Neutral Organometallic Palladium(II) Aquo Complexes

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The reactions of chlorobridged cyclometalated complexes $[Pd(C-N)(\mu\text{-}Cl)]_2$ (C−N = orthometalated *N*,*N*-dimethylbenzylamine, dmba; 2-(*para*-tolyl)pyridine, *p*-tolpy; azobenzene, azb; *N*,*N*-dimethyl-1-naphthylamine, dmna; and 2-benzylpyridine, bzpy) with Li(Fmes) (Fmes = 2,4,6-tris(trifluoromethyl)phenyl or nonafluoromesityl) give, after hydrolysis, neutral aquo complexes $[Pd(C-N)(Fmes)(OH_2)]$, where the *ipso* carbon atoms of the Fmes and the cyclometalated ligand are coordinated *cis*, as shown by an X-ray diffraction study of [Pd(dmba)(Fmes)(OH_2)]. The aquo ligand is readily displaced by other ligands, giving complexes [Pd(C−N)(Fmes)L] (L = PPh_3, 2,6-lutidine, NH_3, CN^{t}Bu, CO) when monodentate ligands are employed or [Pd(dmba-*C*)(Fmes)(2,2′-bipy)], which contains a chelating 2,2′-bipyridyl and a monodentate C-bonded dmba. Different processes in solution are detected for the complexes containing the bulkier ligands: ligand rotation in the complex with PPh_3; inversion of the bipy ligand in [Pd(dmba-*C*)(Fmes)(2,2′-bipy)]; and equilibria with residual water in the solutions of [Pd(C−N)(Fmes)(lut)] and [Pd(dmba-*C*)(Fmes)(2,2′-bipy)].

Introduction

Ligands with high steric demand sometimes stabilize species that are otherwise inaccessible or difficult to obtain. The bulky aryl 2,4,6-tris(trifluoromethyl)phenyl (nonafluoromesityl or Fmes) induces interesting structural features when coordinated to main group[1,2] or transition metals.[3] Some features associated with its high steric demand are hindrance of rotation around the M−Fmes bond, restricted rotation of ancillary ligands, and a high degree of axial protection in square-planar complexes.[4] The *ortho*-CF_3 groups seem to be involved in M···F bonding interactions [M = Li, Na, K, Sn(II)] in many solid state structures,[1] but not in the structures of the fluoromesitylpalladium(II) complexes determined so far.[4] On the other hand, the combination of Fmes and halide ligands in ligand-deficient conditions for palladium(II) led to an unprecedented self-assembly of a pyramidal tetrametallic complex with a chloro ligand in the apex.[5]

We decided to explore the reactivity of Li(Fmes) toward complexes $[Pd(C-N)(\mu\text{-}Cl)]_2$ (C−N = bidentate cyclometalated ligand), where, if the chloro ligands were substituted by Fmes, one coordination position per metal center would still remain available. It was interesting to see whether a three-coordinated Pd(II) complex could be isolated or how the Pd center would otherwise manage to achieve four-coordination. Two possibilities foreseen were coordination of F (forming a favorable five-membered metallacycle) or bridging of the fluoromesityl ligands,[6] since mesityls,[7] and other bridging aryls, including fluoroaryls,[8] are well known. It

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(1) Edelmann, F. T. *Comments Inorg. Chem.* **1992**, *12*, 259.

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

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

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

(5) Bartolomé, C.; de Blas, R.; Espinet, P.; Martín-Álvarez, J. M.; Villafañe, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 2521.

(6) Voelker, H.; Labahn, D.; Bohnen, F. M.; Herbst-Irmer, R.; Roesky, H. W.; Stalke, D.; Edelmann, F. T. *New J. Chem.* **1999**, *23*, 905.

(7) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1079.

(8) (a) Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Navarro, R. *J. Chem. Soc., Dalton Trans.* **1989**, 169. (b) Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R.; Llusar, R. *Organometallics* **1988**, *7*, 2279. (c) Albéniz, A. C.; Espinet, P.; Martín-Ruiz, B. *Chem. Eur. J.* **2001**, *7*, 2481.

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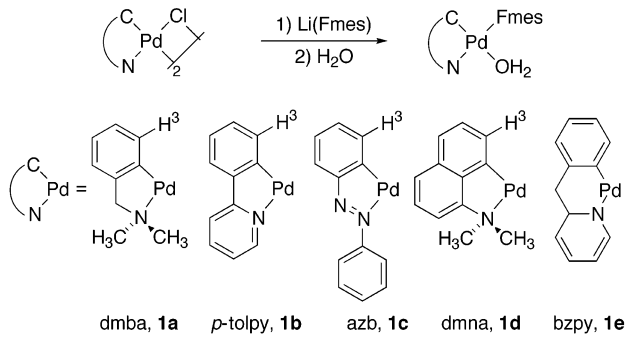
Scheme 1. Synthesis of Complexes 1[a]



[a] H^3 of the five-membered orthometalated ligand is highlighted.

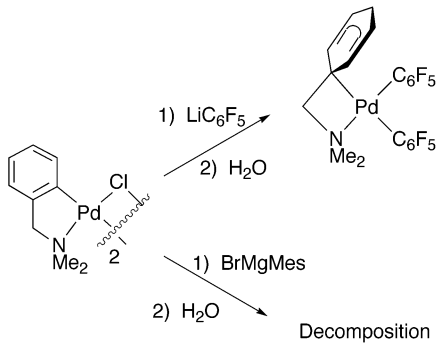
turned out that the availability of water, added for the hydrolysis of the excess Li(Fmes), provided an additional ligand and gave rise to neutral aquo complexes, one of which has been structurally characterized by X-ray diffraction. The formation of stable complexes with the hard ligand water on a very soft metal center (a neutral Pd(II) center with two hydrocarbyl ligands that further enhance its softness) is remarkable and can be related to favorable steric factors.

Results and Discussion

Synthesis of the Aquo Complexes. The reactions of cyclometalated complexes $[Pd(C-N)(\mu\text{-}Cl)]_2$ with Li(Fmes) (Pd/Fmes = 1:2) were carried in Et_2O, at room temperature or 40 °C, for between 15 and 24 h (see Experimental Section). Attempts at treating the solutions in the absence of water gave only intractable oils. However, if a few drops of water were added to hydrolyze the excess of Li(Fmes), the neutral aquo complexes $[Pd(C-N)(Fmes)(OH_2)]$ (C−N = dmba, **1a**; *p*-tolpy, **1b**; azb, **1c**; dmna, **1d**; bzpy, **1e**; Scheme 1) could be isolated. Complexes **1** are somewhat unusual, in that they are remarkably stable toward reductive coupling, despite having two *cis* C-ligands;[9] in fact other reactions of cyclometalated halo-bridged dimers of palladium(II) with different organolithium reagents reported in the literature give the coupling product.[10] Moreover, complexes **1** feature a hard OH_2 ligand coordinated to palladium(II). This is surprising considering that a neutral palladium center having two hydrocarbyl ligands must be very soft. In fact, whereas cationic palladium(II) aquo complexes are not uncommon (the metal center is harder in this case),[11] we have not found precedents in the literature of neutral palladium(II) aquo complexes other than our proposal of their formation in solution.[12,13]

To assess more accurately the role of Fmes in producing these unusual complexes, parallel reactions were carried out with C_6F_5 (a ligand with similar electron-donating properties but smaller steric volume) and mesityl (with similar steric volume but more basic).[14] The reactions with $[Pd(dmba)(\mu\text{-}Cl)]_2$ were carried out under the same conditions as for Li(Fmes): a Pd/C_6F_5 ratio of 1:2, stirred for 24 h at room temperature, and

Scheme 2. Attempts at Synthesizing Complexes Similar to 1 with Other Arylating Reagents



subsequent hydrolysis. The results are shown in Scheme 2. The reaction with $Li(C_6F_5)$ leads in good yield (72%) to the η^1-arene complex *cis*-$[Pd(C_6F_5)_2(C_6H_5CH_2NMe_2)]$, which had been obtained earlier by displacement of the THF ligands by dmba from the complex *cis*-$[Pd(C_6F_5)_2(THF)_2]$.[15] This result can be explained considering that C_6F_5 is not as bulky as Fmes. Thus, a second arylation probably takes place with excess $Li(C_6F_5)$ to give a *cis*-$[Pd(C_6F_5)_2(C_6H_4CH_2NMe_2)]^-$ intermediate, which then undergoes protonolysis by attack at the highly nucleophilic orthopalladated carbon to give the observed product $[Pd(C_6F_5)_2(C_6H_5CH_2NMe_2)]$. Performing the

(9) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1031.

(10) (a) Muharashi, S. I.; Tamba, Y.; Yamamura, M.; Moritani, I. *Tetrahedron Lett.* **1974**, 3749. (b) Muharashi, S. I.; Tamba, Y.; Yamamura, M.; Yoshimura, N. *J. Org. Chem.* **1978**, *43*, 4099.

(11) Crystal structures of cationic organometallic palladium aquo complexes: (a) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans.* **1978**, 1490. (b) Castan, P.; Jaud, P.; Wimmer, S.; Wimmer, F. L. *J. Chem. Soc., Dalton Trans.* **1991**, 1155. (c) Vicente, J.; Arcas, A.; Borrachero, M. V.; Molíns, E.; Miratvilles, C. *J. Organomet. Chem.* **1992**, *441*, 487. (d) Sheehan, J. P.; Spalding, T. R.; Ferguson, G.; Gallagher, J. F.; Kaitner, B.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1993**, 35. (e) Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 738. (f) Maassarani, F.; Davidson, M. F.; Wehman-Ooyevaar, I. C. M.; Grove, D. M.; van Koten, M. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg. Chim. Acta* **1995**, *235*, 327. (g) Vicente, J.; Arcas, A.; Bautista, D. *Organometallics* **1997**, *16*, 2127. (h) Vicente, J.; Arcas, A.; Blasco, M. A.; Lozano, J.; Ramírez de Arellano, M. C. *Organometallics* **1998**, *17*, 5374. (i) Ruiz. J.; Florenciano, F.; Vicente, C.; Ramírez de Arellano, M. C.; López, G. *Inorg. Chem. Commun.* **2000**, *3*, 73. (j) Barco, I. C.; Falvello, L. R.; Fernández, S.; Navarro, R.; Urriolabeitia, E. P. *J. Chem. Soc., Dalton Trans.* **1998**, 1699. (k) Ma, J.-F.; Kojima, Y.; Yamamoto, Y. *J. Organomet. Chem.* **2000**, *616*, 149. Other cationic palladium organometallic aquo complexes reported but not characterized by diffraction methods: (l) Ryabov, A. D.; Kazankov, G. M.; Yatsimirsky, A. K.; Kuz'mina, L. G.; Burtseva, O. Y.; Dvortsova, N. V.; Polyakov, V. A. *Inorg. Chem.* **1992**, *31*, 3083. Crystal structures of cationic coordination palladium aquo complexes: (m) Leoni, P.; Sommovigo, M.; Pasquali, M.; Midollini, S.; Braga, D.; Sabatino, P. *Organometallics* **1991**, *10*, 1038. (n) Stang, P. J.; Cao, D. H.; Poulter, G. T.; Arif, A. T. *Organometallics* **1995**, *14*, 1110. Other cationic palladium coordination aquo complexes reported but not characterized by diffraction methods: (o) Fuss, M.; Siehl, H. U.; Olenyuk, B.; Stang, P. J. *Organometallics* **1999**, *18*, 758.

(12) A reviewer has drawn our attention to the fact that the compound in ref 11b, $[Pd(L)(ONO_2)(OH_2)]ClO_4 \cdot HO_2$, L being the orthometalated *N*-methyl-2,2′-dipyridinium cation, should be considered an essentially neutral Pd aquo complex, since the positive charge must be associated to the methylated nitrogen. Note that the second anionic ligand (nitrate) is a very poor hard donor, which renders the Pd center much harder than ours. Also the positive nitrogen in the heterocycle will still be more electron attracting than a neutral carbon atom and will make the protonated hydrocarbyl harder than a phenyl. Whether neutral or cationic, this must be a rather hard Pd center for which coordination of a hard ligand is not unnatural. Our case is different and remarkable because of the softness of the center where water coordinates.

(13) Espinet, P.; Martínez-Ilarduya, J. M.; Pérez-Briso, C.; Casado, A. L.; Alonso, M. A. *J. Organomet. Chem.* **1998**, *551*, 9.

(14) Although the covalent radii of fluorine (58 pm) and hydrogen (30 pm) differ, their van der Waals radii are similar: 135 vs 120 pm, respectively: Emsley, J. *The Elements*, 2nd ed.; Oxford University Press: Oxford, 1991.

(15) Falvello, L. R.; Forniés, J.; Navarro, R.; Sicilia, V.; Tomás, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 891.

Table 1. IR and ^{1}H NMR Data of Coordinated OH_2 in Complexes 1

aquo complex	δ/ppm (25 °C)	δ/ppm (25 °C)[a]	δ/ppm (−60 °C)[a]	ν/cm^{-1} (solid)
1a	1.89	1.97	2.21	3607m, 3529m
1b	2.10	2.40	2.80	3609w, 3542m
1c	1.95	2.14	2.61	3647m, 3606m
1d	2.09	2.17	2.40	3622w, 3544m
1e	1.70	1.82	2.48	3637m, 3518m

[a] Recorded in dry $CDCl_3$.

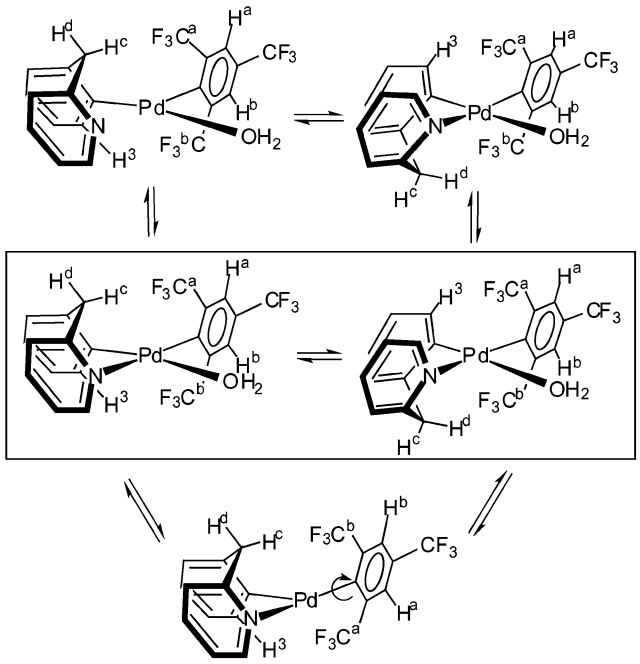
reaction with a Pd/C_6F_5 ratio of 1:1 gives a mixture of *cis*-$[Pd(C_6F_5)_2(C_6H_5CH_2NMe_2)]$ and unidentified minor species that display absorptions in the O−H stretching region. When the parent chloro complex and BrMgMes were subjected to the aforementioned reaction conditions, extensive decomposition took place.

Characterization of the Neutral Aquo Complexes. The IR spectra of complexes **1** show two absorptions in the O−H stretching region.[16] The hydrogens of the coordinated water molecule appear in the range 1.7−2.1 ppm when the spectra are recorded in $CDCl_3$ at room temperature. A slight downfield shift is observed in *dry* $CDCl_3$ (1.8−2.4 ppm range), and even more downfield values are obtained in dry $CDCl_3$ at −60 °C (Table 1). These variations must be a result of fast equilibrium between coordinated water and water in the solvent, the average chemical shift changing with the proportion of free water. The traces of free water are almost completely removed when using dry $CDCl_3$ and should freeze out at −60 °C. Our chemical shift values are unusually low compared to most values reported in the literature,[17] which appear in the range 1.8−5 ppm for cationic complexes[11a,f−k,m,n] and 4.5−7 ppm for neutral complexes.[13] We suspect that most values reported in the literature come from recordings at room temperature in wet $CDCl_3$. Thus, extreme care should be exercised when comparing chemical shifts of aquo complexes.

The signals of the cyclometalated ligand are very similar to those of the parent chloro-bridged dimer, except for H^3 (see Scheme 1), which is clearly shifted upfield in **1a**−**d**. This supports the structure depicted in Scheme 1, where the carbon donor atoms of the Fmes and cyclometalated ligands are *cis*, and the aryl Fmes ring produces anisotropic shielding of H^3. Moreover, this arrangement places the two softer donor atoms mutually *cis*, as expected for Pd(II).[18]

The six-membered metallacycle **1e** differs from the others. The loss of planarity on the cyclometalated ligand results in hydrogen H^3 of the orthometalated ligand not being subjected to anisotropic shielding by the Fmes ligand and appears in the normal range for palladated aryls. The methylene hydrogens of the cyclometalated ligand give rise to a broad signal in the spectrum at room temperature and decoalesce into two doublets at −60 °C. At room temperature the fluorine atoms of the *ortho*-CF_3 groups of **1e** appear as a very broad signal ($\nu_{1/2}$ = ca. 20 Hz), whereas they are fine singlets for **1a**−**d**. On cooling to −60 °C, this broad signal splits into two singlets of equal intensity, indicating that both *ortho*-CF_3 groups are nonequivalent when the dynamic process is frozen. This is attributed to a slow inversion of the boat-shaped six-membered metallacycle (Scheme 3), which has been described for other complexes containing orthometalated 2-benzylpyridine.[19] Direct boat-to-boat inversion of bzpy ligand in the very crowded **1e** complex (Scheme 3, center) looks very unlikely. The most likely mechanism is decoordination and recoordination of the pyridyl group (Scheme 3, upper), since dissociation from an electron-rich bis(hydrocarbyl)palladium(II) center should be easily accessible. Dissociation of OH_2 would require either boat inversion or Fmes rotation in a three-coordinate intermediate, and both are sterically hindered. Moreover, the Fmes rotation does not explain the equivalence of the two methylene hydrogens observed in the room-temperature spectrum of **1e**.

Scheme 3. Mechanisms Proposed for the Boat Inversion Observed for 1e



Structural Characterization of [Pd(dmba)(Fmes)(OH$_2$)], 1a. The structure of the aquo complexes was further supported by the X-ray diffraction study of [Pd(dmba)(Fmes)(OH_2)], **1a**. The molecule is shown in Figure 1. Relevant distances and angles are collected in Table 2. The molecule shows an approximately square-planar palladium atom coordinated by an orthometalated dimethylbenzylamine with its carbon donor atom *cis* to the fluoromesityl ligand and a molecule of water coordinated *cis* to the nitrogen atom. The coordination angles at palladium are not far from the square-planar ideal, although the bite angle of the chelate is noticeably smaller, as expected. The *trans* angles differ slightly from 180° [C(1)−Pd−O(20)

(16) Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Kiss, G.; Hoff, C. D. *Organometallics* **1992**, *12*, 3390, and references therein.

(17) There is only one precedent where the signal corresponding to the hydrogens of the OH_2 ligand appears at 1.8 ppm (ref 11c).

(18) The well-known destabilizing effect of two mutually *trans* soft ligands attached to a soft metal center has been named "antisymbiotic effect" (Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712). More recently the term "transphobia" has been coined for pairs of ligands (see ref 11g and: Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **1999**, *5*, 3067). For *trans* influence of common ligands see: Hartley, F. R. *Chem. Soc. Rev.* **1973**, *2*, 163.

(19) Hiraki, K.; Fuchita, Y.; Takechi, K. *Inorg. Chem.* **1981**, *20*, 4316.

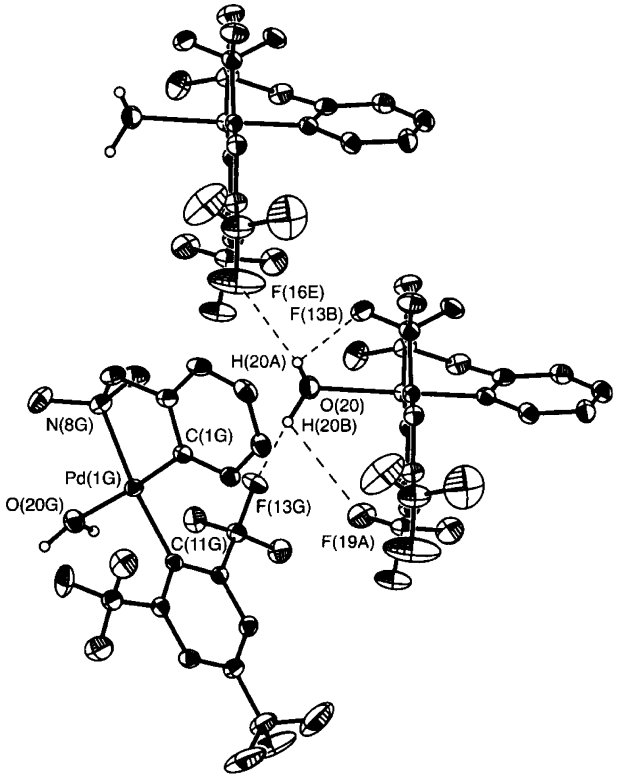


Figure 1. Molecular structure of **1a** showing the atom-numbering scheme. Intermolecular and intramolecular hydrogen bonds observed in **1a**. The ellipsoids are drawn at 30%.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1a

Pd1−C(1)	1.978(2)	C(1)−Pd(1)−N(8)	83.35(10)
		C(1)−Pd(1)−C(11)	92.34(10)
Pd(1)−C(11)	2.006(3)	C(11)−Pd(1)−O(20)	91.57(9)
		N(8)−Pd(1)−O(20)	92.81(9)
Pd(1)−N(8)	2.149(2)	C(1)−Pd(1)−O(20)	176.07(10)
		C(11)−Pd(1)−N(8)	171.83(9)
Pd(1)−O(20)	2.220(2)	C(18)−C(11)−C(12)	114.7(2)

176.07(10)° and C(11)−Pd−N(8) 171.83(9)°], whereas the sum of *cis* angles is almost exactly 360°. The C(18)−C(11)−C(12) angle at the *ipso* carbon is significantly less than 120° [114.7(2)°] as a result of the electronic effects of the electropositive metal and electronegative CF_3 substituents at these positions.[20] The Pd−C(11) distance [2.006(3) Å] is slightly shorter than other Pd−Fmes distances found in bisarylated complexes [from 2.023(3) to 2.114(5) Å].[4] The distances and angles of the orthometalated dmba are essentially similar to those found in other palladium(II) complexes containing this ligand.[11a,f,j,k,21] The Pd−OH_2 distance [2.220(2) Å] is in the range found in cationic Pd(II) aquo complexes, from 2.106(4) to 2.301(6) Å.[11a−k,m,n] The same effect has been observed in platinum(II) aquo complexes, where neutral and cationic complexes present similar Pt−O distances.[22] The fluoromesityl lies virtually perpendicular to the pseudoplane defined by the metal and the donor atoms. The Pd···F_3C-*ortho* distances found in **1a** (3.089 Å, the shortest; 3.463 Å, the largest) are slightly longer than those found in bisarylated "Pd(Fmes)$_2$" complexes, confirming that these are nonbonding contacts, as discussed elsewhere.[4]

The two hydrogen atoms of the OH_2 ligand were located in a difference Fourier map and refined. To correct the systematic shortening of F−H bonds measured by X-ray diffraction, normalized H atom positions were used. An O−H distance of 0.967 Å was imposed, a value that has been observed in alcohols by neutron diffraction.[23] Applying this, four O−H···F contacts have been detected, two of them intramolecular and the other two intermolecular (Figure 1). The distances and angles of these contacts are listed in Table 3. The H(20B)−F(13G) distance is 2.200 Å. Only few cases where these contacts involve H···F distances shorter than 2.3 Å have been described.[24]

Reactivity of the Aquo Complexes. The substitution of **1** with different ligands has been studied (Scheme 4). The aquo ligand is hard and should be easily removed from the coordination sphere of the soft palladium(II) center. The high degree of axial protection to a nucleophilic attack in the bis-arylated [Pd(C−N)(Fmes)(OH_2)] should favor dissociative mechanisms of ligand substitution.[25]

Ligands with different steric and electronic demands were tested. Bulky donors with different steric features were chosen: PPh_3, of conical shape; 2,6-lutidine (lut), highly sterically demanding in the axial positions (like Fmes); and the chelating bidentate ligand 2,2′-bipyridyl (bipy).

Olefins and acetylenes do not react with **1**. ^{t}BuNC and CO replace the water ligand to give **2a** and **3a**, which do not undergo insertion: insertion into the Pd−Fmes bond does not take place easily, while insertion into the *trans*-Pd−C bond is geometrically inaccessible. Ammonia replaces water to give **4a**. Neither **1a** nor **4a** could be deprotonated with NBu_4OH or *N*,*N*,*N*′,*N*′-tetramethyl-1,8-naphthalenediamine ("proton sponge").

The complexes [Pd(C−N)(Fmes)(PPh_3)] (C−N = dmba, **5a**, *p*-tolpy, **5b**) show a septuplet in the $^{31}P\{^1H\}$ NMR spectra, and the *ortho*-CF_3 gives rise to a doublet in their ^{19}F NMR spectra, as expected. These spectra remain invariant from −60 °C to room temperature. H^3 appears shielded as in the parent compounds, suggesting that the substitution has retained the original geometry. The aromatic protons of the phosphines give broad signals in the ^1H NMR spectra at room temperature, while the signals for the hydrogens of the Fmes group (slightly shielded compared with the rest of complexes herein

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

(21) (a) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115. (b) Falvello, L. R.; Fernández, S.; Navarro, R.; Urriolabeitia, E. P. *Inorg. Chem.* **1996**, *35*, 3064.

(22) For some structures of Pt(II) aquo complexes see: ionic: (a) Britten, J. F.; Lippert, B.; Lock, C. J. L.; Pilon, P. *Inorg. Chem.* **1982**, *21*, 1936. (b) Rauter, H.; Hillgeris, E. C.; Erxleben, A.; Lippert, B. *J. Am. Chem. Soc.* **1994**, *116*, 616. (c) Meinema, H. A.; Verbeek, F.; Marsman, J. W.; Bulten, E. J.; Dabrowiak, J. C.; Krishnan, B. S.; Spek, A. L. *Inorg. Chim. Acta* **1986**, *114*, 127. (d) Rochon, F. D.; Melanson, R. *Inorg. Chem.* **1987**, *26*, 989; neutral: (e) Intini, F. P.; Lanfranchi, M.; Natile, G.; Pacifico, C.; Tiripicchio, A. *Inorg. Chem.* **1996**, *35*, 1715.

(23) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

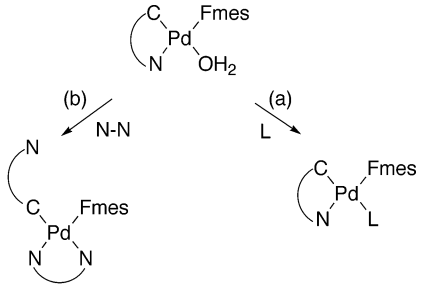
(24) Dunitz, J. D.; Taylor, R. *Chem. Eur. J.* **1997**, *3*, 89.

(25) (a) Bartolomé, C.; Espinet, P.; Martín-Álvarez, J. M.; Villafañe, F. Manuscript in preparation. (b) Romeo, R. *Comments Inorg. Chem.* **1990**, *11*, 21. (b) Minniti, D. *Inorg. Chem.* **1994**, *33*, 2631. (c) Casado, A. L.; Casares, J. A.; Espinet, P. *Inorg. Chem.* **1998**, *37*, 4154.

Table 3. Bond Lengths (Å) and Angles (deg) for Intra- and Intermolecular Hydrogen Bonds Observed in 1a

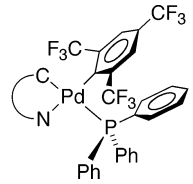
H(20A)−F(13B)	2.358	F(13B)−H(20A)−O(20)	132.0	intramolecular
H(20B)−F(19A)	2.811	F(19A)−H(20B)−O(20)	118.7	intramolecular
H(20A)−F(16E)	2.554	F(16E)−H(20A)−O(20)	109.3	intermolecular
H(20B)−F(13G)	2.200	F(13G)−H(20B)−O(20)	138.5	intermolecular

Scheme 4. Substitution Reactions in [Pd(C−N)(Fmes)(OH$_2$)][a]

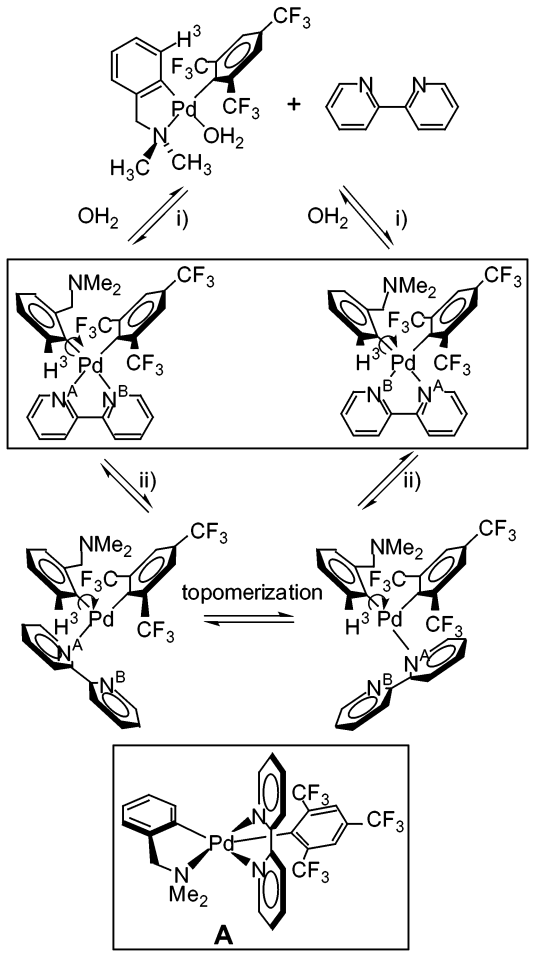


[a] C−N = dmba, L = ^{t}BuNC, **2a**; CO, **3a**; NH_3, **4a**;PPh_3, **5a**; 2,6-lut, **6a**; C−N = dmba, N−N = bipy, **7a**. C-N = *p*-tolpy, L = PPh_3, **5b**.

Chart 1. Low-Temperature Preferred Arrangement in Complexes 5a,b



Scheme 5. Two Possible Mechanisms for the Inversion of the Bipy Ligand in 7a



described: ca. 7.5 in **5** vs ca. 7.9) and the orthometalated ligands are sharp. On cooling the solutions of **5a**,**b** to −60 °C, the phosphine phenyls become nonequivalent, where one phenyl group is highly shielded, with the other two presenting regular chemical shifts. A similar behavior has been previously observed for complexes with Fmes and PPh_3 coordinated *cis* and is due to restricted rotation of the Pd−P bond, which is frozen at low temperature, as shown in Chart 1. In that arrangement the Fmes ligand and one of the phenyl groups of the phosphine exert mutual anisotropic shielding.[4] The activation barrier for the rotation of the PPh_3 is lower in **5a** than in **5b**, suggesting that it takes place in a three-coordinate intermediate. This agrees with the expectation that decoordination of the amine nitrogen in dmba should be easier than for the pyridinic nitrogen in *p*-tolpy.

The ligand 2,6-lutidine is sterically demanding in the same axial positions as Fmes. However, the reaction of **1a** with equimolar amounts of 2,6-lutidine does produce [Pd(dmba)(Fmes)(lut)], **6a**, which is isolated as a white solid. Note that although the axial crowding should be important, it is somewhat less than that in complexes *cis*-[Pd(Fmes)$_2$L$_2$].[4] The IR spectrum and elemental microanalysis support the stoichiometry for the solid obtained, whereas in the NMR spectra at room temperature the signals are very broad, due to the presence of traces of water in $CDCl_3$ and the existence of a slow equilibrium between **6a** and **1a** (eq 1). At −60 °C, the signals of the species present in the equilibrium are resolved and those of **6a** can be assigned. The equilibrium constant at −30 °C in $CDCl_3$ was measured as $K_e = 3.1 \pm 0.7$, using known water concentrations.[26]

$$[Pd(dmba)(Fmes)(L)] + H_2O \rightleftharpoons [Pd(dmba)(Fmes)(OH_2)] + L \quad (1)$$

Finally, the reaction of **1a** with 2,2-bipyridyl (1:1) leads to [Pd(dmba-*C*)(Fmes)(bipy)], **7a**, where the dmba ligand is monodentate. This is supported by the chemical shift of H^3, which is no longer shielded by the Fmes ring, and by the chemical shift of the bipy signals, which support coordination of both pyridyl nitrogens. Two dynamic processes are observed in **7a**. The first is an equilibrium between **7a** and **1a** (*i* in Scheme 5) due to the presence of traces of water in the solvent $CDCl_3$. Below −10 °C the signals of **7a** (major) and **1a** (very minor) can be resolved in the ^{19}F NMR spectrum. At −20 °C signals of **7a**, **1a**, and free bipy can be observed in the ^{1}H NMR spectrum. The equilibrium constant of this process, determined for **7a** using $CDCl_3$ solutions of known water concentration, is temperature dependent, as shown in Table 4.

A second dynamic process is still operative at lower temperatures. On further cooling the fluorine atoms of

(26) $CDCl_3$ solutions with different concentrations of water were titrated by NMR by integration of the water signal versus ferrocene added as reference.

Table 4. Equilibrium Constants for 7a and 1a

temperature/°C	K_{eq}
−30	$(24 \pm 5) \times 10^{-3}$
−25	$(25 \pm 6) \times 10^{-3}$
−20	$(35 \pm 7) \times 10^{-3}$

the *ortho*-CF_3 of **7a** broaden. Below −55 °C this broad signal splits into two singlets, indicating that both *ortho*-CF_3 groups are nonequivalent. In the ^1H spectrum, not only does the singlet of the methylene hydrogens become an AB system at low temperature, but also the signals of the coordinated bipy split, which means that the two halves of the bipyridine are nonequivalent. A dissociative mechanism (*ii* in Scheme 5) involving decoordination of one Py group of the bipy ligand, followed by topomerization in the three-coordinate intermediate and recoordination, could explain the equivalences observed at −20 °C. Alternatively, inversion of the bipy ligand through a five-coordinate intermediate **A** looks less likely because of the high degree of steric hindrance and the inappropriate bite angle of bipy in the five-coordinate transition state and also because of the poor electrophilicity of PdR_2L_2 complexes.[25b]

Both methyls of the amino group are still equivalent at −100 °C. This can be explained assuming that the inversion of the nitrogen is fast on the NMR time scale. This equivalence further proves that the complex does not possess a monodentate bipy and a chelating dmba, as this should produce inequivalence for these methyls.

Conclusions

The reaction of several orthometalated chloro-bridged palladium(II) dimers with Li(Fmes) followed by hydrolysis affords neutral palladium(II) aquo complexes. The electronic and steric features of the Fmes ligand seem to play a decisive role in their stabilization, as attempts at extending this behavior to alternative aryls have failed. The aquo ligand can be readily substituted for a variety of ligands. Those that are sterically demanding allow the observation of dynamic processes in solution due to either hindered rotation of any of the ligands present or equilibrium with the water complex, which is formed even from traces of water. It is noteworthy that the hard ligand water can compete with other much better but bulkier ligands, due to the fact that water relieves structural crowding. The remarkable unusual stability of the CO and NH_3 complexes must also benefit from the small steric requirement of these ligands.

Experimental Section

General Comments. All reactions were carried out under nitrogen atmosphere. The solvents were purified according to standard procedures.[27] Diethyl ether was distilled under nitrogen from sodium/benzophenone ketyl prior to use. [Pd(dmba)(μ-Cl)]$_2$[28] and $Pd_3(OAc)_6$[29] were prepared according to literature procedures. [Pd(*p*-tolpy)(μ-Cl)]$_2$,[30] [Pd(azb)(μ-Cl)]$_2$,[31] [Pd(dmna)(μ-Cl)]$_2$,[28] and [Pd(bzpy)(μ-Cl)]$_2$[10] were prepared by the general method currently used in our group,[32] involving synthesis of the corresponding acetato-bridged complexes[33] and subsequent treatment with a methanolic solution of hydrogen chloride. 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[34] and used immediately in situ without further purification.

Infrared spectra were recorded in Perkin-Elmer 883 or 1720X equipment, as Nujol mulls between polystyrene plates, from 4000 to 200 cm^{-1}. NMR spectra were recorded on Bruker AC-300 or ARX-300 instruments, in $CDCl_3$ at room temperature unless otherwise stated. NMR spectra are referenced to TMS, $CFCl_3$, or 85% aqueous H_3PO_4, and coupling constants are measured in Hz. Elemental analyses were performed on a Perkin-Elmer 2400B microanalyzer.

General Method for the Preparation of the Aquo Complexes. The orthometalated palladium(II) chloro-bridged dimer (0.5 mmol) was added to a freshly prepared solution of Li(Fmes) (2.0 mmol; [Pd(C−N)(μ-Cl)]$_2$/Li(Fmes) = 1:4) in Et_2O (20 mL). After stirring the mixture for 24 h at the temperature indicated, two drops of water were added to hydrolyze the excess of organolithium reagent. The volatiles were removed in a vacuum, and the dark residue was extracted with CH_2Cl_2 (ca. 50 mL) and filtered on dry Celite. *n*-Hexane (ca. 20 mL) was added to the filtrate, which was concentrated and cooled to −20 °C. The microcrystalline solid obtained was decanted, washed with *n*-hexane (3 × 5 mL), and dried in a vacuum. The reaction details (temperature and yield), color, and spectroscopic data of the products obtained are given below. The aquo complexes were analized by ATG. Above 110 °C the compounds started to lose water slowly, but before the loss was complete the compounds started to decompose gradually. For this reason no well-defined melting or decomposition temperatures can be given.

[Pd(dmba)(Fmes)(OH_2)], 1a. Reaction at room temperature, 88% yield, pale brown. ^{19}F NMR: δ −60.00 (s, *ortho*-C*F*$_3$, 6F), −62.90 (s, *para*-C*F*$_3$, 3F). ^1H NMR: δ 7.88 (s, $C_6H_2(CF_3)_3$, 2H), 6.86 (m, C_6H_4, 2H), 6.59 (td, *J* 7.0 and 2.0, C_6H_4, 1H), 5.85 (d, *J* 7.5, H^3, C_6H_4, 1H), 3.82 (s, C*H*$_2$, 2H), 2.69 (s, NC*H*$_3$, 6H), 1.97 (s, *H*$_2$O, 2H). IR: 3607 m, 3529 m, 1616 s, 1580 s, 1563 s, 1403 m, 1283 vs, 1127 vs, 1022 s, 996 s, 976 m, 918 s, 868 m, 852 s, 835 s, 684 s, 564 w, 511 w, 491 w, 467 m, 438 m. Anal. Calcd for $C_{18}H_{16}F_9NOPd$: C, 40.06; H, 2.99; N, 2.60. Found: C, 40.18; H, 2.97; N, 2.88.

[Pd(*p*-tolpy)(Fmes)(OH_2)], 1b. Reaction at 40 °C, 50% yield, pale brown. ^{19}F NMR: δ −59.71 (br, *ortho*-C*F*$_3$, 6F), −62.79 (s, *para*-C*F*$_3$, 3F). ^1H NMR: δ 8.38 (br, NC_5H_4, 1H), 7.95 (s, $C_6H_2(CF_3)_3$, 2H), 7.72 (m, NC_5H_4, 1H), 7.65 (d, *J* 8.0, NC_5H_4, 1H), 7.33 (d, *J* 8.0, $CH_3C_6H_3$, 1H), 7.11 (br, NC_5H_4, 1H), 6.79 (d, *J* 7.5, $CH_3C_6H_3$, 1H), 5.80 (s, $CH_3C_6H_3$, H^3, 1H), 2.41 (br, *H*$_2$O, 2H), 2.03 (s, C*H*$_3$C$_6$H$_3$, 3H). IR: 3607 w, 3542 m, 1620 s, 1601 s, 1573 m, 1299 s, 1279 vs, 1189 vs, 1181 vs, 1146 vs, 1130 vs, 1118 vs, 1081 s, 1029 m, 911 s, 852 m, 833 m, 776 s, 693 m, 684 m, 667 w, 466 w, 418 w. Anal. Calcd for $C_{21}H_{14}F_9NOPd$: C, 43.96; H, 2.46; N, 2.44. Found: C, 44.11; H, 2.60; N, 2.60.

[Pd(azb)(Fmes)(OH_2)], 1c. Reaction at 40 °C, 72% yield, deep red. ^{19}F NMR: δ −60.02 (s, *ortho*-C*F*$_3$, 6F), −62.97 (s, *para*-C*F*$_3$, 3F). ^1H NMR: δ 7.97 (s, $C_6H_2(CF_3)_3$, 2H), 7.95 (partially hidden dd, *J* unknown and 1.5, C_6H_4, 1H), 7.78 (dd, *J* 8.0 and 1.5, C_6H_5, 2H), 7.57 (m, C_6H_5, 3H), 7.14 (td, *J* 7.5 and 1, C_6H_4, 1H), 6.92 (td, *J* 7.5 and 1.0, C_6H_4, 1H), 6.06 (dd, *J* 7.5 and 1.0, C_6H_4, H^3, 1H), 2.14 (s, *H*$_2$O, 2H). IR: 3647 m,

(27) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.
(28) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.
(29) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.
(30) Gutiérrez, M. A.; Newkome, G. R.; Selbin, J. *J. Organomet. Chem.* **1980**, *202*, 341.
(31) Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272.
(32) Buey, J.; Espinet, P. *J. Organomet. Chem.* **1996**, *507*, 137. Based on the method described in: Onoue, H.; Moritani, I. *J. Organomet. Chem.* **1972**, *43*, 431.
(33) Thompson, J. M.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 2667.
(34) (a) Carr, G. E.; Chambers, R. D.; Holmes, T. F.; Parker, D. G. *J. Org. Chem.* **1987**, *325*, 13. (b) Scholz, M.; Roesky, H. W.; Stalke, D.; Keller, K.; Edelmann, F. T. *J. Organomet. Chem.* **1989**, *366*, 73.

3606 w, 1618 m, 1567 w, 1553 w, 1299 vw, 1278 vw, 1239 m, 1190 vw, 1121 w, 1081 m, 1022 m, 910 m, 851 w, 834 m, 769 s, 684 m, 666 w, 598 w, 439 w. Anal. Calcd for $C_{21}H_{13}F_9N_2OPd$: C, 42.99; H, 2.23; N, 4.77. Found: C, 43.02; H, 2.33; N, 4.74.

[Pd(dmna)(Fmes)(OH$_2$)], 1d. Reaction at room temperature, 32% yield, dark yellow. ^{19}F NMR: δ −59.72 (s, *ortho*-CF_3, 6F), −62.84 (s, *para*-CF_3, 3F). ^{1}H NMR: δ 7.94 (s, $C_6H_2(CF_3)_3$, 2H), 7.61 (m, $C_{10}H_6$, 1H), 7.39 (m, $C_{10}H_6$, 3H), 6.92 (t, *J* 7.5, $C_{10}H_6$, 1H), 5.89 (d, *J* 7.0, $C_{10}H_6$, H^3, 1H), 3.24 (s, CH_3, 6H), 2.17 (s, H_2O, 2H). IR: 3622 w, 3548 m, 1619 m, 1560 m, 1357 s, 1216 w, 1190 s, 1111 s, 1082 s, 1032 w, 1019 w, 937 w, 915 m, 861 w, 852 w, 834 w, 818 w, 781 m, 772 m, 755 w, 694 m, 684 m, 636 m, 565 w, 468 m, 440 m, 396 w. Anal. Calcd for $C_{21}H_{16}F_9NOPd$: C, 43.81; H, 2.80; N, 2.78. Found: C, 44.07; H, 2.93; N, 2.75.

[Pd(bzpy)(Fmes)(OH$_2$)], 1e. Reaction at 40 °C, 17% yield, pale brown. ^{19}F NMR: δ −59.97 (br, *ortho*-CF_3, 6F), −62.96 (s, *para*-CF_3, 3F). ^{19}F NMR (−60 °C): δ −59.82 (s, *ortho*-CF_3, 3F), −60.4 (s, *ortho*-CF_3, 3F), −62.46 (s, *para*-CF_3, 3F). ^{1}H NMR: δ 8.61 (d, *J* 5.0, C_6H_4N, 1H), 7.86 (s, $C_6H_2(CF_3)_3$, 2H), 7.72 (td, *J* 6.0 and 1.5, C_6H_4N, 1H), 7.47 (d, *J* 7.5, C_6H_4, 1H), 7.22 (t, *J* 6.5, C_6H_4N, 1H), 6.97 (d, *J* 7.0, C_6H_4, 1H), 6.80 (td, *J* 7.0 and 1.5, C_6H_4, 1H), 6.60 (td, *J* 7.0 and 1.5, C_6H_4, 1H), 6,50 (dd, *J* 6.5 and 1.0, C_6H_4N, 1H), 4.40 (br, CH_2, 2H), 1.82 (s, H_2O, 2H). ^{1}H NMR (−60 °C): δ 8.63 (d, *J* 5.0, C_6H_4N, 1H), 7.98 (s, $C_6H_2(CF_3)_3$, 1H), 7.75 (t, *J* 7.5, C_6H_4N, 1H), 7.70 (s, $C_6H_2(CF_3)_3$, 1H), 7.50 (d, *J* 8.0, C_6H_4, 1H), 7.26 (hidden by the $CHCl_3$ signal, C_6H_4N, 1H), 7.00 (d, *J* 7.0, C_6H_4, 1H), 6.84 (t, *J* 7.0, C_6H_4, 1H), 6,62 (m, C_6H_4 and C_6H_4N, 2H), 4.79 (d, *J* 14.0, CH_2, 1H), 3.97 (d, *J* 13.0, CH_2, 1H), 2.48 (s, H_2O, 2H). IR: 3637 m, 3518 m, 1610 s, 1578 s, 1566 s, 1339 s, 1191 s, 1095 s, 1082 m, 102 w, 966 m, 946 w, 924 w, 913 m, 890 m, 871 w, 851 m, 832 m, 693 m, 684 m, 667 m, 650 w, 622 m, 577 m, 508 w, 468 m, 447 m, 373 w. Anal. Calcd for $C_{21}H_{14}F_9NOPd$: C, 43.96; H, 2.46; N, 2.44. Found: C, 43.83; H, 2.60; N, 2.62.

[Pd(dmba)(Fmes)(CN^{t}Bu)], 2a. CN^{t}Bu (57 μL, 0.5 mmol) was added to a solution of **1a** (0.270 g, 0.5 mmol) in toluene (25 mL). The solution was stirred at room temperature for 1 h. The solvent was removed in a vacuum, *n*-hexane (10 mL) was added to the oily residue, and the volatiles were removed in a vacuum again. This was repeated twice, and the solid residue was recrystallized from CH_2Cl_2/hexane, yielding 0.223 g (74%) of **2a** as a white microcrystalline solid. ^{19}F NMR: δ −61.40 (s, *ortho*-CF_3, 6F), −62.68 (s, *para*-CF_3, 3F). ^{1}H NMR: δ 7.86 (s, $C_6H_2(CF_3)_3$, 2H), 6.95 (d, *J* 7.0, C_6H_4 of dmba, 1H), 6.86 (td, *J* 7.0 and 1.0, C_6H_4 of dmba, 1H), 6.67 (td, *J* 7.5 and 1.0, C_6H_4 of dmba, 1H), 5.92 (dd, *J* 7.5 and 1, H^3 of dmba, 1H), 3.89 (s, CH_2 of dmba, 2H), 2.83 (s, CH_3 of dmba, 6H), 1.33 (s, CNC_4H_9, 9H). IR (CH_2Cl_2): 2188. IR: 2186 vs, 1620 s, 1581 m, 1560 m, 1407 w, 1300 s, 1278 m, 1186 m, 1128 m, 1081 w, 1025 m, 991 m, 972 w, 937 w, 928 w, 912 s, 873 w, 853 s, 833 m, 755 w, 748 m, 694 m, 685 s, 667 w, 620 w, 581 w, 525 w, 470 w, 439 w. Anal. Calcd for $C_{23}H_{23}F_9N_2Pd$: C, 45.74; H, 3.83; N, 4.63. Found: C, 45.43; H, 3.74; N, 4.70.

[Pd(dmba)(Fmes)(CO)], 3a. Carbon monoxide was bubbled through a solution of **1a** (0.540 g, 1.0 mmol) in toluene (40 mL), while the solution was stirred, at room temperature for 30 min. The solvent was removed in a vacuum, and the solid residue was washed with *n*-hexane (3 × 5 mL), yielding an off-white solid, which was recrystallized from CH_2Cl_2/hexane, yielding 0.461 g (84%) of **3a** as an off-white microcrystalline solid. ^{19}F NMR: δ −61.43 (s, *ortho*-CF_3, 6F), −62.95 (s, *para*-CF_3, 3F). ^{1}H NMR: δ 7.95 (s, $C_6H_2(CF_3)_3$, 2H), 7.00 (d, *J* 7.5, C_6H_4 of dmba, 1H), 6.93 (t, *J* 7.5, C_6H_4 of dmba, 1H), 6.71 (t, *J* 7.0, C_6H_4 of dmba, 1H), 5.85 (d, *J* 7.5, H^3 of dmba, 1H), 3.99 (s, CH_2 of dmba, 2H), 2.96 (s, CH_3 of dmba, 6H). IR (CH_2Cl_2): 2105. IR: 2111 vs, 2061 w, 1623 vw, 1585 m, 1574 m, 1407 m, 1369 w, 1300 s, 1194 s, 1156 w, 1119 s, 1049 m, 1025 m, 992 w, 939 w, 915 s, 873 m, 854 s, 835 s, 747 s, 694 m, 684 s, 667 w, 580 w, 518 w, 469 w, 451 w, 438 w, 396 w, 334 w, 278 w. Anal. Calcd for $C_{19}H_{14}F_9NOPd$: C, 41.51; H, 2.57; N, 2.55. Found: C, 41.58; H, 2.78; N, 2.52.

[Pd(dmba)(Fmes)(NH$_3$)], 4a. Ammonia was bubbled through a solution of **1a** (0.162 g, 0.3 mmol) in toluene (15 mL), while the solution was stirred at room temperature for 15 min. The solvent was removed in a vacuum, and the oily residue was extracted with CH_2Cl_2 (30 mL) and filtered on dry Celite. *n*-Hexane (ca. 30 mL) was added to the filtrate, which was concentrated and cooled to −20 °C. The microcrystalline solid obtained was decanted, washed with hexane (3 × 5 mL), and dried in a vacuum, yielding 0.117 g (72%) of **4a** as a white microcrystalline solid. ^{19}F NMR: δ −60.65 (s, *ortho*-CF_3, 6F), −62.79 (s, *para*-CF_3, 3F). ^{1}H NMR: δ 7.86 (s, $C_6H_2(CF_3)_3$, 2H), 6.92 (d, *J* 6.0, C_6H_4 of dmba, 1H), 6.84 (td, *J* 7.5 and 1.0, C_6H_4 of dmba, 1H), 6.63 (td, *J* 7.5 and 1.0, C_6H_4 of dmba, 1H), 5.90 (dd, *J* 7.5 and 1.0, H^3 of dmba, 1H), 3.87 (s, CH_2 of dmba, 2H), 2.67 (s, CH_3 of dmba, 6H), 1.39 (br, NH_3, 3H). IR: 3383 w, 3294 m, 1617 s, 1580 m, 1563 m, 1402 w, 1298 vs, 1282 vs, 1233 m, 1213 m, 1181 s, 1132 vs, 1079 m, 1025 m, 996 m, 974 vw, 909 m, 868 w, 852 m, 832 m, 746 s, 694 m, 684 m, 666 w, 622 w, 579 w, 508 w, 470 w, 438 w. Anal. Calcd for $C_{18}H_{17}F_9N_2Pd$: C, 40.13; H, 3.18; N, 5.20. Found: C, 40.32; H, 3.26; N, 4.98.

[Pd(dmba)(Fmes)(PPh$_3$)], 5a. PPh_3 (0.052 g, 0.2 mmol) was added to a solution of **1a** (0.108 g, 0.2 mmol) in toluene (10 mL). The solution was stirred at room temperature for 16 h, during which time a white solid had precipitated. The solid was filtered off, washed with *n*-hexane (3 × 5 mL), and recrystallized from CH_2Cl_2/hexane, yielding 0.095 g (60%) of **5a** as white crystals. ^{19}F NMR: δ −59.27 (d, J_{PF} 4.0, *ortho*-CF_3, 6F), −62.79 (s, *para*-CF_3, 3F). ^{31}P{^{1}H} NMR: δ 16.7 (sept). ^{1}H NMR: δ 7.53 (s, $C_6H_2(CF_3)_3$, 2H), 7.3 (br, C_6H_5, 15H), 7.02 (dt, *J* 7.0 and 1.0, $C_6H_4CH_2NMe_2$, 1H), 6.91 (t, *J* 7.0, C_6H_4-CH_2NMe_2, 1H), 6.69 (tt, *J* 7.0 and 2.0, $C_6H_4CH_2NMe_2$, 1H), 6.01 (m, H^3, $C_6H_4CH_2NMe_2$, 1H), 3.97 (s, $C_6H_4CH_2NMe_2$, 2H), 2.29 (s, CH_3, 6H). ^{1}H NMR (−60 °C): δ 7.69 (t, *J* 8.0, C_6H_5, 4H), 7.52 (m, 2H of $C_6H_2(CF_3)_3$ and 6H of C_6H_5), 6.99 (m, 2H of $C_6H_4CH_2NMe_2$ and 1H of C_6H_5), 6.76 (m, 1H of $C_6H_4CH_2$-NMe_2 and 2H of C_6H_5), 6.44 (t, *J* 8.0, C_6H_5, 2H), 6.01 (t, *J* 3.0, H^3, dmba, 1H), 4.00 (s, $C_6H_4CH_2NMe_2$, 2H), 2.28 (s, CH_3, 6H). IR: 1619 m, 1582 m, 1566 w, 1404 w, 1302 s, 1279 m, 1186 s, 1156 w, 1141 w, 1128 w, 1097 w, 1078 m, 1021 m, 974 w, 915 s, 865 w, 847 m, 830 m, 790 w, 752 w, 699 w, 684 m, 619 w, 561 m, 527 m, 511 w, 494 w, 466 w, 449 w, 435 s, 396 w, 310 m. Anal. Calcd for $C_{36}H_{29}F_9NPPd$: C, 55.15; H, 3.73; N, 1.79. Found: C, 55.07; H, 3.82; N, 1.80.

[Pd(*p*-tolpy)(Fmes)(PPh$_3$)], 5b. PPh_3 (0.052 g, 0.2 mmol) was added to a solution of **1b** (0.115 g, 0.2 mmol) in toluene (10 mL). The solution was stirred at room temperature for 15 min. The solvent was removed in a vacuum, and the solid was dissolved in 10 mL of Et_2O. After 3 h stirring at room temperature a white solid had precipitated spontaneously. The solvent was decanted, and the solid was washed with Et_2O (3 × 5 mL) and recrystallized from CH_2Cl_2/hexane, yielding 0.113 g (69%) of **5b** as white crystals. ^{19}F NMR: δ −59.80 (d, J_{PF} 4.5, *ortho*-CF_3, 6F), −62.76 (s, *para*-CF_3, 3F). ^{31}P{^{1}H} NMR: δ 21.1 (sept). ^{1}H NMR: δ 7.93 (br, C_6H_5, 4H), 7.80 (m, *p*-tolpy, 2H), 7.67 (t, *J* 8.0, *p*-tolpy, 1H), 7.53 (m, *p*-tolpy, 1H), 7.51 (s, $C_6H_2(CF_3)_3$, 2H), 7.4 (br, C_6H_5, 6H), 7.0 (br, C_6H_5, 3H), 6.86 (d, *J* 8.0, *p*-tolpy, 1H), 6.55 (t, *J* 7.0, *p*-tolpy, 1H), 6.5 (br, C_6H_5, 2H), 6.03 (d, *J* 6.0, H^3, 1H), 2.04 (s, CH_3 of *p*-tolpy, 3H). ^{1}H NMR (−60 °C): δ 7.94 (t, *J* 8.5, C_6H_5, 4H), 7.84 (m, *p*-tolpy, 2H), 7.72 (t, *J* 8.0, *p*-tolpy, 1H), 7.57 (d, *J* 7.5, *p*-tolpy, 1H), 7.48 (m, 2H of $C_6H_2(CF_3)_3$ and 2H of C_6H_5), 7.39 (m, C_6H_5, 4H), 7.02 (t, *J* 7.0, C_6H_5, 1H), 6.88 (d, *J* 8.0, *p*-tolpy, 1H), 6.81 (t, *J* 7.0, C_6H_5, 2H), 6.64 (t, *J* 7.0, *p*-tolpy, 1H), 6.40 (t, *J* 9.0, C_6H_5, 2H), 6.03 (d, *J* 6.0, H^3 of *p*-tolpy, 1H), 2.03 (s, CH_3 of *p*-tolpy, 3H). IR: 1620 m, 1608 m, 1591 w, 1569 m, 1371 s, 1297 m, 1280 s, 1189 m, 1114 s, 1096 w, 1076 w, 1023 m, 913 s, 852 m, 830 w, 814 w, 775 m, 752 m, 746 w, 684 m, 667 w, 528 m,

506 m, 490 m, 466 w, 441 w. Anal. Calcd for $C_{39}H_{27}F_9NPPd$: C, 57.26; H, 3.33; N, 1.71. Found: C, 57.14; H, 3.51; N, 1.95.

[Pd(dmba)(Fmes)(lut)], 6a. 2,6-Lutidine (24 μL, 0.2 mmol) was added to a solution of **1a** (0.108 g, 0.2 mmol) in toluene (10 mL). The solution was stirred at room temperature for 15 h. Workup as for **2a** yielded 0.085 g (68%) of **6a** as a white microcrystalline solid. ^{19}F NMR: δ −59.48 (br, *ortho*-CF_3, 6F), −62.89 (s, *para*-CF_3, 3F). ^{19}F NMR (−60 °C): δ −58.13 (s, *ortho*-CF_3, 6F), −62.49 (s, *para*-CF_3, 3F). ^{1}H NMR (−60 °C): δ 7.73 (s, $C_6H_2(CF_3)_3$, 2H), 7.51 (t, *J* 7.5, $NC_5H_3(CH_3)_2$, 1H), 7.03 (d, *J* 7.5, $NC_5H_3(CH_3)_2$, 2H), 6.9 (m, C_6H_4 of dmba, 2H), 6.68 (t, *J* 7.5, C_6H_4 of dmba, 1H), 6.06 (d, *J* 7.5, C_6H_4, H^3 of dmba, 1H), 3.99 (s, CH_2 of dmba, 2H), 3.02 (s, CH_3 of dmba, 6H), 2.35 (s, CH_3, $NC_5H_3(CH_3)_2$, 6H). These NMR spectra show also signals of **1a** and free 2,6-lutidine (see Discussion). IR: 1619 s, 1584 s, 1565 m, 1403 m, 1369 s, 1355 w, 1295 s, 1187 s, 1072 s, 1048 w, 1018 m, 988 m, 971 w, 920 s, 863 w, 853 w, 843 m, 828 m, 781 m, 754 w, 692 w, 683 m, 667 w, 567 w, 520 w, 462 w, 440 w, 395 w, 326 w. Anal. Calcd for $C_{25}H_{23}F_9N_2Pd$: C, 47.75; H, 3.69; N, 4.45. Found: C, 47.70; H, 3.77; N, 4.25.

[Pd(dmba-*C*)(Fmes)(bipy)], 7a. 2,2′-Bipyridyl (0.031 g, 0.2 mmol) was added to a solution of **1a** (0.108 g, 0.2 mmol) in toluene (10 mL). The solution was stirred at room temperature for 20 h. Workup as for **2a**, yielded 0.065 g (48%) of **7a** as a pale yellow microcrystalline solid. ^{19}F NMR: −59.31 (s, *ortho*-CF_3, 6F), −62.92 (s, *para*-CF_3, 3F). ^{19}F NMR (CD_2Cl_2, −95 °C): δ −59.01 (s, *ortho*-CF_3, 3F), −59.85 (s, *ortho*-CF_3, 3F), −62.09 (s, *para*-CF_3, 3F). These NMR spectra show also signals of **1a** (see Discussion). ^{1}H NMR: δ 8.20 (br, $N_2C_{10}H_8C_5H_4N$, 2H), 8.10 (br, C_5H_4N, 2H), 7.93 (t, *J* 7,5, C_5H_4N, 2H), 7.84 (s, $C_6H_2(CF_3)_3$, 2H), 7.30 (m, C_5H_4N, 2H), 7.20 (br, C_6H_4 of dmba, 1H), 6.92 (t, *J* 7.5, C_6H_4 of dmba, 1H), 6.8 (br, C_6H_4 of dmba, 1H), 6.71 (st, *J* 7.5, C_6H_4 of dmba, 1H), 3.86 (s, CH_2 of dmba, 2H), 2.21 (br, CH_3 of dmba, 6H). ^{1}H NMR (CD_2Cl_2, −95 °C): δ 8.13 (m, $N_2C_{10}H_8$, 2H), 8.00 (m, $N_2C_{10}H_8$, 2H), 7.96 (s, $C_6H_2(CF_3)_3$, 1H), 7.75 (s, $C_6H_2(CF_3)_3$, 1H), 7.71 (d, *J* 5.0, $N_2C_{10}H_8$, 1H), 7.57 (d, *J* 5.0, $N_2C_{10}H_8$, 1H), 7.28 (m, 2H of $N_2C_{10}H_8$ and 1H of C_6H_4 of dmba), 7.01 (d, *J* 7.5, C_6H_4 of dmba, 1H), 6.85 (t, *J* 7.5, C_6H_4 of dmba, 1H), 6.61 (t, *J* 7.5, C_6H_4 of dmba, 1H), 4.04 (d, *J* 15.0, CH_2 of dmba, 1H), 3.42 (d, *J* 15.0, CH_2 of dmba, 1H), 2.06 (s, CH_3 of dmba, 6H). These NMR spectra show also signals of **1a** and free 2,2′-bipyridyl (see Discussion). IR: 1617 s, 1603 s, 1570 m, 1294 vs, 1280 vs, 1260 vs, 1188 vs, 1127 vs, 1075 m, 1022 s, 916 s, 852 m, 832 m, 759 s, 747 s, 693 w, 685 w, 666 w, 567 w, 465 w, 440 w, 426 w. Anal. Calcd for $C_{28}H_{22}F_9N_3Pd$: C, 49.61; H, 3.27; N, 6.19. Found: C, 49.65; H, 3.40; N, 5.94.

X-ray Diffraction Study of 1a. Plate-shaped crystals were grown by slow diffusion of concentrated dichloromethane solutions of the complex into hexane at −20 °C. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo Kα radiation (λ = 0.71073 Å).[35] Intensities were integrated[36] from several series of exposures, each exposure covering 0.3° in ω, and the total data set being a hemisphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[37] The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 5).[38] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms H(20A) and H(20B) were located in the electron density difference map, assigned isotropic displacement parameters and refined without positional constraints. All other hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded smoothly to give residuals shown in Table 5. Complex neutral-atom scattering factors were used.[39]

Table 5. Crystal Data and Structure Refinement for 1a

empirical formula	$C_{18}H_{16}F_9NOPd$
fw	539.72
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	9.286(1)
b (Å)	17.095(3)
c (Å)	12.895(2)
β (deg)	100.24(1)
V (Å^3)	2014.2(5)
Z	4
D_{calc} (g cm^{-3})	1.780
abs coeff (mm^{-1})	1.011
F(000)	1064
cryst size (mm)	0.30 × 0.10 × 0.05
temperature (K)	173(2)
θ range for data collection	2.00 to 27.48°
wavelength (Å)	0.71073 (Mo Kα)
index ranges	$-6 \le h \le 12$, $-22 \le k \le 22$, $-16 \le l \le 16$
no. of reflns collected	12 520
no. of ind reflns	4598 (R_{int} = 0.0302)
no. of obsd reflns [$I > 2\sigma(I)$]	3604
abs corr	SADABS
max. transmn	0.962
min. transmn	0.846
no. of data/restraints/params	4598/0/282
goodness-of-fit on F^2	0.971
final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0292, wR_2 = 0.0642
R indices (all data)	R_1 = 0.0456, wR_2 = 0.0693
extinction coeff	0.0011(2)
largest diff peak and hole (e Å^{-3})	0.839 and −0.568

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Supporting Information Available: Atomic positional parameters for the freely refined atoms, bond lengths and interbond angles, atomic displacement parameters, and hydrogen atom parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) *SMART* diffractometer control software; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.

(36) *SAINT* integration software; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

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

(38) *SHELXTL program system version 5.1*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.

(39) *International Tables for Crystallography*; Kluwer: Dordrecht, 1992; Vol. C.