, 1572 m, 1298 vs, 1284 vs, 1262 s, 1187 s, 1132 vs (br), 1083 m, 1028 s, 912 s, 857 m, 833 w, 788 vw, 752 m, 696 m, 684 m, 667 m, 539 w (br), 486 vw, 419 w, 437 m, 425 w, 313 vw, 287 vw, 240 vw cm^{-1}. ^{1}H NMR: δ = 8.11 [s, $NC_5H_3(CH_3)_2$, H^1 and H^5, 2 H, *cis*], 8.08 [s, $NC_5H_3(CH_3)_2$, H^1 and H^5, 2 H, *trans*], 7.78 [s, $C_6H_2(CF_3)_3$, 2 H, *trans*], 7.70 [s, $C_6H_2(CF_3)_3$, 2 H, *cis*], 7.32 [s, $NC_5H_3(CH_3)_2$, H^3, 1 H, *cis*], 7.30 [s, $NC_5H_3(CH_3)_2$, H^3, 1 H, *trans*], 2.28 [s, $NC_5H_3(CH_3)_2$, 3 H, *cis*], 2.19 [s, $NC_5H_3(CH_3)_2$, 3 H, *trans*], (*trans*/*cis*, 78:22) ppm. ^{19}F NMR: δ = −58.01 (s, *ortho*-CF$_3$, 6 F, *trans*), −58.06 (s, *ortho*-CF$_3$, 6 F, *cis*), −63.21 (s, *para*-CF$_3$, 3 F, *trans*), −63.31 (s, *para*-CF$_3$, 3 F, *cis*), (*trans*/*cis*, 78:22) ppm. $C_{32}H_{22}Cl_2F_{18}N_2Pd_2$: calcd. C 36.25, H 2.09, N 2.64; found C 36.40, H 2.25, N 2.84.

[Pd(μ-Cl)(Fmes){P(*o*-Tol)$_3$}]$_2$ (1f): P(*o*-Tol)$_3$ (0.122 g, 0.4 mmol) was added to a solution of **1a** (0.186 g, 0.2 mmol) in toluene (30 mL) and the resultant solution stirred 24 h at room temperature. The volatiles were then pumped off, freshly distilled *n*-hexane was added and the mixture kept under nitrogen. The yellow solid thus obtained was decanted, washed with hexane and vacuum dried, yielding 0.197 g (68%) of **1f**. IR: $\tilde{\nu}$ = 1617 m, 1591 w, 1569 w, 1281 vs, 1180 vs, 1153 s, 1080 m, 1021 m, 910 m, 854 w, 832 w, 807 w, 753 m, 694 w, 683 m, 565 w, 536 w, 517 vw, 469 m, 292 w, 284 w, 271 w cm^{-1}. ^{1}H NMR: δ = 7.54 [br., $C_6H_2(CF_3)_3$], 7.47 [br., $C_6H_2(CF_3)_3$], 7.5−6.5 [br., C_6H_4, P(*o*-Tol)$_3$], 3.5−1.5 [br., CH$_3$, P(*o*-Tol)$_3$] ppm. ^{19}F NMR: δ = −56.8 (br., *ortho*-CF$_3$, 12 F, *trans*), −58.1 (br., *ortho*-CF$_3$, 12 F, *cis*), −63.18 (br., *para*-CF$_3$, 6 F, *trans*), −63.27 (br., *para*-CF$_3$, 6 F, *cis*) (*trans*/*cis*, 62:38) ppm. ^{31}P{^{1}H} NMR: δ = 22.1 (br) ppm. $C_{60}H_{46}Cl_2F_{18}P_2Pd_2$ (1454.6): calcd. C 49.54, H 3.19; found C 49.70, H 3.39.

[Pd(μ-Cl)(Fmes)(tht)]$_2$ (1g): [PdCl(Fmes)(tht)$_2$],[4] (0.060 g, 0.1 mmol) was dissolved in *n*-hexane (10 mL), and the solution boiled under reflux overnight. The yellow crystals thus formed were decanted, washed with *n*-hexane (3 × 5 mL) and dried to afford 0.036 g (71%) of **1g**. IR: $\tilde{\nu}$ = 1617 s, 1574 m, 1300 vs, 1278 vs, 1177 vs, 1132 vs (br), 1084 s, 959 w, 916 s, 880 w, 854 m, 836 m, 804 w, 751 m, 695 m, 684 s, 669 w, 582 vw, 517 vw, 470 w, 438 w, 326 vw, 297 vw. ^{1}H NMR: δ = 7.84 [s, $C_6H_2(CF_3)_3$, 2 H, *trans*], 7.74 [s, $C_6H_2(CF_3)_3$, 2 H, *cis*], 3.00 (br., SC_4H_8, H^α, 4 H, *cis* and *trans*), 2.00 (br., SC_4H_8, H^β, 4 H, *cis* and *trans*), (*trans*/*cis*, 90:10) ppm. ^{19}F NMR: δ = −58.84 (s, *ortho*-CF$_3$, 6 F, *cis* and *trans*), −63.13 (s, *para*-CF$_3$, 3 F, *trans*), −63.29 (s, *para*-CF$_3$, 3 F, *cis*), (*trans*/*cis*, 90:10) ppm. $C_{26}H_{20}Cl_2F_{18}Pd_2S_2$ (1022.2): calcd. C 30.55, H 1.97; found C 30.53, H 1.98.

[Pd(μ-Cl)(Fmes)(SMe$_2$)]$_2$ (1h): Compound **2a** (0.110 g, 0.2 mmol) was dissolved in toluene (10 mL) and the resultant solution was boiled under reflux. After 8 h the solution became yellow. It was then filtered through dry Celite, and hexane was added to the filtrate, which was concentrated and cooled to −20 °C. The yellow crystals thus obtained were decanted, washed with *n*-hexane (3 × 5 mL) and vacuum dried to yield 0.079 g (81%) of product. IR: $\tilde{\nu}$ = 1621 m, 1568 w, 1621 m, 1569 w, 1297 s, 1277 vs, 1192 vs, 1180 s, 1135 vs, 1115 vs, 1087 s, 1027 m, 950 w, 914 m, 880 vw, 851 m, 830 m, 805 vw, 754 m, 692 m, 682 s, 520 s, 462 w, 437 w, 310 vw cm^{-1}. ^{1}H NMR: δ = 7.85 [s, $C_6H_2(CF_3)_3$, 2 H, *trans*], 7.75 [s, $C_6H_2(CF_3)_3$, 2 H, *cis*], 2.23 [s, $S(CH_3)_2$, 6 H, *trans*], 2.17 [s, $S(CH_3)_2$, 6 H, *cis*], (*trans*/*cis*, 86:14) ppm. ^{19}F NMR: δ = −58.99 (s, *ortho*-CF$_3$, 6 F, *trans*), −59.10 (s, *ortho*-CF$_3$, 6 F, *cis*), −63.19 (s, *para*-CF$_3$, 3 F, *trans*), −63.32 (s, *para*-CF$_3$, 3 F, *cis*), (*trans*/*cis*, 86:14) ppm. $C_{22}H_{16}Cl_2F_{18}Pd_2S_2$ (970.2): calcd. C 27.24, H 1.66; found C 27.43, H 1.78.

[Pd(μ-Cl)(Fmes)(PPh$_3$)]$_2$ (1i): PPh$_3$ (0.052 g, 0.2 mmol) was added to a yellow solution of **2a** (0.110 g, 0.2 mmol) in toluene (20 mL) and boiled under reflux for 24 h. The volatiles were then pumped off to afford a yellow solid that was dissolved in dichloromethane; *n*-hexane was then added and the mixture concentrated and cooled to −20 °C. The yellow crystals thus obtained were decanted, washed with *n*-hexane (3 × 5 mL) and vacuum dried to furnish 0.065 g (47%) of **1i**. IR: $\tilde{\nu}$ = 1619 s, 1588 w, 1574 m, 1297 vs, 1277 vs, 1186 vs, 1143 vs (br), 1097 s, 1082 s, 1024 s, 1000 m, 972 w, 912 s, 855 m, 833 m, 747 s, 693 vs, 667 w, 532 vs, 509 s, 499 s, 469 w, 450 w, 436 w, 283 w, 277 w cm^{-1}. ^{31}P{^{1}H} NMR: δ = 27.3 (m, *trans*) (*cis* isomer signal not observed) ppm. ^{1}H NMR: δ = 7.44 [s, $C_6H_2(CF_3)_3$, 4 H, *trans*], 8.2−6.2 (br., C_6H_5, 30 H) (*cis* isomer signals not observed) ppm. ^{19}F NMR: δ = −57.74 (d, $J_{P,F}$ = 4.6 Hz, *ortho*-CF$_3$, 12 F, *trans*), −57.93 (d, $J_{P,F}$ = 5.0 Hz, *ortho*-CF$_3$, 12 F, *cis*), −63.33 (s, *para*-CF$_3$, 6 F, *trans*), −63.40 (s, *para*-CF$_3$, 6 F, *cis*), (*trans*/*cis*, 95:5) ppm. $C_{54}H_{34}Cl_2F_{18}P_2Pd_2$ (1370.5): calcd. C 47.33, H 2.50; found C 47.48, H 2.70.

[Pd(μ-Br)(Fmes){P(*o*-Tol)$_3$}]$_2$ (1j): P(*o*-Tol)$_3$ (0.018 g, 0.06 mmol) was added to a solution of **1b** (0.031 g, 0.03 mmol) in toluene (10 mL) and the solution was stirred at room temperature for 8 h. The volatiles were then pumped off to give a deep-yellow oil that was crystallized from dichloromethane/hexane under an inert atmosphere. The yellow crystals thus obtained were decanted, washed with cold hexane (2 × 5 mL) and vacuum dried to yield 0.020 g (43%) of **1j**. IR: $\tilde{\nu}$ = 1617 m, 1591 w, 1568 w, 1280 vs, 1261 s, 1161 vs, 1152 vs, 1084 s (br), 1019 s, 910 m, 855 w, 805 s, 754 s, 694 w, 683 m, 564 w, 536 w, 516 vw, 482 m, 469 m cm^{-1}. ^{1}H NMR: δ = 7.50 [br., $C_6H_2(CF_3)_3$, *cis* and *trans*], 7.5−6.5 [br., C_6H_4, P(*o*-Tol)$_3$], 3.5−1.5 [br., CH$_3$, P(*o*-Tol)$_3$] ppm. ^{19}F NMR: δ = −53.93 (br., *ortho*-CF$_3$), −57.44 (br., *ortho*-CF$_3$), −63.20 (s, *para*-CF$_3$, *trans*), −62.56 (s, *para*-CF$_3$, 6 F, *cis*) (*cis*/*trans*, 90:10) ppm. ^{31}P{^{1}H}: δ = 21.8 (s) ppm. $C_{60}H_{46}Br_2F_{18}P_2Pd_2$ (1543.5): calcd. C 46.69, H 3.00; found C 46.67, H 3.04.

[Pd(Fmes)(μ-I){P(*o*-Tol)$_3$}]$_2$ (1k): P(*o*-Tol)$_3$ (0.031 g, 0.1 mmol) was added to a solution of K[Pd$_4$(Fmes)$_4$I$_5$][5a] (0.056 g, 0.0025 mmol) in toluene (10 mL) and the resultant solution was stirred at room temperature for 9 h. The deep yellow solution thus obtained was filtered through dry Celite and then concentrated; hexane was then added under an inert atmosphere. The resultant orange crystals were decanted, washed with cold hexane (2 × 5 mL) and vacuum dried to furnish 0.047 g (57%) of **1k**. IR: $\tilde{\nu}$ = 2019 vw, 1616 m, 1590 w, 1568 w, 1281 vs, 1191 s, 1181 s, 1149 s, 1137 s, 1078 m, 1015 m, 910 m, 854 w, 831 w, 805 w, 754 m, 684 m, 564 w, 536 w, 517 w, 468 m, 438 w, 395 vw, 292 vw cm^{-1}. ^{1}H NMR: δ = 9.3 [br.,

C_6H_4, P(*o*-Tol)$_3$], 8.0−6.5 [br., C_6H_4, P(*o*-Tol)$_3$ and $C_6H_2(CF_3)_3$], 3.3 [br., CH_3, P(*o*-Tol)$_3$], 1.4 [br., CH_3, P(*o*-Tol)$_3$] ppm. ^{19}F NMR: δ = −52.97 (br., *ortho*-CF_3), −57.09 (br., *ortho*-CF_3), −63.20 (s, *para*-CF_3) ppm. ^{31}P{^{1}H} NMR: δ = 18.3 (s) ppm. $C_{60}H_{46}F_{18}I_2P_2Pd_2$: calcd. C 44.01, H 2.83; found C 44.03, H 2.83.

***trans*-[PdCl(Fmes)(SMe$_2$)$_2$] (2a):** *trans*-[PdCl$_2$(SMe$_2$)$_2$] (0.603 g, 2 mmol) was added to a freshly prepared solution of Li(Fmes) (4.26 mmol) in Et_2O (40 mL). The reaction mixture was then maintained at 40 °C for 24 h, after which two drops of water were added to hydrolyze the excess of organolithium reagent. The volatiles were then pumped off, and the residue extracted with toluene and then filtered through silica gel. This solution afforded, after evaporation and crystallization, a mixture of **1h** and [Pd(Fmes)$_2$(SMe$_2$)$_2$].[30] The rest of the residue was extracted with dichloromethane and filtered through silica gel. The solvent was then evaporated and the resultant yellow residue was recrystallized from dichloromethane/hexane at −20 °C giving pale yellow crystals of **2a** that were decanted, washed with hexane and vacuum-dried. Yield 0.529 g (48%). IR: ṽ = 1621 s, 1572 m, 1287 vs (sh), 1262 vs, 1188 vs (sh), 1132 vs, 1085 s, 1035 s, 1026 s, 995 m, 980 s, 915 s, 853 m, 835 m, 754 m, 695 m, 684 m, 668 w, 468 w, 439 w, 377 vw, 358 vw, 306 vw, 285 w cm^{-1}. ^{1}H NMR: δ = 7.90 [s, $C_6H_2(CF_3)_3$, 2 H], 2.24 [s, S(CH_3)$_2$, 12 H] ppm. ^{19}F NMR: δ = −60.81 (s, *ortho*-CF_3, 6 F), −63.18 (s, *para*-CF_3, 3 F) ppm. $C_{13}H_{14}ClF_9PdS_2$ (547.2): calcd. C 28.53, H 2.58; found C 28.69, H 2.49.

***cis*-[PdCl(Fmes)(4-pic)$_2$] (2b):** 4-Pic (43 µL, 0.041 g, 0.44 mmol) was added to a yellow solution of **1a** (0.093 g, 0.1 mmol) in dichloromethane (10 mL) and stirred at room temperature for 15 min. Then *n*-hexane was added to the resultant colorless solution, and this was then concentrated and cooled to −20 °C. The white solid thus obtained was decanted, washed with *n*-hexane (3 × 5 mL) and vacuum dried, yielding 0.045 g (37%) of **2b**. IR: ṽ = 1617 s, 1569 w, 1504 m, 1298 vs, 1278 vs (br), 1214 m, 1195 vs (sh), 1126 vs (sh), 1083 s, 1071 s, 1040 m, 1028 m, 938 w, 914 m, 871 vw, 852 w, 834 m, 815 w, 753 w, 695 w, 683 s, 667 vw, 550 vw, 498 m, 470 vw, 436 vw, 329 w cm^{-1}. ^{1}H NMR: δ = 8.42 [d, *J* = 6.0 Hz, $NC_5H_4(CH_3)$, 2 H], 8.13 [d, *J* = 6.0 Hz, $NC_5H_4(CH_3)$, 2 H], 7.76 [s, $C_6H_2(CF_3)_3$, 2 H], 7.14 [d, *J* = 5.6 Hz, $NC_5H_4(CH_3)$, 2 H], 7.02 [d, *J* = 5.6 Hz, $NC_5H_4(CH_3)$, 2 H], 2.36 [s, $NC_5H_4(CH_3)$, 3 H], 2.31 [s, $NC_5H_4(CH_3)$, 3 H] ppm. ^{19}F NMR: δ = −58.89 (s, *ortho*-CF_3, 6 F), −63.13 (s, *para*-CF_3, 3 F) ppm. $C_{21}H_{16}ClF_9N_2Pd$ (609.2): calcd. C 41.40, H 2.65, N 4.60; found C 41.23, H 2.59, N 4.43. A solution of pure *cis*-**2b** maintained at 50 °C in $CDCl_3$ solution showed, with time, the following *cis*-**2b**/**1d**/*trans*-**2b** ratios by ^{19}F NMR: after 24 h, 20:12:68; after 48 h: 9:10:81; after 5 days: 5:9:86.

***trans*-[PdCl(Fmes)(CN*tBu*)$_2$] (2c):** *t*BuNC (23 µL, 0.017 g, 0.2 mmol) was added to a solution of [PdCl(Fmes)(COD)][4] (0.053 g, 0.1 mmol) in acetone (10 mL), and the mixture was boiled under reflux for 3 h. The solution was then filtered through dry Celite and concentrated; *n*-hexane was subsequently added and the solution cooled to −20 °C. The colorless crystals thus obtained were decanted, washed with *n*-hexane (3 × 5 mL) and vacuum dried to yield 0.035 g (59%) of **2c**. IR: ṽ = 2221 s, 1618 m, 1571 m, 1400 w, 1299 vs, 1279 vs, 1236 m, 1196 s, 1033 s (sh), 1085 m, 1043 mw, 1024 m, 934 vw, 922 m, 852 m, 835 m, 753 m, 693 m, 683 vs, 672 w, 580 vw, 534 m, 468 m, 451 w, 438 m, 291 vw cm^{-1}. ^{1}H NMR: δ = 7.91 [s, $C_6H_2(CF_3)_3$, 2 H], 1.33 (s, CNC_4H_9, 18 H) ppm. ^{19}F NMR: δ = −61.31 (s, *ortho*-CF_3, 6 F), −63.06 (s, *para*-CF_3, 3 F) ppm. $C_{19}H_{20}ClF_9N_2Pd$: calcd. C 38.73, H 3.42, N 4.75; found C 38.75, H 3.27, N 4.74. For the same reaction in CH_2Cl_2 at −50 °C, the ^{19}F NMR spectrum of a $CDCl_3$ solution of the crude product obtained after removing immediately the volatiles in vacuo, maintaining the low temperature, showed a mixture of *cis*-**2c** (72%) and *trans*-**2c** (28%). The ^{19}F NMR spectrum of the same sample after 15 h at room temperature showed 31% of *cis*-**2c** and 69% *trans*-**2c**. This crude product was stored as a solid at room temperature and, after several weeks, the ^{19}F NMR of a $CDCl_3$ solution showed only signals due to *trans*-**2c**.

***cis*-[Pd(Fmes)Cl(NCMe)$_2$] (2d):** This complex cannot be isolated pure because it loses MeCN. It was characterized by ^{19}F NMR in CH_3CN solution: ^{19}F NMR (CH_3CN/[D$_6$]Me$_2$CO): δ = −57.63 (s, *ortho*-CF_3, 6 F), −62.17 (s, *para*-CF_3, 3 F) ppm.

***cis*-[PdCl(Fmes)(PMe$_3$)$_2$] (*cis*-2e):** This complex was detected upon addition of PMe$_3$ to a solution of **1a** in acetonitrile (PMe$_3$/**1a**, 2:1) by ^{19}F NMR (CH_3CN/[D$_6$]Me$_2$CO): δ = −58.44 (d, $J_{P,F}$ = 6.0 Hz, *ortho*-CF_3, 6 F), −62.13 (s, *para*-CF_3, 3 F) ppm. ^{31}P{^{1}H} NMR (CH_3CN/[D$_6$]Me$_2$CO): δ = −6.7 (d sept, $J_{P,P}$ = 36.0, $J_{P,F}$ = 6.0 Hz), −15.9 (d, $J_{P,P}$ = 36.0 Hz) ppm.

***trans*-[PdCl(Fmes)(PMe$_3$)$_2$] (*trans*-2e):** This was detected in similar fashion to *cis*-**2e**.^{19}F NMR (CH_3CN/[D$_6$]Me$_2$CO): δ = −61.41 (t, $J_{P,F}$ = 6.0 Hz, *ortho*-CF_3, 6 F), −62.19 (s, *para*-CF_3, 3 F) ppm. ^{31}P{^{1}H} NMR (CH_3CN/[D$_6$]Me$_2$CO): δ = −11.2 (sept, $J_{P,F}$ = 6.0 Hz). Ratios of *trans*-**2e** to *cis*-**2e**: 3:97 immediately after addition of PMe$_3$; 55:45 after 7 h at room temperature; 70:30 after 24 h at room temperature

[PdCl(Fmes)(tmeda)] (3a): [PdCl$_2$(tmeda)] (0.292 g, 1 mmol) was added to a recently prepared solution of Li(Fmes) (4 mmol) in Et_2O (30 mL). After stirring the solution at room temperature for 24 h, two drops of water were then added to hydrolyze the excess organolithium reagent, and the volatiles were removed in vacuo. The resultant dark residue was extracted with CH_2Cl_2 (ca. 50 mL) and filtered through dry Celite. *n*-Hexane (ca. 20 mL) was then added to the orange filtrate, which was concentrated, and cooled to −20 °C. The orange microcrystalline solid thus obtained was decanted, washed with *n*-hexane (3 × 5 mL), and dried in vacuo to furnish 0.339 g (63%) of **3a**. IR: ṽ = 1620 m, 1571 w, 1286 vs, 1262 s, 1191 vs, 1140 vs, 1128 vs, 1046 m, 957 w, 917 s, 855 m, 833 m, 804 s, 772 w, 754 w, 696 w, 684 m, 667 w, 437 w, 329 m cm^{-1}. ^{1}H NMR: δ = 7.76 [s, $C_6H_2(CF_3)_3$, 2 H], 2.73 [m, {$(CH_3)_2NCH_2$}$_2$, 6 H], 2.70 [m, {$(CH_3)_2NCH_2$}$_2$, 4 H], 2.40 [s, {$(CH_3)_2NCH_2$}$_2$, 6 H] ppm. ^{19}F NMR: −56.74 (s, *ortho*-CF_3, 6 F), −63.17 (s, *para*-CF_3, 3 F) ppm. $C_{15}H_{18}ClF_9N_2Pd$ (539.2): calcd. C 33.42, H 3.37, N 5.20; found C 32.37, H 3.46, N 5.72.

[PdCl(Fmes)(4,4′-Me$_2$bipy)] (3b): 4,4′-Me$_2$bipy (0.022 g, 0.12 mmol) was added to a yellow solution of **1a** (0.047 g, 0.05 mmol) in dichloromethane (15 mL) and stirred for 3 h at room temperature. Then *n*-hexane was added to the colorless solution and concentrated. The resultant white solid was washed with *n*-hexane (3 × 5 mL), vacuum dried and recrystallized from dichloromethane/hexane to yield 0.025 g (42%) of **3b** as colorless crystals. IR: ṽ = 1616 s, 1567 w, 1297 vs, 1283 vs, 1262 vs, 1242 m, 1223 w, 1187 s, 1127 vs (sh), 1083 s, 1028 s (sh), 927 w, 913 s, 896 w, 853 w, 832 s, 756 w, 696 m, 684 s, 667 vw, 564 vw, 519 m, 469 vw, 438 vw, 427 w, 337 w cm^{-1}. ^{1}H NMR: δ = 9.11 [d, $J_{H^6H^5}$ = 5.5 Hz, {$NC_5H_3(CH_3)$}$_2$, H^6 *cis* to Cl, 1 H], 7.89 [s, $C_6H_2(CF_3)_3$, 2 H], 7.87 [s, H^3, {$NC_5H_3(CH_3)$}$_2$, 1 H], 7.39 [d, $J_{H^5H^6}$ = 5.5 Hz, H^5, {$NC_5H_3(CH_3)$}$_2$, 1 H], 7.35 [d, $J_{H^5H^6}$ = 5.8 Hz, H^5, {$NC_5H_3(CH_3)$}$_2$, 1 H], 7.06 [d, *J* = 5.8 Hz, H^6, {$NC_5H_3(CH_3)$}$_2$, 1 H], 2.54 (s, CH_3, 3 H), 2.48 [s, {$NC_5H_3(CH_3)$}$_2$, 3 H] ppm. ^{19}F NMR: δ = −59.21 (s, *ortho*-CF_3, 6 F), −63.00 (s, *para*-CF_3, 3 F) ppm. $C_{21}H_{14}N_2ClF_9Pd$ (607.2): calcd. C 41.54, H 2.32, N 4.61; found C 41.58, H 2.44, N 4.64.

[PdCl(Fmes)(biquinolyl)] (3c): 2,2′-Biquinolyl (0.056 g, 0.22 mmol) was added to a yellow solution of **1a** (0.093 g, 0.1 mmol) in dichloromethane (15 mL) and stirred for 7 h at room temperature to give a cloudy solution. The volatiles were then pumped off and the yellow residue was washed with *n*-hexane (3 × 5 mL) and vacuum dried to furnish 0.109 g (80%) of **3c**. IR: ṽ = 1619 m, 1600 m, 1575 w, 1344 m, 1300 s, 1282 vs, 1265 s, 1188 vs, 1131 vs (br), 1083 m, 1031 m, 992 w, 972 w, 915 m, 872 w, 855 w, 830 s, 784 m, 750 s, 684 m, 506 vw, 490 vw, 470 vw, 439 vw, 328 w cm^{-1}. ^1H NMR: δ = 9.37 [d, J = 8.2 Hz, $(NC_9H_6)_2$, H^6 *cis* to Cl, 1 H], 8.57 [t, J = 8.8 Hz, $(NC_9H_6)_2$, 2 H], 8.35 [d, J = 8.7 Hz, $(NC_9H_6)_2$, 1 H], 8.25 [d, J = 8.8 Hz, $(NC_9H_6)_2$, 1 H], 7.93 [m, $(NC_9H_6)_2$, 2 H], 7.85 [d, J = 7.8 Hz, $(NC_9H_6)_2$, 1 H], 7.73 [m, $C_6H_2(CF_3)_3$ and $(NC_9H_6)_2$, 4 H], 7.49 [m, $(NC_9H_6)_2$, 2 H] ppm. ^{19}F NMR: δ = −58.44 (s, *ortho*-CF_3, 6 F), −63.01 (s, *para*-CF_3, 3 F) ppm. $C_{27}H_{14}N_2ClF_9Pd$ (679.3): calcd. C 47.73, H 2.08, N 4.12; found C 47.56, H 2.12, N 4.10.

[PdCl(Fmes)(OPPhPy₂-*N,N′*)] (3d): $OPPhPy_2$ (0.031 g, 0.11 mmol) was added to a yellow solution of **1a** (0.047 g, 0.05 mmol) in dichloromethane (10 mL) and stirred at room temperature for 8 h to give a colorless solution. *n*-Hexane was then added and the solution was concentrated. The resultant white solid was washed with *n*-hexane (3 × 5 mL), vacuum dried and recrystallized from dichloromethane/hexane to yield 0.045 g (64%) of **3d** as colorless crystals. IR: ṽ = 1617 s, 1591 m, 1569 w, 1298 vs, 1275 vs, 1217 s, 1194 vs, 1136 vs, 1060 m, 1024 s, 997 w, 928 w, 906 s, 853 m, 835 m, 777 m, 756 s, 744 s, 702 m, 692 s, 684 s, 667 vw, 646 vw, 547 s, 504 w, 471 vw, 451 w, 438 vw, 326 vw, 305 vw, 285 vw cm^{-1}. ^1H NMR: δ = 9.69 (d, J = 5.5 Hz, C_5H_4N, H^6 *cis* to Cl, 1 H), 8.81 (t, J = 7.5 Hz, C_5H_4N, H^3, 1 H), 8.47 (t, J = 7.0 Hz, C_5H_4N, H^3, 1 H), 8.18 (m, C_5H_4N, H^4, 1 H), 8.08 (m, C_5H_4N, H^4, 1 H), 7.93 (d, J = 6.5 Hz, C_5H_4N, H^6, 1 H), 7.92 [s, $C_6H_2(CF_3)_3$, 1 H], 7.80 (m, C_6H_5, 4 H), 7.71 (m, C_5H_4N, H^5, 1 H), 7.6 (m, $H^5$of C_5H_4N, and C_6H_5, 2 H), 7.54 [s, $C_6H_2(CF_3)_3$, 1 H] ppm. ^{19}F NMR: δ = −57.13 (s, *ortho*-CF_3, 3 F), −62.42 (s, *ortho*-CF_3, 3 F), −63.19 (s, *para*-CF_3, 3 F) ppm. $^{31}P\{^1H\}$ NMR: δ = 20.4 (s) ppm. $C_{25}H_{15}ClF_9N_2OPPd$ (703.2): calcd. C 42.70, H 2.15, N 3.98; found C 43.04, H 2.35, N 3.91.

[PdCl(Fmes){(OH)(CH₃)CPy₂-*N,N′*}] (3e): $(OH)(CH_3)CPy_2$ (0.024 g, 0.12 mmol) was added to a yellow solution of **1a** (0.047 g, 0.05 mmol) in dichloromethane (10 mL) and stirred at room temperature for 2 h. Then *n*-hexane was added and the solution concentrated. The resultant yellow solid was washed with *n*-hexane (3 × 5 mL), vacuum dried and recrystallized from dichloromethane/hexane to yield 0.061 g (88%) of **3e**·CH_2Cl_2 as yellow crystals. IR: ṽ = 3371 m, 1619 m, 1603 m, 1569 w, 1283 vs, 1262 s, 1189 vw, 1126 vs, 1097 m, 1083 m, 1060 m, 1027 m, 944 w, 913 m, 854 w, 834 w, 791 w, 761 m, 694 w, 684 m, 667 vw, 654 vw, 590 vw, 468 vw, 436 vw, 332 vw cm^{-1}. ^1H NMR ([D₆]Me₂CO): δ = 9.30 (m, C_5H_4N, H^6 *cis* to Cl, 1 H), 8.36 (m, C_5H_4N, 1 H), 8.10 (m, C_5H_4N, 3 H), 8.01 [s, $C_6H_2(CF_3)_3$, 1 H], 7.91 (m, C_5H_4N, 1 H), 7.84 [s, $C_6H_2(CF_3)_3$, 1 H], 7.60 (m, C_5H_4N, 1 H), 7.23 (m, C_5H_4N, 1 H), 6.40 (s, OH, 1 H), 3.00 (s, CH_3, 3 H) ppm. ^{19}F NMR ([D₆]Me₂CO): δ = −56.17 (br., *ortho*-CF_3, 3 F), −58.86 (br., *ortho*-CF_3, 3 F), −61.96 (s, *para*-CF_3, 3 F) ppm. $C_{22}H_{16}Cl_3F_9N_2OPd$ (708.1): calcd. C 38.12, H 2.33, N 4.05; found C 38.08, H 2.34, N 3.94.

[PdCl(Fmes)(pte)] (3f): 1,2-Bis(phenylthio)ethane (0.041 g, 0.165 mmol) was added to a yellow solution of **1a** (0.067 g, 0.075 mmol) in dichloromethane (10 mL) and stirred for 5 h at room temperature. *n*-Hexane (10 mL) was then added and the dichloromethane evaporated off to give a yellow solid that was washed with *n*-hexane (3 × 5 mL), vacuum dried and recrystallized from dichloromethane/hexane [yield: 0.073 g (73%)]. IR: ṽ = 1616 m, 1571 w (sh), 1406 w, 1299 s, 1284 vs, 1262 s, 1185 vs, 1144 s, 1118 vs (sh), 1083 m, 1024 m, 924 w, 907 m, 853 vw, 834 m, 753 m, 744 s, 693 m, 684 m, 666 vw, 506 vw, 478 w, 467 vw, 455 vw, 436 vw, 322 w cm^{-1}. ^1H NMR: δ = 8.04 (m, C_6H_5, 2 H), 7.76 [s, $C_6H_2(CF_3)_3$, 2 H], 7.51 (m, C_6H_5, 3 H), 7.47 (m, C_6H_5, 5 H), 3.32 (m, CH_2, 2 H), 3.09 (m, CH_2, 2 H) ppm. ^{19}F NMR: δ = −57.78 (s, *ortho*-CF_3, 6 F), −63.22 (s, *para*-CF_3, 3 F) ppm. $C_{23}H_{16}ClF_9PdS_2$ (669.3): calcd. C 41.27, H 2.41; found C 41.00, H 2.42.

[PdCl(Fmes)(dppe)] (3g): The ligand dppe (0.040 g, 0.1 mmol) was added to a solution of **1a** (0.047 g, 0.05 mmol) in toluene (10 mL). The solution was then boiled under reflux for 2 h, after which the volatiles were pumped off and the resultant white residue was dissolved in dichloromethane filtered through dry Celite. Hexane (10 mL) was then added to the filtrate, which was concentrated and cooled to −20 °C. The thus obtained colorless crystals were decanted, washed with *n*-hexane (3 × 5 mL) and vacuum dried to yield 0.052 g (63%) of **3g**. IR: ṽ = 1618 m, 1569 vw, 1438 m, 1298 s, 1279 vs, 1261 s, 1186 vs, 1130 vs (sh), 1106 s, 1079 m, 1021 w, 1000 vw, 925 vw, 890 w, 852 vw, 826 w, 745 s, 706 s, 692 s, 666 w, 530 m, 498 m, 481 w, 439 vw, 329 vw, 298 vw cm^{-1}. ^1H NMR: δ = 8.00 (m, C_6H_5, *para*-H, 4 H), 7.60 [d, $J_{P_{trans}H_{Fmes}}$ = 1.0 Hz, $C_6H_2(CF_3)_3$, 2 H], 7.51 (m, C_6H_5, 6 H), 7.37 (m, C_6H_5, 2 H), 7.18 (m, C_6H_5, 8 H), 2.58 (m, CH_2, 2 H), 2.15 (m, CH_2, 2 H) ppm. ^{19}F NMR: δ = −58.29 (d, $J_{P,F}$ = 5.5 Hz, *ortho*-CF_3, 6 F), −63.12 (s, *para*-CF_3, 3 F) ppm. $^{31}P\{^1H\}$ NMR: δ = 52.9 (d sept., $J_{P,P}$ = 23.2, $J_{P,F}$ = 5.5 Hz, P_{cis} of dppe), 39.67 (d, $J_{P,P}$ = 23.2 Hz, P_{trans} of dppe) ppm. $C_{35}H_{26}ClF_9P_2Pd$ (821.4): calcd. C 51.18, H 3.19; found C 51.03, H 3.29.

[PdCl(Fmes)(2,6-lut)(NCMe)] (4a): 2,6-Lut (25 µL, 0.023 g, 0.22 mmol) was added to a yellow solution of **1a** (0.093 g, 0.1 mmol) in dichloromethane (10 mL) and stirred for 5 h at room temperature to give a colorless solution, to which *n*-hexane was added. This solution was then concentrated and cooled to −20 °C to give a white solid that was washed with *n*-hexane (3 × 5 mL) and vacuum dried to yield 0.094 g (82%) of **4a**. IR: ṽ = 2343 m, 2303 w, 1616 m, 1583 m, 1571 m, 1300 vs, 1288 vs, 1264 vs, 1180 vs (br), 1119 vs (br), 1095 m, 1029 m, 915 s, 854 m, 837 m, 781 s, 757 m, 695 m, 684 s, 668 vw, 577 vw, 470 vw, 438 w, 374 w, 340 w cm^{-1}. ^1H NMR: δ = 7.84 [s, $C_6H_2(CF_3)_3$, 2 H], 7.56 [t, $J_{H^3H^4}$ = 7.7 Hz, $NC_5H_3(CH_3)_2$, H^4, 1 H], 7.11 [d, $J_{H^3H^4}$ = 7.7 Hz, $NC_5H_3(CH_3)_2$, H^3, 2 H], 3.29 [s, $NC_5H_3(CH_3)_2$, 6 H], 2.08 (s, CH_3CN, 3 H) ppm. ^{19}F NMR: δ = −58.22 (s, *ortho*-CF_3, 6 F), −63.06 (s, *para*-CF_3, 3 F) ppm. $C_{18}H_{14}ClF_9N_2Pd$ (571.2): calcd. C 37.85, H 2.47, N 4.90; found C 37.97, H 2.54, N 4.70.

[PdCl(Fmes)(3,5-lut)(NCMe)] (4b): 3,5-Lut (25 µL, 0.023 g, 0.22 mmol) was added to a yellow solution of **1a** (0.093 g, 0.1 mmol) in dichloromethane (10 mL) and stirred for 15 min at room temperature to give a colorless solution. Then *n*-hexane was added and the solution was concentrated and cooled to −20 °C. The colorless crystals thus obtained were decanted, washed with *n*-hexane (3 × 5 mL) and vacuum dried to yield 0.060 g (53%) of **4b**. IR: ṽ = 2329 w, 2303 w, 1618 m, 1599 w, 1572 w, 1304 vs, 1292 vs, 1263 s, 1184 vs, 1157 s, 1143 s, 1117 vs, 1084 m, 1032 w, 913 m, 865 w, 856 vw, 835 w, 774 w, 755 w, 700 m, 684 m, 667 vw, 471 vw, 439 vw, 344 vw cm^{-1}. ^1H NMR: δ = 8.35 [s, $NC_5H_3(CH_3)_2$, H^2, 2 H], 7.80 [s, $C_6H_2(CF_3)_3$, 2 H], 7.42 [s, $NC_5H_3(CH_3)_2$, H^4, 1 H], 2.35 [s, $NC_5H_3(CH_3)_2$, 6 H], 2.14 (s, CH_3CN, 3 H) ppm. ^{19}F NMR: δ = −58.48 (s, *ortho*-CF_3, 6 F), −63.04 (s, *para*-CF_3, 3 F) ppm.

Table 3. Crystal data and structure refinement for $[Pd(Fmes)(\mu\text{-}Br)\{P(o\text{-}Tol)_3\}]_2$ (**1j**) and $[PdCl(Fmes)\{(OH)(CH_3)CPy_2\text{-}N,N'\}]$ (**3e**)

	1j	**3e**
Empirical formula	$C_{30}H_{23}BrF_9PPd$	$C_{21}H_{14}ClF_9N_2OPd$
Molecular weight	771.76	623.19
Temperature	302(2) K	298(2) K
Wavelength [Å]	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a [Å]	15.753(5)	11.567(5)
b [Å]	9.369(3)	9.696(4)
c [Å]	21.184(7)	23.001(10)
β [°]	107.803(5)	95.748(9)
V [Å^3]	2976.8(15)	2566.7(19)
Z	4	4
$D_{calcd.}$ [g·cm^{-3}]	1.722	1.613
Absorption coefficient [mm^{-1}]	2.095	0.908
$F(000)$	1520	1224
Crystal size [mm]	0.11 × 0.04 × 0.03	0.23 × 0.13 × 0.04
Theta range for data collection	1.36 to 23.42°	1.78 to 23.40°
Reflections collected	27367	12107
Independent reflections	4323 (R_{int} = 0.1050)	3717 (R_{int} = 0.0373)
Absorption correction	SADABS	SADABS
Data/restraints/parameters	4323/0/382	3717/0/322
Goodness-of-fit on F^2	1.000	1.002
R_1 [$I > 2\sigma(I)$]	0.0528	0.0507
wR_2 (all data)	0.1312	0.1864

$C_{18}H_{14}ClF_9N_2Pd$ (571.2): calcd. C 37.85, H 2.47, N 4.91; found C 37.62, H 2.31, N 4.72. A $CDCl_3$ solution of **4b** maintained at −20 °C for 5 days showed a **4b/1e** ratio of 81:19 by ^{19}F NMR spectroscopy. In a separate experiment, a $CDCl_3$ solution of **4b** maintained at room temperature during 24 h showed a **4b/1e** ratio of 60:40 by ^{19}F NMR spectroscopy.

[PdCl(Fmes)(NCMe)(PPh$_3$)] (4c): PPh_3 (0.058 g, 0.22 mmol) was added to a yellow solution of **1a** (0.093 g, 0.1 mmol) in dichloromethane (10 mL) and stirred at room temperature for 8 h to give a colorless solution, to which *n*-hexane was added. The resultant solution was then concentrated and cooled to −20 °C. The colorless crystals thus obtained were decanted, washed with *n*-hexane (3 × 5 mL) and vacuum dried to yield 0.060 g (52%) of **4c**·CH_2Cl_2. IR: $\tilde{\nu}$ = 2329 m, 2322 w, 1616 s, 1570 m, 1300 vs, 1286 vs, 1261 vs, 1186 vs (br), 1121 vs (br), 1099 s, 1082 s, 1024 s, 1000 m, 913 s, 852 m, 834 m, 695 vs, 684 s, 668 w, 529 s, 512 s, 494 m, 456 w, 436 w, 330 w cm^{-1}. ^1H NMR: δ = 7.85 [d, $J_{P,H}$ = 2.4 Hz, $C_6H_2(CF_3)_3$, 2 H], 7.76 (m, *ortho*-H, C_6H_5, 6 H), 7.46 (m, *meta*-H and *para*-H, C_6H_5, 9 H), 1.59 (d, $J_{P,H}$ = 1.3 Hz, CH_3CN, 3 H) ppm. ^{19}F NMR: δ = −58.40 (s, *ortho*-CF_3, 6 F), −62.98 (s, *para*-CF_3, 3 F) ppm. $^{31}P\{^1H\}$ NMR: δ = 17.6 (s) ppm. $C_{30}H_{22}Cl_3F_9NPd$ (780.3): calcd. C 44.42, H 2.73, N 1.72; found C 44.25, H 2.77, N 1.76. A $CDCl_3$ solution of **4c** maintained at room temperature for 2 days showed a **4c/1i** ratio of 58:42 by ^{19}F NMR spectroscopy.

[(μ-dppe){PdCl(Fmes)(NCMe)}$_2$] (4d): The ligand dppe (0.080 g, 0.2 mmol) was added to a yellow solution of **1a** (0.093 g, 0.1 mmol) in dichloromethane (10 mL) and stirred at room temperature for 12 h. The white solid so-formed was decanted, washed with diethyl ether (3 × 5 mL) and vacuum dried to yield 0.079 g (59%) of **4d**. IR: $\tilde{\nu}$ = 2331 w, 2304 vw, 1616 s, 1569 m, 1339 m, 1299 vs, 1278 vs, 1186 vs, 1126 vs, 1082 s, 1023 m, 1001 m, 977 vw, 913 s, 852 m, 835 m, 772 vw, 746 s, 705 s, 692 s, 682 s, 535 w, 520 s, 492 m, 450 m, 437 w, 350 w, 302 w cm^{-1}. ^1H NMR ($[D_6]Me_2CO$): δ = 8.2−7.7 (m, C_6H_5, 20 H), 7.94 [d, $J_{P,H}$ = 1.0 Hz, $C_6H_2(CF_3)_3$, 4 H], 3.26 (m, CH_2, 4 H), 1.93 (s, CH_3CN, 6 H) ppm. ^{19}F NMR ($[D_6]Me_2CO$): δ = −56.99 (s, *ortho*-CF_3, 6 F), −61.91 (s, *para*-CF_3, 3 F) ppm. $^{31}P\{^1H\}$ NMR ($[D_6]Me_2CO$): δ = 18.1 (s) ppm. $C_{48}H_{34}Cl_2F_{18}N_2P_2Pd_2$ (1326.4): calcd. C 43.46, H 2.58, N 2.11; found C 43.73, H 2.66, N 1.97. The filtrate was dried and the white solid thus obtained was washed with diethyl ether (3 × 5 mL) and vacuum dried to furnish 0.047 g of **3g** (29%).

X-ray Crystallographic Study: Suitable crystals of **1j** and **3e** were grown by slow diffusion of a concentrated dichloromethane (for **1j**) or acetone (for **3e**) solution of the complex into *n*-hexane at −20 °C. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K_α radiation (λ = 0.71073 Å).[31] Intensities were integrated from several series of exposures,[32] each exposure covering 0.3° in ω, the total data set being a hemisphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[33] The structure was solved by direct methods and refined by least-squares on weighted F^2 values for all reflections (Table 3).[34] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters except for the hydrogen of the alcohol group in **3e**, which was located in a difference Fourier map and refined. Refinement proceeded smoothly to give the residuals shown in Table 3. Complex neutral-atom scattering factors were used.[35]
CCDC-192421 (**1j**) and -192420 (**3e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union

Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors thank the DGI (BQU2001−2015) and the JCyL (VA17/00B) for financial support.

---

[1] F. T. Edelmann, *Comments Inorg. Chem.* **1992**, *12*, 259.

[2] [2a] D. Stalke, K. H. Whitmire, *J. Chem. Soc., Chem. Commun.* **1990**, 833. [2b] S. Brooker, J.-K. Buijink, F. T. Edelmann, *J. Chem. Soc., Chem. Commun.* **1991**, *10*, 25. [2c] H. Grützmacher, H. Pritzkow, F. T. Edelmann, *Organometallics* **1991**, *10*, 23. [2d] K. H. Whitmire, D. Labahn, H. W. Roesky, M. Noltemeyer, G. M. Sheldrick, *J. Organomet. Chem.* **1991**, *402*, 55. [2e] U. Lay, H. Pritzkow, H. Grützmacher, *Chem. Commun.* **1992**, 260. [2f] S. Brooker, N. Bertel, D. Stalke, M. Noltemeyer, H. W. Roesky, G. M. Sheldrick, F. T. Edelmann, *Organometallics* **1992**, *11*, 192. [2g] R. D. Schulter, A. H. Cowley, D. A. Atwood, R. A. Jones, M. R. Bond, C. J. Carrano, *J. Am. Chem. Soc.* **1993**, *115*, 2070. [2h] R. D. Schulter, H. S. Isom, A. H. Cowley, D. A. Atwood, R. A. Jones, F. Olbrich, S. Corbelin, R. J. Lagow, *Organometallics* **1994**, *163*, 4058. [2i] A. Vij, R. L. Kirchmeier, R. D. Willett, J. M. Shreeve, *Inorg. Chem.* **1994**, *33*, 5456. [2j] J.-T. Ahlemann, A. Künzel, H. W. Roesky, M. Noltemeyer, L. Markovskii, H.-G. Schmidt, *Ibid* **1996**, *35*, 6644. [2k] J. E. Bender IV, M. M. B. Holl, J. W. Kampf, *Organometallics* **1997**, *16*, 2743. [2l] J. E. Bender IV, M. M. B. Holl, A. Mitchell, N. J. Wells, J. W. Kampf, *Organometallics* **1998**, *17*, 5166. [2m] K. W. Klinkhammer, T. F. Fässler, H. Grützmacher, *Angew. Chem. Int. Ed.* **1998**, *37*, 124. [2n] J. E. Bender IV, A. J. Shusterman, M. M. B. Holl, J. W. Kampf, *Organometallics* **1999**, *18*, 1547. [2o] N. Burford, C. L. B. Macdonald, D. J. LeBlanc, T. S. Cameron, *Organometallics* **2000**, *19*, 152.

[3] [3a] M. Belay, F. T. Edelmann, *J. Organomet. Chem.* **1994**, *479*, C21. [3b] V. C. Gibson, C. Redshaw, L. J. Sequeira, K. B. Dillon, W. Clegg, M. R. J. Elsegood, *Chem. Commun.* **1996**, 2151. [3c] K. B. Dillon, V. C. Gibson, J. A. K. Howard, C. Redshaw, L. Sequeira, J. W. Yao, *J. Organomet. Chem.* **1997**, *528*, 179. [3d] P. Espinet, S. Martín-Barrios, F. Villafañe, P. G. Jones, *Organometallics* **2000**, *19*, 290. [3e] A. S. Batsanov, K. B. Dillon, V. C. Gibson, J. A. K. Howard, L. Sequeira, J. W. Yao, *J. Organomet. Chem.* **2001**, *631*, 181. [3f] G. M. Benedikt, B. L. Goodall, S. Iyer, L. H. McIntosh, III, R. Mimna, L. F. Rhodes, C. S. Day, V. W. Day, *Organometallics* **2001**, *20*, 2565.

[4] C. Bartolomé, P. Espinet, F. Villafañe, S. Giesa, A. Martín, A. G. Orpen, *Organometallics* **1996**, *15*, 2019.

[5] [5a] C. Bartolomé, R. de Blas, P. Espinet, J. M. Martín-Alvarez, F. Villafañe, *Angew. Chem. Int. Ed.* **2001**, *40*, 2521. [5b] C. Bartolomé, P. Espinet, L. Vicente, F. Villafañe, J. P. H. Charmant, G. A. Orpen, *Organometallics* **2002**, *21*, 3536. [5c] C. Bartolomé, P. Espinet, J. M. Martín-Alvarez, F. Villafañe, *Inorg. Chim. Acta* **2003**, *347*, 49.

[6] [6a] F. T. Ladipo, G. K. Anderson, *Organometallics* **1994**, *13*, 303. [6b] C. Eaborn, K. J. Odell, A. Pidcock, *J. Chem. Soc., Dalton Trans.* **1978**, 1288. [6c] R. J. Puddephatt, P. J. Thomson, *J. Chem. Soc., Dalton Trans.* **1977**, 1219. [6d] G. K. Anderson, R. J. Cross, L. Manojlovic-Muir, K. W. Muir, T. Solomun, *J. Organomet. Chem.* **1979**, *170*, 385.

[7] For R = C_6F_5, the monomer *cis*-[PdBr(C_6F_5)(NCMe)$_2$] is isolated as a solid and the dimer has not been obtained: A. C. Albéniz, P. Espinet, C. Foces-Foces, R. H. Cano, *Organometallics* **1990**, *9*, 1079. This suggests that the *trans* effect of Fmes is higher than that of C_6F_5, which implies that Fmes is a stronger σ-donor than C_6F_5.

[8] K. F. Purcell, J. C. Kotz, *Inorganic Chemistry*, 1st ed., W. B. Saunders C. **1977**, Cap. 13, page 694.

[9] Fmes is a soft σ-donor ligand with a high *trans* influence, which facilitates the release of the leaving ligand in an associative ligand substitution, i.e. the high *trans* influence of Fmes induces a high *trans* effect by destabilizing the fundamental state. Probably, some π-acceptor contribution in the five-coordinate transition state will further increase the *trans* effect of Fmes.

[10] R. G. Pearson, *Inorg. Chem.* **1973**, *12*, 712.

[11] [11a] J. Vicente, A. Arcas, D. Bautista, *Organometallics* **1997**, *16*, 2127. [11b] J. Vicente, J. A. Abad, A. D. Frankland, M. C. Ramírez de Arellano, *Chem. Eur. J.* **1999**, *5*, 3066. [11c] J. Vicente, J. A. Abad, E. Martinez-Viviente, P. G. Jones, *Organometallics*, in press.

[12] [12a] P. K. Biers, A. J. Canty, *Organometallics* **1990**, *9*, 210. [12b] R. E. Rülke, J. N. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen, K. Brieze, *Inorg. Chem.* **1993**, *32*, 5769.

[13] J. A. Casares, P. Espinet, J. M. Martínez-Ilarduya, Y.-S. Lin, *Organometallics* **1997**, *16*, 770.

[14] [14a] A. Domenicano, A. Vaciago, C. A. Coulson, *Acta Crystallogr., Sect. B* **1975**, *31*, 221. [14b] A. Domenicano, P. Murray-Rust, A. Vaciago, *Acta Crystallogr., Sect. B* **1983**, *39*, 457, and references therein. [14c] R. Norrestam, L. Schepper, *Acta Chem. Scand., Ser. A* **1981**, *35*, 91. [14d] A. Domenicano, P. Mazzeo, A. Vaciago, *Tetrahedron Lett.* **1976**, 1029.

[15] To correct the systematic shortening of O−H bonds measured by X-ray diffraction, normalized H-atom positions were used. An O−H distance of 0.967 Å was imposed. This value has been observed in alcohols by neutron-diffraction: F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

[16] G. Aullón, D. Bellamy, L. Brammer, E. A. Bruton, A. G. Orpen, *Chem. Commun.* **1998**, 653.

[17] J. P. Rourke, F. P. Fanizzi, N. J. S. Salt, D. W. Bruce, D. A. Dunmur, P. Maitlis, *J. Chem. Soc., Chem. Commun.* **1990**, 229.

[18] [18a] F. Paul, J. Patt, J. F. Hartwig, *J. Am. Chem. Soc.* **1994**, *116*, 5969. [18b] F. Paul, J. Patt, J. F. Hartwig, *Organometallics* **1995**, *14*, 3030. [18c] M. Chentit, M. Geoffroy, G. Bernardinelli, *Acta Crystallogr., Sect. C* **1997**, *53*, 866.

[19] [19a] D. A. Albisson, R. B. Bedford, S. E. Lawrence, P. N. Scully, *Chem. Commun.* **1998**, 2095. [19b] V. Dufaut, J. Thivolle-Cazat, J. M. Basset, R. Mathieu, J. Jaud, J. Waissermann, *Organometallics* **1991**, *10*, 4005. [19c] K. Tsutsumi, S. Ogoshi, S. Nishiguchi, H. Kurosawa, *J. Am. Chem. Soc.* **1998**, *120*, 1938. [19d] S. J. Geib, A. L. Rheingold, *Acta Crystallogr., Sect. C* **1987**, *43*, 1427.

[20] J. A. S. Howell, M. G. Palin, P. C. Yates, P. McArdle, D. Cunningham, Z. Goldschmidt, H. G. Gottlieb, D. Hezroni-Langerman, *J. Chem. Soc., Perkin Trans. 2* **1992**, 1769.

[21] C. A. McAuliffe, in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, A. A. McCleverty), Pergamon, Oxford; **1987**, vol. 2., p. 1012.

[22] [22a] R. A. Widenhoefer, H. A. Zhong, S. L. Buchwald, *Organometallics* **1996**, *15*, 2745. [22b] J. A. S. Howell, M. G. Palin, P. McArdle, D. Cunningham, Z. Goldschmidt, H. G. Gottlieb, D. Hezroni-Langerman, *Organometallics* **1993**, *12*, 1694. [22c] J. A. S. Howell, M. G. Palin, P. McArdle, D. Cunningham, Z. Goldschmidt, H. G. Gottlieb, D. Hezroni-Langerman, *Inorg. Chem.* **1993**, *32*, 3493.

[23] [23a] A. K. Colter, I. I. Schuster, R. J. Kurland, *J. Am. Chem. Soc.* **1965**, *87*, 2278. [23b] A. K. Colter, I. I. Schuster, R. J. Kurland, *J. Am. Chem. Soc.* **1965**, *87*, 2279.

[24] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, U. K., **1988**.

[25] [25a] G. E. Carr, R. D. Chambers, T. F. Holmes, D. G. Parker, *Ibid* **1987**, *325*, 13. [25b] M. Scholz, H. W. Roesky, D. Stalke, K. Keller, F. T. Edelmann, *J. Organomet. Chem.* **1989**, *366*, 73.

[26] R. Usón, J. Forniés, F. Martínez, M. Tomás, *J. Chem. Soc., Dalton Trans.* **1980**, 888.

[27] F. L. Wimmer, S. Wimmer, P. Castan, *Inorg. Synth.* **1992**, *29*, 185.

[28] G. R. Newkome, D. C. Hager, *J. Org. Chem.* **1978**, *43*, 947.

[29] Treatment of $OCPy_2$ with LiMe and further hydrolysis yields $(OH)(CH_3)CPy_2$, which can be recrystallized from dichloromethane/hexane. Spectroscopic data agree with those previously reported: S. Bhaduri, N. Y. Sapre, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1991**, 2539.

[30] C. Bartolomé, P. Espinet, J. M. Martín-Alvarez, F. Villafañe, manuscript in preparation.

[31] SMART V5.051 diffractometer control software, Bruker Analytical X-ray Instruments Inc., Madison, WI, **1998**.

[32] SAINT V6.02 integration software, Siemens Analytical X-ray Instruments Inc., Madison, WI, **1999**.

[33] G. M. Sheldrick. *SADABS: A program for absorption correction with the Siemens SMART system*; University of Göttingen: Germany, **1996**.

[34] *SHELXTL program system version 5.1*; Bruker Analytical X-ray Instruments Inc., Madison, WI, **1998**.

[35] *International Tables for Crystallography*, Kluwer, Dordrecht, **1992**, vol. C.

Received April 7, 2003