ChemPubSoc Europe

DOI: 10.1002/chem.201501984

CHEMISTRY A European Journal Full Paper

Coordination Chemistry |*Hot Paper*|

# Coordination Properties of Perfluoroethyl- and Perfluorophenyl-Substituted Phosphonous acids, $R^fP(OH)_2$

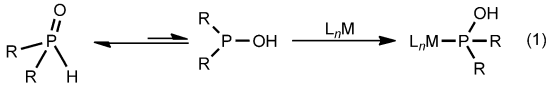
Nadine Allefeld,[a] Boris Kurscheid,[a] Beate Neumann,[a] Hans-Georg Stammler,[a] Nikolai Ignat'ev,[b] and Berthold Hoge*[a]

**Abstract:** Phosphinic acids, $R^fP(O)(OH)H$ ($R^f = CF_3$, $C_2F_5$, $C_6F_5$), turned out to be excellent preligands for the coordination of phosphonous acids, $R^fP(OH)_2$. Addition of $C_2F_5P(O)(OH)H$ to solid $PtCl_2$ under different reaction conditions allows the isolation and full characterization of the mononuclear complexes $[ClPt\{P(C_2F_5)(OH)O\}\{P(C_2F_5)(OH)_2\}_2]$ and $[Pt\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}]$ containing hydrogen-bridged $[R^fP(OH)O]^-$ and $R^fP(OH)_2$ units. Further deprotonation of $[Pt\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$ leads to the formation of the dianionic platinate, $[Pt\{P(C_2F_5)(OH)O\}_4]^{2-}$, revealing four intramolecular hydrogen bridges. With $PdCl_2$ the dinuclear complex $[Pd_2(\mu\text{-}Cl)_2\{[P(C_2F_5)(OH)O]_2H\}_2]$ was isolated and characterized. The $Cl^-$ free complex $[Pd\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$ was also prepared and deprotonated to the dianionic palladate, $[Pd\{P(C_2F_5)(OH)O\}_4]^{2-}$. Both compounds were characterized by NMR spectroscopy, IR spectroscopy, and X-ray analyses. In addition, the $C_6F_5$ derivatives $[ClPt\{P(C_6F_5)(OH)O\}\{P(C_6F_5)(OH)_2\}_2]$ and $[Pd_2(\mu\text{-}Cl)_2\{[P(C_6F_5)(OH)O]_2H\}_2]$ as well as the $CF_3$ derivative $[Pd_2(\mu\text{-}Cl)_2\{[P(CF_3)(OH)O]_2H\}_2]$ were synthesized and fully characterized. Phosphonous acid complexes are inert towards air and moisture and can be stored for several months without decomposition. The catalytic activity of the palladium complexes in the Suzuki cross-coupling reaction between 1-bromo-3-fluorobenzene and phenyl boronic acid was demonstrated.

## Introduction

A number of chemical reactions in the laboratory as well as in industry are based upon the use of catalysts. The search for catalysts well suited for a planned transformation is usually not trivial. Apart from a high catalytic activity, the catalyst has to be selective, easy to handle, and resistant towards air and moisture. Commonly used transition-metal complexes of high catalytic activity often bear phosphorus-based ligands, for example, alkyl- or aryl-substituted phosphanes. A serious drawback, however, is that these compounds are in general sensitive towards oxygen and moisture. Another popular approach is the employment of secondary phosphane oxides (SPOs), $R_2P(O)H$, as preligands for the synthesis of phosphinous acid complexes.[1,2] Diorganylphosphane oxides, $R_2P(O)H$, are in a tautomeric equilibrium with the corresponding phosphinous acid, $R_2POH$. For electron-donating alkyl or aryl substituents, the equilibrium is in general completely shifted to the pentavalent phosphane oxide. Chatt and Heaton demonstrated in 1968 that by coordination to suitable metals the phosphinous acid can be trapped and removed from the equilibrium.[3] A whole variety of such complexes is known in the literature and was successfully tested as catalysts for, for example, cross-coupling reactions.[1,2]

Formal substitution of one organyl group by a hydroxyl group leads to the formation of a water-stable phosphinic acid. Likewise, a tautomerization into the corresponding phosphonous acid can be formulated. The equilibrium in Equation (1) is, in general, completely shifted to the phosphinic acid, for electron-donating as well as for electron-withdrawing groups. Therefore there are no reports on a free phosphonous acid in the literature.




R = $CF_3$, $C_2F_5$

The attempted coordination of phosphinic acids to a suitable metal leads to the formation of phosphonous acid complexes. The coordinating properties of phosphonous acids are not well investigated and only a small number of complexes thereof are described.[4] The topic of this work is the study of the ligating properties of phosphonous acids with electron-withdrawing groups, especially the pentafluoroethyl group, towards the catalytically relevant metals palladium and platinum. The employment of the new phosphonous acid complexes of palladium as catalysts in Suzuki-type reactions will be discussed.

[a] *Dr. N. Allefeld, Dr. B. Kurscheid, B. Neumann, Dr. H.-G. Stammler, Prof. Dr. B. Hoge*
*Centrum für Molekulare Materialien*
*Fakultät für Chemie, Anorganische Chemie II*
*Universität Bielefeld, Universitätsstrasse 25*
*33619 Bielefeld (Germany)*
*E-mail: b.hoge@uni-bielefeld.de*

[b] *Dr. N. Ignat'ev*
*PM-APR-FT, Merck KGaA*
*Frankfurter Strasse 250, 64293 Darmstadt (Germany)*

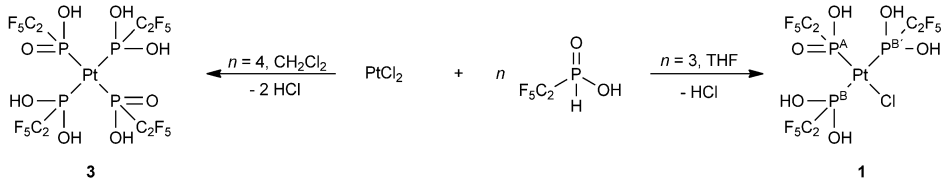
## Results and Discussion

### Platinum complexes

A slurry of platinum(II) chloride in THF smoothly reacts with 3.5 equivalents of pentafluoroethylphosphinic acid affording $[ClPt\{P(C_2F_5)(OH)O\}\{P(C_2F_5)(OH)_2\}_2]$, **1** (Scheme 1). After filtration and removal of all volatile compounds in vacuo, the product is obtained as a viscous oil. Its $^{31}P$ NMR spectrum shows the existence of two chemically inequivalent phosphorus atoms. The resonance for the phosphorus atom $P^A$ at $\delta = 61.3$ ppm reveals platinum satellites with a $^1J(Pt,P^A)$ coupling constant of 4277 Hz, characteristic for a phosphorus-based ligand in a *trans* position to a chloro ligand. Furthermore, a triplet of triplets splitting due to the $^2J(P,F)$ coupling of 99 Hz and the $^2J(P^A,P^B)$ coupling of 28 Hz, respectively, is observed. The resonance for the phosphorus atom $P^B$ at $\delta = 94.7$ ppm exhibits platinum satellites with a significantly lower $^1J(Pt,P^B)$ coupling constant of 3172 Hz. In square-planar platinum complexes, such a value is characteristic of a phosphane ligand in *trans* position to a second phosphane ligand. Because of a long-range $^4J(P,F)$ coupling of a phosphorus atom $P^B$ to the $CF_2$ group of the phosphonous acid in the *trans* position, the phosphorus atoms are magnetically inequivalent resulting in a high-order multiplet. By $^{19}F$-decoupling of the $^{31}P$ NMR spectrum, the spin system can be simplified and the resonance at $\delta = 94.7$ ppm reveals a doublet splitting with a $^2J(P^AP^B)$ coupling constant of 27 Hz. Consistently, the $^{195}Pt$ NMR spectrum is characterized by a doublet of triplets at $\delta = -4694.1$ ppm with a $^1J(Pt,P^A)$ coupling constant of 4276 Hz and a $^1J(Pt,P^B)$ coupling constant of 3177 Hz. Single crystals of **1**, suitable for an X-ray structure determination, were grown from THF solution. Complex **1** crystallizes with one solvent molecule in the triclinic space group $P\bar{1}$ (no. 2). The molecular structure is shown in Figure 1. Formally, compound **1** features two phosphonous acids and one phosphonito unit, which should be distinguishable from each other based on the P–O bond lengths. A differentiation is difficult in solution because of fast proton exchange. In the solid state, however, the phosphonous acids at P2 and P3 exhibit two longer P–O bonds of about 155.7 pm in accordance with single bonds. The ligand at P1 exhibits one short P1–O1 bond of 152.1(2) pm and one long P1–O2 bond of 158.8(2) pm due to the double and single bond of a phosphonito unit.

The short O3···O1 distance of 254.1(1) pm as well as the O4···O5 distance of 286.3(3) pm are characteristic for a hydrogen bridge between a phosphonous acid and a phosphonito unit.[5] The solvent THF molecule is coordinated by a hydrogen bridge resulting in a short O7···O4 separation of 242.6(1) pm. All hydrogen atoms were refined isotropically and the distance O7–H7 of 104(5) pm indicates a protonation of THF by **1** at least in solid state. The oxygen atoms O1 and O6 are coordinated to an adjacent molecule through intermolecular hydrogen bridges featuring O1···O6(a) and O1(a)···O6 distances of 256.5(3) pm, respectively, building a dimer.

Similarly, pentafluorophenylphosphinic acid, $(C_6F_5)P(O)(OH)H$, functions as a precursor for the corresponding phosphonous acid as a ligand in transition-metal complexes. Thus treatment of a slurry of $PtCl_2$ in diethyl ether with $(C_6F_5)P(O)(OH)H$ in a molar ratio of 1:3 at room temperature affords the mononuclear complex $[ClPt\{P(C_6F_5)(OH)O\}\{P(C_6F_5)(OH)_2\}_2]$ (**2**) as a light-yellow solid in 76% yield. The $^{31}P$ NMR spectrum of **2** exhibits two resonances at $\delta = 49.3$ and 97.1 ppm for two chemically inequivalent phosphorus atoms $P^A$ and $P^B$, respectively. The $^1J(Pt,P)$ coupling constants of 4606 Hz for the phosphorus atom $P^A$ *trans* to a chloro ligand and 3223 Hz for the phosphorus atoms $P^B$ *cis* to the chloro ligand are in agreement




**Scheme 1.** Synthesis of the platinum complexes **1** and **3**.

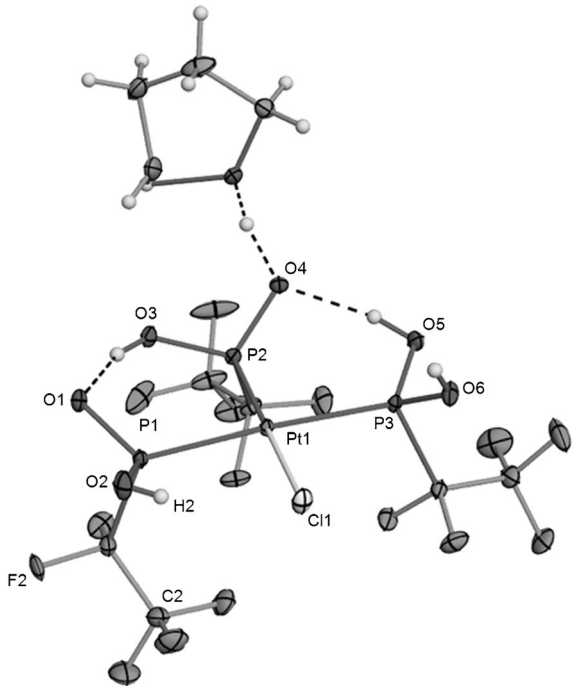



**Figure 1.** Molecular structure of $[H\text{-}THF]^+[ClPt\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}]^-$ (**1**); 50% probability amplitude displacement ellipsoids are shown; selected bond lengths [pm] and angles [°]: P1–Pt1 229.53(6), P1–O1 152.1(2), P1–O2 158.8(2), P2–Pt1 221.95(6), P2–O3 155.9(2), P2–O4 154.0(2), P3–Pt1 231.13(6), P3–O5 157.2(2), P3–O6 155.6(2), Pt1–Cl1 235.86(6), O1-P1-O2 107.5(1), O3-P2-O4 108.5(1), O5-P3-O6 107.2(1).

with the values obtained for complex **1**. Accordingly, the $^{195}$Pt NMR spectrum reveals a doublet of triplets at $\delta = -4692.2$ ppm.

Single crystals of **2** were grown from diethyl ether. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with two (unprotonated) solvent molecules $Et_2O$ per formula unit linked by hydrogen bridges. The molecular structure in the solid state (Figure 2) reveals a square-planar platinum center coordinated by two phosphonous acids, one phosphonito unit and a chloro ligand. The P–O bond lengths vary between 155.6 and 156.6 pm, making a differentiation between phosphonous acid and phosphonito unit impossible as well as the distances inside the intramolecular hydrogen bridge of H2–O2 113(4) pm and H2–O3 131(4) pm.

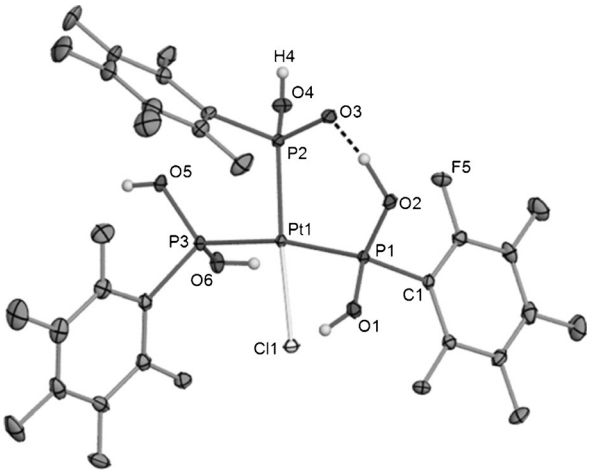



**Figure 2.** Molecular structure of $[ClPt\{P(C_6F_5)(OH)O\}\{P(C_6F_5)(OH)_2\}_2]$, **2**·2($Et_2O$); 50% probability amplitude displacement ellipsoids are shown, solvent molecules omitted for clarity; selected bond lengths [pm] and angles [°]: P1–Pt1 228.74(6), P1–O1 156.3(2), P1–O2 155.8(2), P2–Pt1 221.37(6), P2–O3 155.6(2), P2–O4 156.3(2), P3–Pt1 229.82(6), P3–O5 156.6(2), P3–O6 156.1(2), O1-P1-O2 106.04(9), O3-P2-O4 108.73(9), O5-P3-O6 107.4(1); disorder of solvent molecule on two positions.

As shown in Scheme 1, the treatment of $(C_2F_5)P(O)(OH)H$ with platinum dichloride in THF selectively yields the tris-substituted complex **1** in 58% yield, whereas in dichloromethane the $Cl^-$ free complex $[Pt\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$, **3**, is obtained in 70% yield. Two equivalents of hydrogen chloride are eliminated under the formation of two phosphonous acid phosphonito units, $[P(C_2F_5)(OH)O\cdots H\cdots O(OH)(C_2F_5)P]^-$. Complex **3** is also prepared from $[Pt(acac)_2]$ (acac = acetylacetonato). Both acetylacetonato ligands are protonated and replaced by two $[P(C_2F_5)(OH)O\cdots H\cdots O(OH)(C_2F_5)P]^-$ units. The proton NMR spectrum reveals one resonance at $\delta = 13.7$ ppm because of the rapid exchange of the hydrogen atoms. The $^{31}$P NMR spectrum is characterized by one resonance at $\delta = 93.0$ ppm with platinum satellites ($^1J$(Pt,P) = 3048 Hz). Because of the long range coupling of the phosphorus atoms to the $CF_2$ groups of the adjacent ligands, the phosphorus atoms are magnetically inequivalent. This is reflected in a multiplet of higher order in the $^{31}$P NMR spectrum. The formation of a corresponding pentafluorophenyl derivative under similar reaction conditions was not observed. Recrystallization of the $C_2F_5$ derivative from diethyl ether solution yielded colorless crystals. Complex **3** lies at a center of inversion and crystallizes in the monoclinic space group $C2/c$ (No. 15) with two solvent molecules per formula unit. The molecular structure reveals short O1···O3# and O1#···O3 separations of 245.8(4) pm, indicating an intramolecular hydrogen bridge of a quasichelating unit. The platinum center deviates slightly from an ideal square-planar geometry (Figure 3).

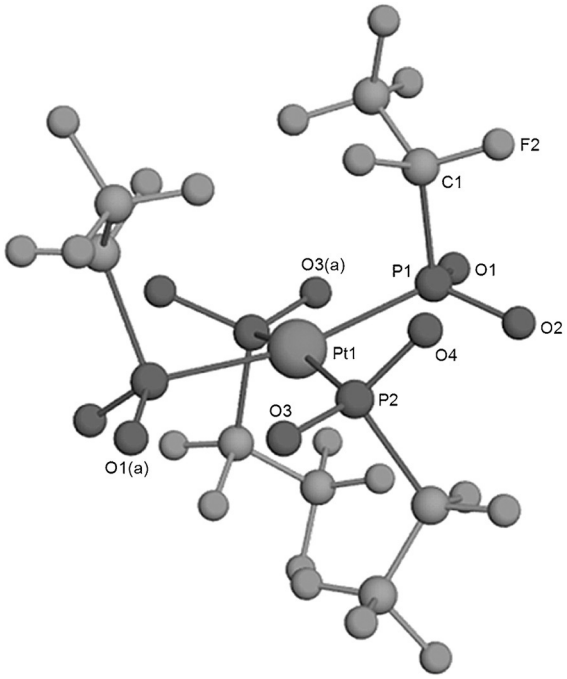
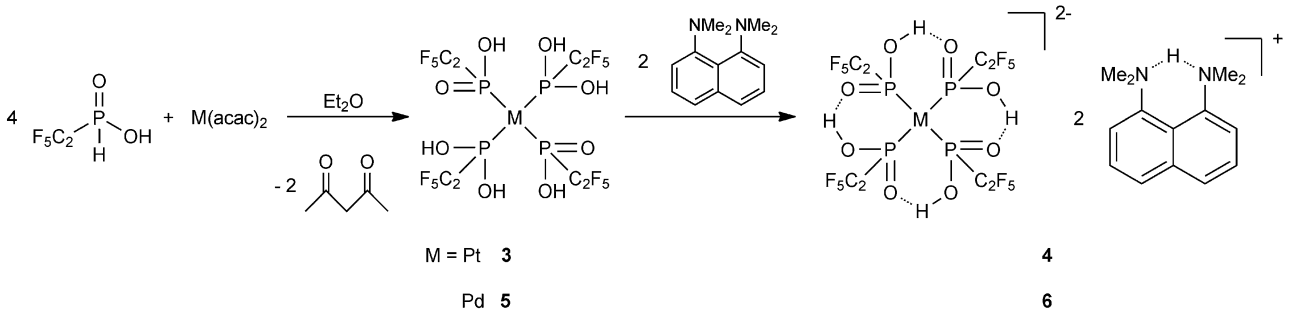



**Figure 3.** Molecular structure of $[Pt\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$, **3**·2$Et_2O$; H atoms and solvent molecules omitted for clarity; selected bond lengths [pm] and angles [°]: P1–Pt1 231.0(1), P1–O1 154.9(3), P1–O2 153.5(3), P2–Pt1 231.86(8), P2–O3 153.3(3), P2–O4 155.5(3), O1-P1-O2 107.8(2), O3-P2-O4 110.3(2); disorder of $C_2F_5$ groups on two positions.

The treatment of platinum(II) acetylacetonate, $[Pt(acac)_2]$ with bis(pentafluoroethyl)phosphinous acid, $(C_2F_5)_2POH$, gives rise to the selective substitution of only one acetylacetonato ligand by a phosphinous acid phosphinito quasichelating unit.[6] An explanation for this different reactivity could be the decreased steric demand of the OH group compared with that of the pentafluoroethyl group. The O···O distance of the quasichelating unit $[P(C_2F_5)_2O\cdots H\cdots O(C_2F_5)_2P]^-$ of 242.02(3) pm is comparable to the O1···O3 distance of complex **3**.[6]

The pronounced tendency of the complexes **1, 2**, and **3** to coordinate solvent molecules through strong hydrogen bridges reflects their high acidity. Deprotonation leads to the formation of four intramolecular hydrogen bridges (Scheme 2). The addition of two equivalents of 1,8-bis(dimethylamino)-naphthalene to a freshly prepared solution of $[Pt\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$, **3**, in diethyl ether results in the precipitation of a colorless solid. The $^1$H NMR spectrum ex-




**Scheme 2.** Synthesis of complexes **3** and **5**, as well as of the metallates **4** and **6**.

**Table 1.** $^{1}H$, $^{31}P$, and $^{195}Pt$ NMR spectroscopic data of **1**, **2**, **3**, and **4**.

| | $\delta(^{1}H)$ | $\delta(^{31}P)$ [ppm] | $\delta(^{195}Pt)$ | $^{1}J(Pt,P)$ [Hz] |
|---|---|---|---|---|
| $[ClPt\{P(C_2F_5)(OH)O\}\{P(C_2F_5)(OH)_2\}_2]$, **1**[a] | 11.9 | 61.3 ($P^A$)<br>94.7 ($P^B$) | −4694.1 | 4277<br>3172 |
| $[ClPt\{P(C_6F_5)(OH)O\}\{P(C_6F_5)(OH)_2\}_2]$, **2**[b] | 11.6 | 49.3 ($P^A$)<br>97.1 ($P^B$) | −4692.2 | 4606<br>3223 |
| $[Pt\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$, **3**[c] | 13.7 | 93.0 | – | 3048 |
| $2[C_{14}H_{19}N_2]^+[Pt\{P(C_2F_5)(OH)O\}_4]^{2-}$, **4**[d] | 16.5 | 85.9 | −5191.1 | 2751 |

[a] [D]Chloroform. [b] $Et_2O$. [c] [$D_8$]THF. [d] [$D_3$]Acetonitrile.

hibits two signals in the ratio of 2:1 for acidic protons at $\delta =$ 16.5 ($[Pt\{P(C_2F_5)(OH)O\}_4]^{2-}$) and 18.7 ppm for protonated 1,8-bis(dimethylamino)naphthalene. The NMR spectroscopic data of **4** show significant deviations from the corresponding data of the neutral complex **3** (Table 1).

The treatment of palladium(II) acetylacetonate, $[Pd(acac)_2]$, with four equivalents of $(C_2F_5)P(O)(OH)H$ smoothly affords $[Pd\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$ (**5**) as a colorless oil because of solvent impurities. The $^{31}P$ NMR spectrum of the compound is characterized by one complex multiplet ($\delta(^{31}P) = 80.0$ ppm). The $^{1}H$ NMR spectrum shows one signal at $\delta = 13.4$ ppm. The $^{19}F$ NMR spectrum reveals two sets of signals at $\delta = -121.9$ ($CF_2$) and −79.7 ppm ($CF_3$) for the $C_2F_5$ unit. $[Pd\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$ (**5**) is readily deprotonated by 1,8-bis(dimethylamino)naphthalene. The product, $2[C_{14}H_{19}N_2]^+[Pd\{P(C_2F_5)(OH)O\}_4]^{2-}$ (**6**), was isolated as a colorless solid. The twofold deprotonation is clearly reflected in the $^{31}P$ NMR spectrum. Thus, the resonance of the phosphonous acid ligands is shifted from $\delta = 80.0$ ppm for the neutral compound **5** to $\delta =$ 97.7 ppm for the dianion **6**. The proton NMR spectrum reveals two singlets at $\delta = 12.3$ ppm for the protons of the palladate unit and at $\delta = 18.7$ ppm for the acidic proton of the cation. Single crystals of **6** were grown from dichloromethane solution. The crystal structure (Figure 4) exhibits four intramolecular hydrogen bridges, as evidenced by four short O···O distances of about 243.6 pm. The hydrogen atoms could not be refined isotropically and were included at calculated positions.

The oxygen atoms are bent out of the plane defined by the metal and the four phosphorus atoms allowing hydrogen bonding over all eight oxygen atoms. The $C_2F_5$ units are perpendicular to the complex plane in the opposite direction of

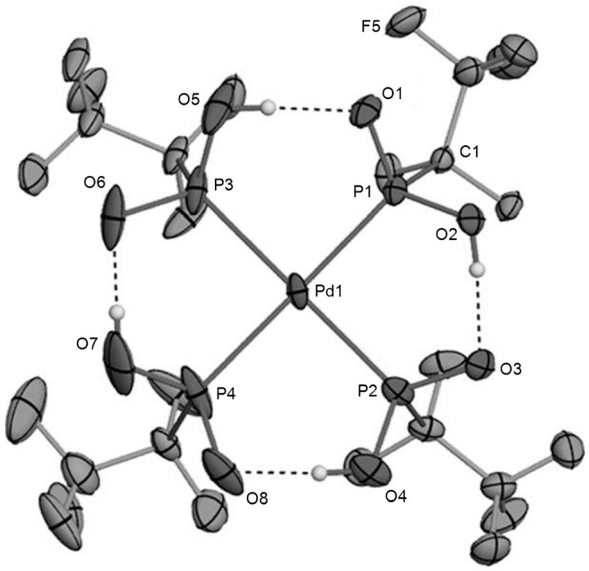



**Figure 4.** Molecular structure of $2[C_{14}H_{19}N_2]^+[Pd\{P(C_2F_5)(OH)O\}_4]^{2-}$, **6**·$CH_2Cl_2$; cations and solvent molecule omitted for clarity; selected bond lengths [pm] and angles [°]: Pd1—P1 234.16(6), Pd1—P3 235.47(7), P1—O1 152.4(2), P1—O2 155.6(2), P3—O5 155.6(2), P3—O6 153.2(2), O1-P1-O2 108.5(1), Pd1-P1-O1 116.64(7), Pd1-P1-O2 114.24(7), O5-P3-O6 108.1(1), Pd1-P3-O5 116.72(8), Pd1-P3-O6 115.1(1).

the oxygen atoms. The solid-state structure of the neutral complexes **1**, **2**, **3**, **8a**, **8b**, and **8c** is dominated by intra- and intermolecular hydrogen bridges to neighboring complex units or solvent molecules are prominent. In contrast to this, compound **6** exhibits in the solid-state isolated palladate units without any intermolecular hydrogen bridges. In the phosphonito units one shorter (152.9 pm) and one slightly elongated P—O bond (155.2 pm) differing by only 2 pm are obvious.

The treatment of palladium(II) chloride with $(C_2F_5)P(O)(OH)H$ resulted in a less selective reaction. The $^{31}P$ NMR spectrum of the reaction mixture is characterized by three resonances (Figure 5). The signals at $\delta = 88.3$ ($P^A$) and 103.4 ppm ($P^B$) belong to the mononuclear palladium complex $[ClPd\{P(C_2F_5)(OH)O\}\{P(C_2F_5)(OH)_2\}_2]$ (**7a**), evidenced by the $^{2}J(P^A,P^B)$ coupling constant of 11 Hz. Accordingly the $^{31}P\{^{19}F\}$ NMR spectrum shows a triplet for $P^A$ and a doublet for the phosphorus atoms $P^B$. The second product detected in the reaction mixture is the dinuclear palladium complex **8a** with

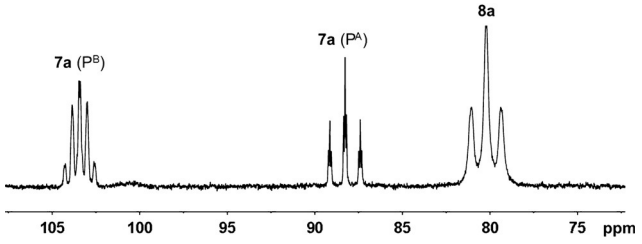
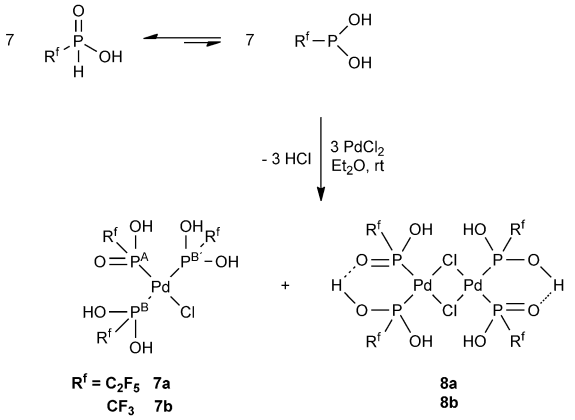



**Figure 5.** $^{31}P$ NMR spectrum of the diethyl ether solution of $PdCl_2$ and $(C_2F_5)P(O)(OH)H$.

a broad multiplet at $\delta = 80.2$ ppm. Removal of all volatile components and heating the residue in vacuo shifted the product ratio in favor of the dinuclear complex, however, neither excess $(C_2F_5)P(O)(OH)H$ nor **7a** could be completely removed.

Satisfying results were achieved by a change of the solvent from diethyl ether to dichloromethane. The treatment of a palladium(II) chloride slurry in dichloromethane with $(C_2F_5)P(O)(OH)H$ results in the precipitation of a colorless solid identified as the dinuclear compound **8a**. Excess phosphinic acid was removed by washing the precipitate thoroughly with dichloromethane. It should be noted that attempts to dissolve **8a** in the presence of $(C_2F_5)P(O)(OH)H$ always furnished **7a** as a byproduct (Scheme 3).




**Scheme 3.** Treatment of $(C_2F_5)P(O)(OH)H$ and $(CF_3)P(O)(OH)H$ with solid $[PdCl_2]$ to form the complexes **7a**, **b** and **8a**, **b**, respectively.

Previously, the treatment of $PdCl_2$ with 2,4-bis(trifluoromethyl)phenylphosphinic acid was reported to give a mixture of a mononuclear ($\delta(^{31}P) = 94.6$ ppm) and a dinuclear complex ($\delta(^{31}P) = 77.8$ ppm).[5] The latter resonance is well comparable with that of complex **8a** in diethyl ether ($\delta(^{31}P) = 80.2$ ppm)).

The attempts to separate preparative amounts of either **7a** or **8a** from the reaction mixture by recrystallization were unsuccesful. Single crystals suitable for X-ray diffraction analysis, however, were obtained. The structure reveals the dinuclear palladium complex **8a** (Figure 6), which cocrystallized with a mononuclear dianionic complex unit (comp. **6**). The O1···O3 distance (248.7(1) pm) and O6···O7 distance (249.5(1) pm) of **8a** are characteristic for hydrogen-bridged quasichelating

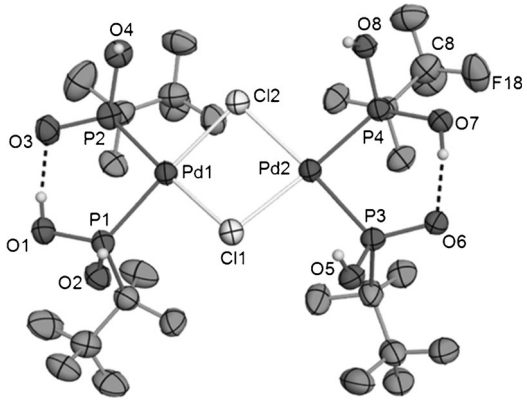



**Figure 6.** Molecular structure of $[Pd_2(\mu\text{-}Cl)_2\{[P(C_2F_5)(OH)O|_2H\}_2]$, **8a** (co-crystal with $2[H_3O\cdot(OEt_2)_2]^+[Pd\{P(C_2F_5)(OH)O\}_4]^{2-}$ (comp. the dianion of **6**)); H atoms omitted for clarity; selected bond lengths [pm] and angles [°]: Pd1–P1 223.1(1), Pd1–P2 223.3(1), P1–O1 154.4(3), P1–O2 154.3(3), P2–O3 152.1(3), P2–O4 154.9(3), O1–O3 248.6(4), O6–O7 249.5(4), Pd1-P1-O1 119.7(1), Pd1-P2-O3 116.9(1).

$[P(C_2F_5)(OH)O\cdots H\cdots O(OH)(C_2F_5)P]^-$ units. The P–O bond lengths are relatively short and vary between 151.8(3) and 155.6(3) pm.

The treatment of solid palladium(II) chloride with $(CF_3)P(O)(OH)H$ in diethyl ether furnished a mixture of $[ClPd\{P(CF_3)(OH)O\}\{P(CF_3)(OH)_2\}_2]$ (**7b**), ($\delta(^{31}P) = 80.4$ ($P^A$), 97.4 ppm ($P^B$), $^2J(P,P) = 26$ Hz) and the dinuclear complex $[Pd_2(\mu\text{-}Cl)_2\{[P(CF_3)(OH)O]_2H\}_2]$ (**8b**) ($\delta(^{31}P) = 74.8$ ppm; Table 2)).

**Table 2.** $^1H$ and $^{31}P$ NMR spectroscopic data of **5**, **6**, **7a**, **b**, **8a**, **b**, and **c**.

| | $\delta(^1H)$[a] | $\delta(^{31}P)$ [ppm] |
|---|---|---|
| $[Pd\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$, **5**[b] | 13.4 | 80.0 |
| $2[C_{14}H_{19}N_2]^+[Pd\{P(C_2F_5)(OH)O\}_4]^{2-}$, **6**[c] | 12.3 | 97.7 |
| $[ClPd\{P(C_2F_5)(OH)O\}\{P(C_2F_5)(OH)_2\}_2]$, **7a**[b] | – | 88.3 ($P^A$)<br>103.4 ($P^B$)<br>80.4 ($P^A$) |
| $[ClPd\{P(CF_3)(OH)O\}\{P(CF_3)(OH)_2\}_2]$, **7b**[b] | – | 97.4 ($P^B$) |
| $[Pd_2(\mu\text{-}Cl)_2\{[P(C_2F_5)(OH)O]_2H\}_2]$, **8a**[d] | 13.1 | 79.5 |
| $[Pd_2(\mu\text{-}Cl)_2\{[P(CF_3)(OH)O]_2H\}_2]$, **8b**[b] | 13.5 | 74.8 |
| $[Pd_2(\mu\text{-}Cl)_2\{[P(C_6F_5)(OH)O]_2H\}_2]$, **8c**[b] | 11.3 | 73.2 |

[a] OH function. [b] $Et_2O$. [c] $[D_3]$Acetonitrile. [d] Dioxane.

The selective synthesis of the dinuclear complex **8b** was achieved in a two-phase system of diethyl ether and water. After 3 h the reaction mixture was filtered and all volatile compounds were removed in vacuo affording a light-yellow solid identified as compound **8b**. If diethylamine was condensed onto a freshly prepared solution of $[Pd_2(\mu\text{-}Cl)_2\{[P(CF_3)(OH)O]_2H\}_2]$ (**8b**), single crystals of $2[H_2NEt_2]^+[Pd_2(\mu\text{-}Cl)_2\{[P(CF_3)O_2]_2H\}_2]^{2-}$ slowly separated. The molecular structure in the solid state (Figure 7) is dominated by inter- and intramolecular hydrogen bridges. The O1···O4 (246.9(4) pm) and O5···O8 distance (243.0(4) pm) are characteristic for a hydrogen-bridged quasi-chelating unit. One complex unit is connected to a second unit by intermolecular hydrogen bridges (O2···O7# 249.3(4) and O3···O6# 248.1(3) pm). The $CF_3$ groups

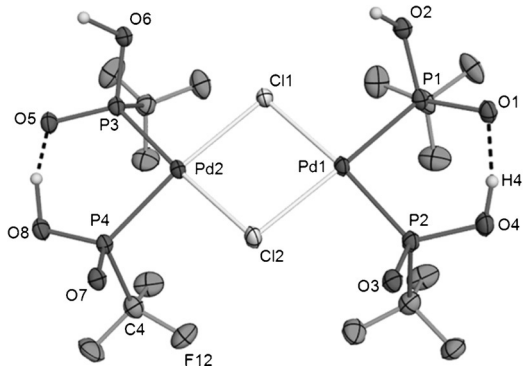



**Figure 7.** Molecular structure of $2[H_2NEt_2]^+[Pd_2(\mu\text{-}Cl)_2\{[P(CF_3)O_2]_2H\}_2]^{2-}$; cations omitted for clarity; selected bond lengths [pm] and angles [°]: Pd1—P1 223.54(9), Pd1—P2 223.27(9), P1—O1 152.1(3), P1—O2 154.9(3), P2—O3 151.8(3), P2—O4 155.8(3), Pd1—P1-O1 119.5(1), Pd1-P2-O4 118.2(1); disorder of the cation on two positions.

are located on one side perpendicular to the complex plane. Comparable to those of the $C_2F_5$ derivative **8a**, the P—O bond lengths vary between 151.6(3) and 156.2(3) pm.

As compared with the reaction of the $CF_3$ and $C_2F_5$ derivatives, the treatment of $(C_6F_5)P(O)(OH)H$ with $PdCl_2$ in diethyl ether proceeds much slower and selectively yields one product. Stirring of the reaction mixture at room temperature for three days afforded the dinuclear complex $[Pd_2(\mu\text{-}Cl)_2\{[P(C_6F_5)(OH)O]_2H\}_2]$ (**8c**), and single crystals separated from THF solutions. Compound **8c** crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with two solvent molecules per formula unit. The X-ray analysis discloses a dinuclear palladium complex (Figure 8) featuring two quasichelating phosphonous acid phosphonito units with an O1···O4 distance of 250.0(1) pm. A solvent molecule is coordinated through a hydrogen bridge to O3. Intermolecular hydrogen bridges between O1···O2# and O2···O1# lead to a zigzag structure of the complex units in the crystal. In contrast to the $C_2F_5$ and the $CF_3$ derivatives in which the perfluoroalkyl groups are orientated perpendicular to the complex plane, the pentafluorophenyl substituents of the quasichelating units are orientated to different sides of the complex plane.

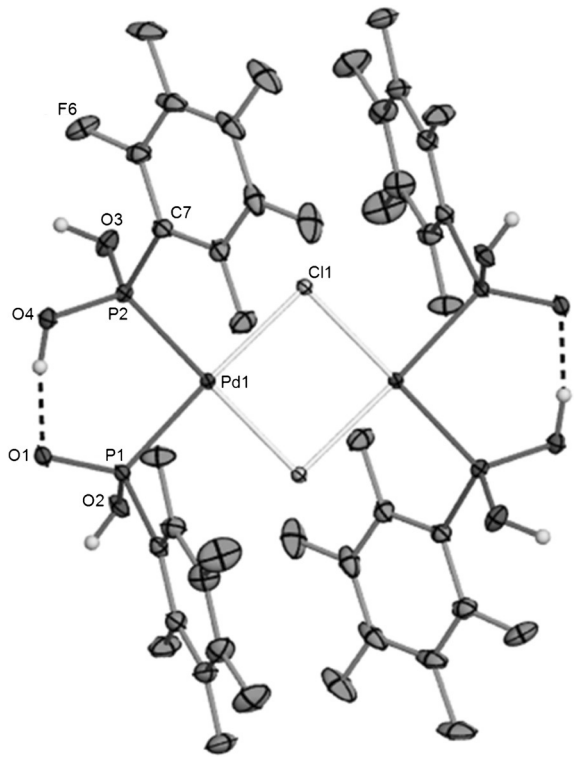



**Figure 8.** Molecular structure of $[Pd_2(\mu\text{-}Cl)_2\{[P(C_6F_5)(OH)O]_2H\}_2]$, **8c**·2 THF; solvent molecules omitted for clarity; selected bond lengths [pm] and angles [°]: Pd1—Cl1 240.93( 3), Pd1—P1 221.86(3), Pd1—P2 222.55(3), P1—O1 152.94(9), P1—O2 155.84(9), P2—O3 155.0(1), P2—O4 156.57(9), Pd1-P1-O1 119.97(4), Pd1-P2-O4 118.81(4).

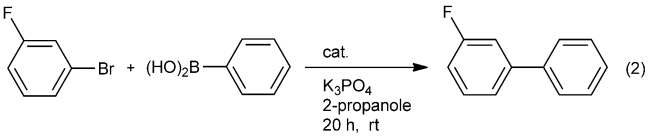
**Table 3.** Results of the Suzuki cross-coupling reaction.[a]

| Catalyst | Turnover [%] | TON | TOF |
|---|---|---|---|
| $[Pd\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$, **5** | 91 | 9100 | 455 |
| $[Pd_2(\mu\text{-}Cl)_2\{[P(C_2F_5)(OH)O]_2H\}_2]$, **8a** | 87 | 8700 | 435 |
| $[Pd_2(dba)_3]$ | 55 | 5500 | 275 |
| $[Pd_2(dba)_3]/P(t\text{Bu})_3$ | 78 | 7800 | 390 |

[a] After 20 h with a catalyst loading of 0.01 mol% Pd (0.005 mol% of the dinuclear complex **8a** and $[Pd_2(dba)_3]$). TON = turnover number; TOF = turnover frequency.

### Catalytic activity in the Suzuki cross coupling reaction

The Suzuki reaction is a well-known and frequently used cross-coupling commonly catalyzed by palladium complexes. It is therefore an excellent system to explore the catalytic activity of new compounds. Previous work has shown that phosphinous acid complexes bearing electron-withdrawing groups exhibit a very high catalytic activity in the Suzuki reaction of 1-bromo-3-fluorobenzene and phenyl boronic acid.[7] The most efficient system proved to be 2-propanole as the solvent and potassium phosphate as the base [Eq. (2)].




Based on this work, we investigated the catalytic activity of $[Pd_2(\mu\text{-}Cl)_2\{[P(C_2F_5)(OH)O]_2H\}_2]$ (**8a**) and $[Pd\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$ (**5**) (Table 3). The reaction proceeds even at room temperature and the conversion was determined by $^{19}F$ NMR spectroscopy after 20 h at room temperature. Even with a catalyst loading of only 0.01 mol% Pd (0.005 mol% of the dinuclear complex **8a**) a turnover of 91% for **8a** and 87% for **5** was achieved. For comparison, the literature-known catalyst systems of $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) and $[Pd_2(dba)_3]/P(t\text{Bu})_3$ gave only turnovers of 78 and 55%, respectively.[7]

## Conclusion

A tautomeric equilibrium between phosphinic, RP(O)(OH)H, and phosphonous acids, $RP(OH)_2$, is evidenced by this work. Calculations at the B3LYP/6-311+G(2df,p) level of theory revealed an energy difference of 7.6 kJ mol$^{-1}$ for the $CF_3$ and 9.9 kJ mol$^{-1}$ for the $C_2F_5$ derivative in favor of the phosphinic acid. In this work we described the diverse coordinative properties of phosphinic acids with the electron-withdrawing groups $CF_3$, $C_2F_5$, and $C_6F_5$. For the pentafluoroethylphosphinic acid, a three- or fourfold coordination to $PtCl_2$ under HCl elimination occurs, depending on the used solvent. Stabilizing intramolecular hydrogen bridges between phosphonous acid-phosphonito quasichelating units with a characteristic O···O distance of 240 to 250 pm are formed. With the pentafluorophenyl-substituted phosphinic acid, only a threefold coordination could be achieved under the same reaction conditions. The $Cl^-$ free complexes $[M\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]^{2-}$ (M = Pt (**3**), Pd (**5**)) are highly acidic and can easily be deprotonated to the dianionic complexes $[M\{P(C_2F_5)(OH)O\}_4]$ (M = Pt (**4**), Pd (**6**)) in which two additional stabilizing intramolecular hydrogen bridges are formed.

The treatment of $PdCl_2$ with $R^fP(O)(OH)H$ ($R^f = CF_3$, $C_2F_5$, $C_6F_5$) further underlines the different reactivity of perfluoroalkyl- and perfluoroaryl-substituted phosphinic acids. The dinuclear complex $[Pd_2(\mu\text{-}Cl)_2\{[P(R^f)(OH)O]_2H\}_2]$ is accessible for all derivatives. Complex $[ClPd\{P(R^f)(OH)O\}\{P(R^f)(OH)_2\}_2]$ is obtained as the only product with the perfluoroalkyl phosphinic acids. A possible explanation could be the decreased electron-withdrawing effect of the pentafluorophenyl group, which results in a larger energy difference between phosphinic and phosphonous acid and a decreased acidity as compared with the $CF_3$ and $C_2F_5$ derivatives.

In summary, perfluoroalkyl- and perfluoroaryl-substituted phosphinic acids are useful preligands for the synthesis of transition-metal complexes of phosphonous acids. The phosphinic acids as well as their platinum and palladium complexes are remarkably stable towards oxygen and moisture. In addition, the palladium complexes $[Pd\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$ and $[Pd_2(\mu\text{-}Cl)_2\{[P(C_2F_5)(OH)O]_2H\}_2]$ proved to be excellent catalysts for the Suzuki reaction of 1-bromo-2-fluorobenzene and phenyl boronic acid. Both complexes exhibit a high catalytic activity even under mild conditions.

## Experimental Section

All chemicals were obtained from commercial sources and used without further purification. Standard high-vacuum techniques were employed throughout all preparative procedures. Non-volatile compounds were handled in a dry $N_2$ atmosphere using Schlenk techniques. The NMR spectra were recorded on a Bruker Model Avance III 300 spectrometer ($^{31}P$ 111.92 MHz; $^{19}F$ 282.40 MHz; $^{13}C$ 75.47 MHz, $^1H$ 300.13 MHz) with positive shifts being downfield from the external standards (85% orthophosphoric acid ($^{31}P$), $CCl_3F$ ($^{19}F$) and TMS ($^1H$)). IR spectra were recorded on an ALPHA-FTIR spectrometer (Bruker). ESI mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. Nitrogen was generated by a Bruker nitrogen generator NGM 11. Helium served as the cooling gas for the ion trap and collision gas for MS experiments. The spectra were recorded with a Bruker Daltonik esquireNT 5.2 esquireControl software by the accumulation and averaging of several single spectra. Data analysis software 3.4 was used for processing the spectra. C, H, and N analyses were carried out with a HEKAtech Euro EA 3000. The crystal data for compounds **1**·THF, **2**·2THF, **3**·2THF and the cocrystal were collected on a Bruker Nonius Kappa CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm). Data collection for X-ray structure determination for compound $2[H_2NEt_2]^+[Pd_2(\mu\text{-}Cl)_2\{[P(CF_3)O_2]_2H\}_2]^{2-}$ was performed on a Bruker KAPPA APEX II diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm). The crystal data for compounds **6**·$CH_2Cl_2$ and **8c**·2THF were collected on a SuperNova, Single source at offset, Eos using $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm). Suitable crystals were selected, coated with paratone oil and mounted onto the diffractometer. The structures were solved by Direct Methods and refined by full-matrix least-squares cycles (programs SHELXS-97 and SHELXL-97 (Sheldrick, G. M. SHELXL-97; Programs for Crystal Structure Analysis, University of Göttingen, 1997)). The CCDC depositions numbers for all complexes are given in Table 4 and Table 5. CCDC 1016495 (**1**), 1016496 (**2**), 1016497 (**3**), 1016498 (**8a**), 1016499 (**8b**), 1016500 (**6**), and 1016501 (**8c**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

**Synthesis of $(C_2F_5)P(NEt_2)_2$:** ***CAUTION!!!*** *$LiC_2F_5$ is highly reactive and tends to violently decompose above temperatures of −50 °C.* A 1.6 M *n*-butyl lithium solution in *n*-hexane (119.0 mL, 190.0 mmol) diluted in diethyl ether (200 mL) was degassed at −78 °C and stirred for 30 min in an atmosphere of pentafluoroethane (228.0 mmol). After the addition of bis(diethylamino)chlorophosphane (36.0 g, 171.0 mmol) at −78 °C, the mixture was warmed to room temperature and stirred overnight. The precipitate was filtered off. After evaporation of the solvent, 43.2 g (147.0 mmol, 86%) $(C_2F_5)P(NEt_2)_2$ were obtained by vacuum distillation at 28 °C and $1\times10^{-3}$ mbar as a colorless liquid. $^1H$ NMR ([D]chloroform, RT): $\delta = 1.1$ (t, $^3J(H,H) = 7$ Hz, 3H, $CH_3$), 3.2 ppm (m, 2H, $CH_2$); $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, RT): $\delta = 14.1$ (d, $^3J(C,P) = 3$ Hz, $CH_3$), 44.2 ppm (d, $^2J(C,P) = 21$ Hz, $CH_2$); $^{13}C\{^{19}F\}$ NMR ([D]chloroform, RT): $\delta = 119.5$ (d, $^1J(C,P) = 52$ Hz, $CF_2$), 120.1 ppm (d, $^2J(C,P) = 25$ Hz, $CF_3$); $^{19}F$ NMR ([D]chloroform, rt): $\delta = -117.6$ (d, $^2J(P,F) = 71$ Hz, 2F, $CF_2$), −81.7 ppm (s, 3F, $CF_3$); $^{31}P$ NMR ([D]chloroform, RT): $\delta = 72.4$ ppm (m, ***P***); IR (gas phase): $\tilde{\nu} = 746$ (w), 947 (w), 1146 (m), 1224 (s), 1308 (m), 1388 (w), 2882 (w), 2946 (w), 2979 cm$^{-1}$ (w).

**Synthesis of $(C_2F_5)P(O)(OH)H$**: Water (1.47 g, 81.86 mmol) was added to a solution of $(C_2F_5)P(NEt_2)_2$ (12.04 g, 40.93 mmol) in diethyl ether (200 mL). The reaction mixture was cooled to −78 °C and degassed before the addition of gaseous HBr (6.54 g, 81.84 mmol). The temperature was slowly raised to room temperature and the white precipitate was filtered off. The solvent was distilled off and the product (6.44 g; 35.01 mmol, 86%) was obtained by vacuum distillation at 43 °C and $1\times10^{-3}$ mbar as a colorless liquid. $^1H$ NMR (neat, RT): $\delta = 7.3$ (d, $^1J(P,H) = 640$ Hz, 1H, P***H***), 14.0 ppm (s, 1H, O***H***); $^1H\{^{31}P\}$ NMR (neat, RT): $\delta = 7.3$ (s, 1H, P***H***), 14.0 ppm (s, 1H, O***H***); $^{13}C\{^1H\}$ NMR (neat, RT): $\delta = 109.9$ (t, d, quart, $^1J(C,F) = 275$ Hz, $^1J(C,P) = 139$, $^2J(C,F) = 40$ Hz, $CF_2$), 118.3 ppm (quart, t, d, $^1J(C,F) = 285$ Hz, $^2J(C,F) = 31$, $^2J(C,P) = 19$ Hz, $CF_3$); $^{19}F$ NMR (neat, RT): $\delta = -132.3$ (d, $^2J(P,F) = 96$ Hz, 2F, $CF_2$), −82.5 ppm (s, 3F, $CF_3$); $^{31}P$ NMR (neat, RT): $\delta = 9.4$ ppm (d, t, $^1J(P,H) = 639$, $^2J(P,F) = 96$ Hz, ***P***).

**Table 4.** Crystal data and refinement characteristics for **1**·THF, **2**·2THF, **3**·2$Et_2O$ and the cocrystal.[a]

| | **1**·THF | **2**·2$Et_2O$ | **3**·2$Et_2O$ | 2$[H_3O{\cdot}(Et_2O)_2]^+[Pd\{P(C_2F_5)O_2\}_4H_4]^{2-}$ $[Pd_2(\mu\text{-}Cl)_2\{[P(C_2F_5)(OH)O]_2H\}_2]$ (**8a**) |
|---|---|---|---|---|
| empirical formula | $C_6H_4ClF_{15}O_6P_3Pt$, $C_4H_9O$ | $C_{18}H_5ClF_{15}O_6P_3Pt$, 2($C_4H_{10}O$) | $C_8H_6F_{20}O_8P_4Pt$, 2($C_4H_{10}O$) | $C_{32}H_{56}Cl_2F_{40}O_{22}P_8Pd_3$ |
| $a$ [pm] | 978.47(1) | 890.14(9) | 2339.31(3) | 1033.9(1) |
| $b$ [pm] | 1108.73(1) | 2909.7(4) | 952.98(1) | 1267.3(1) |
| $c$ [pm] | 1183.48(1) | 1432.9(2) | 1729.66(2) | 1312.1(1) |
| $\alpha$ [°] | 68.75(1) | | | 81.5(1) |
| $\beta$ [°] | 84.35(1) | 105.79 (1) | 114.30(1) | 80.2(1) |
| $\gamma$ [°] | 71.97(1) | | | 81.9(1) |
| $V$ [$10^6$ pm$^3$] | 1137.76(1) | 3571.2(8) | 3514.21(7) | 1663.9(1) |
| Z | 2 | 4 | 4 | 1 |
| $\rho_x$ [g cm$^{-3}$] | 2.492 | 1.997 | 2.036 | 1.638 |
| crystal system | triclinic | monoclinic | monoclinic | triclinic |
| space group | $P\bar{1}$ (no. 2) | $P2_1/n$ (no. 14) | $C2/c$ (no. 15) | $P\bar{1}$ (no. 2) |
| color | colorless | colorless | colorless | colorless |
| crystal size [mm$^3$] | 0.30×0.25×0.20 | 0.30×0.30×0.20 | 0.27×0.10×0.10 | 0.28×0.13×0.10 |
| diffractometer | Bruker Nonius Kappa CCD | | | |
| radiation | $Mo_{K\alpha}$ (graphite monochromator, $\lambda$ = 71.073 pm) | | | |
| $T$ [K] | 100(2) | 100(2) | 200(2) | 100(2) |
| $\theta$ range [°] | 3.51/30.00 | 2.43/30.00 | 3.38/29.99 | 3.12/30.0 |
| index range | $-13 \le h \le 13$<br>$-15 \le k \le 15$<br>$-16 \le l \le 16$ | $-12 \le h \le 12$<br>$-40 \le k \le 40$<br>$-20 \le l \le 20$ | $-32 \le h \le 32$<br>$-13 \le k \le 13$<br>$-24 \le l \le 24$ | $-14 \le h \le 14$<br>$-17 \le k \le 17$<br>$-18 \le l \le 18$ |
| total data collected | 46167 | 72241 | 57121 | 48600 |
| $R$(int) | 0.055 | 0.0375 | 0.052 | 0.041 |
| unique data | 6636 | 10433 | 5115 | 9642 |
| observed data ($I > 2\sigma$) | 6457 | 9236 | 4606 | 9512 |
| $\mu$ [mm$^{-1}$] (numerical) | 6.650 | 4.262 | 4.325 | 2.349 |
| $T$ min/max | 0.2403/0.3497 | 0.3612/0.4827 | 0.3881/0.6716 | 0.559/0.799 |
| $R_1/wR_2$ [$I > 2\sigma(I)$] | 0.0212/0.0530 | 0.0241/0.0454 | 0.0319/0.0855 | 0.028/0.069 |
| $R_1/wR_2$ (all data) | 0.0220/0.0533 | 0.0312/0.0471 | 0.0370/0.0889 | 0.029/0.069 |
| goodness of fit ($S_{all}$) | 1.077 | 1.099 | 1.041 | 1.027 |
| $\Delta\rho_{max/min}$ [$10^6$ e pm$^{-3}$] | 0.963/−2.381 | 0.713/−1.307 | 2.192/−1.165 | 0.988/−1.089 |
| $F$(000) | 808 | 2080 | 2080 | 820 |
| CCDC number | 1016495 | 1016496 | 1016497 | 1016498 |

[a] Using SIR-97 and ShelXL-97.[8]

**Synthesis of [ClPt{P($C_2F_5$)(OH)O}{P($C_2F_5$)(OH)$_2$}$_2$] (1)**: ($C_2F_5$)P(O)(OH)H (0.24 g, 1.33 mmol) was added to a suspension of $PtCl_2$ (0.10 g, 0.38 mmol) in tetrahydrofuran (5 mL) and stirred at room temperature for 1 h. The resulting solution was filtered and all volatile compounds were removed in vacuo yielding a red oil. After recrystallization from dichloromethane solution colorless crystals (0.17 g; 0.22 mmol, 58%) were obtained. $^1$H NMR ([D]chloroform, RT): $\delta$ = 11.9 ppm (s, ***H***); $^{13}$C{$^{19}$F} NMR ([D]chloroform, RT): $\delta$ = 111.8 (d, $^1J$(C,P) = 86 Hz, ($CF_3$***C***$F_2$)P *trans* to Cl), 113.9 (t, $^{1/3}J$(C,P) = 48 Hz, ($CF_3$***C***$F_2$)P *cis* to Cl), 119.6 (d, $^2J$(C,P) = 13 Hz, (***C***$F_3CF_2$)P *trans* to Cl), 119.9 ppm (t, $^{2/4}J$(C,P) = 7 Hz, (***C***$F_3CF_2$)P *cis* to Cl); $^{19}$F NMR ([D]chloroform, RT): $\delta$ = −124.4 (d, $^2J$(P,F) = 98, $^3J$(Pt,F) = 37 Hz, 2F, C***F***$_2$), −122.2 (m, 4F, C***F***$_2$), −79.8 (s (br), $^4J$(Pt,F) = 12 Hz, 6F, C***F***$_3$), −79.7 ppm (s (br), $^4J$(Pt,F) = 23 Hz, 3F, C***F***$_3$); $^{31}$P NMR ([D]chloroform, RT): $\delta$ = 61.3 (t, t, $^2J$(P,F) = 99, $^2J$(P,P) = 28 Hz, $^1J$(Pt,P) = 4277 Hz, 1 P, ***P*** *trans* to Cl), 94.7 ppm (m, $^1J$(Pt,P) = 3172 Hz, 2 P, ***P*** *cis* to Cl); $^{31}$P{$^{19}$F} NMR ([D]chloroform, RT): $\delta$ = 61.3 (t, $^2J$(P,P) = 27, $^1J$(Pt,P) = 4279 Hz, 1 P, ***P*** *trans* to Cl), 94.7 ppm (d, $^2J$(P,P) = 27, $^1J$(Pt,P) = 3172 Hz, 2 P, ***P*** *cis* to Cl); $^{195}$Pt NMR ([D]chloroform, RT): $\delta$ = −4694.1 ppm (d, t, $^1J$(Pt,P) = 4276, $^1J$(Pt,P) = 3177 Hz, ***Pt***).

**Synthesis of [ClPt{P($C_6F_5$)(OH)O}{P($C_6F_5$)(OH)$_2$}$_2$] (2)**: ($C_6F_5$)P(O)(OH)H (0.24 g, 1.03 mmol) was dissolved in diethyl ether (5 mL) and $PtCl_2$ (0.09 g, 0.34 mmol) was added. The reaction mixture was stirred at room temperature for 7 days and filtered. The residue was washed with diethyl ether (5 mL). Evaporation of the filtrate to dryness yielded 0.24 g (0.26 mmol, 76%) of light-yellow solid **2**. $^1$H NMR ($Et_2O$, RT): $\delta$ = 11.6 ppm (s, ***H***); $^{13}$C{$^{19}$F} NMR ($Et_2O$, RT): $\delta$ = 137.5 (m, 6 C, *meta*-C), 142.8 (m, 1 C, *para*-C), 143.2 (s, 2 C, *para*-C), 146.8 (s, 2 C, *ortho*-C), 147.2 ppm (s, 4 C, *ortho*-C); $^{19}$F NMR ($Et_2O$, RT): $\delta$ = −164.0 (m, 2F, *meta*-F), −163.5 (m, 4F, *meta*-F), −153.6 (m, 1F, *para*-F), −151.8 (m, 2F, *para*-F), −133.8 (m, 2F, *ortho*-F), −133.1 ppm (m, 4F, *ortho*-F); $^{31}$P NMR ($Et_2O$, RT): $\delta$ = 49.3 (t, m, $^2J$(P,P) = 27, $^1J$(Pt,P) = 4606 Hz, 1 P, ***P*** *trans* to Cl), 97.1 ppm (d (br), $^2J$(P,P) = 27, $^1J$(Pt,P) = 3223 Hz, 2 P, ***P*** *cis* to Cl); $^{31}$P{$^{19}$F} NMR ([D]chloroform, RT): $\delta$ = 49.3 (t, $^2J$(P,P) = 27, $^1J$(Pt,P) = 4607 Hz, 1 P, ***P*** *trans* to Cl), 97.1 ppm (d, $^2J$(P,P) = 27, $^1J$(Pt,P) = 3223 Hz, 2 P, ***P*** *cis* to Cl); $^{195}$Pt NMR ([D]chloroform, RT): $\delta$ = −4692.2 ppm (d, t, $^1J$(Pt,P) = 4619, $^1J$(Pt,P) = 3236 Hz, ***Pt***).

**Synthesis of [Pt{P($C_2F_5$)(OH)O}$_2${P($C_2F_5$)(OH)$_2$}$_2$] (3)**: (a) ($C_2F_5$)P(O)(OH)H (0.35 g, 1.90 mmol) was added to a suspension of [Pt(acac)$_2$] (0.18 g, 0.46 mmol) in diethyl ether (5 mL) and stirred at room temperature for 5 days. The resulting yellow solution was filtered and all volatile compounds were removed in vacuo yielding 0.43 g (0.46 mmol, 100%) of light-yellow solid **3**. (b) ($C_2F_5$)P(O)(OH)H (0.20 g, 1.09 mmol) was added to a suspension of $PtCl_2$ (0.08 g, 0.30 mmol) in dichloromethane (5 mL) and stirred at room temperature for 12 days. After the removal of the solvent, excess phosphinic acid was distilled off. The residue was dissolved in diethyl ether and filtered. Evaporation of the filtrate to dryness yielded 0.19 g (0.21 mmol, 70%) of colorless solid **3**. $^1$H NMR ([D$_8$]THF, RT): $\delta$ = 13.7 ppm (s, ***H***); $^{13}$C{$^{19}$F} NMR ([D$_8$]THF, RT): $\delta$ = 113.4 (m, ***C***$F_2$), 119.9 ppm (m, ***C***$F_3$); $^{19}$F NMR ([D$_8$]THF, RT): $\delta$ = −123.0 (m, 2F, C***F***$_2$), −80.1 ppm (m, 3 F, C***F***$_3$); $^{31}$P NMR ([D$_8$]THF, RT): $\delta$ = 93.0 ppm (m, $^1J$(Pt,P) = 3048 Hz, ***P***); $^{31}$P{$^{19}$F} NMR ([D$_8$]THF, RT): $\delta$ = 93.0 ppm (s, $^1J$(Pt,P) = 3048 Hz, ***P***); IR

**Table 5.** Crystal data and refinement characteristics for $2[H_2NEt_2]^+[Pd_2(\mu\text{-}Cl)_2\{[P(CF_3)O_2]_2H\}_2]^{2-}$,[a] **6**·$CH_2Cl_2$,[b] and **8c**·2THF[b].

| | $2[H_2NEt_2]^+[Pd_2(\mu\text{-}Cl)_2\{[P(CF_3)O_2]_2H\}_2]^{2-}$ **8b** | **6**·1/2 $CH_2Cl_2$ | **8c**·2THF |
|---|---|---|---|
| empirical formula | $C_{12}H_{28}Cl_2F_{12}N_2O_8P_4Pd_2$ | $C_{36.5}H_{43}ClF_{20}N_4O_8P_4Pd$ | $C_{24}H_6Cl_2F_{20}O_8P_4Pd_2$, $2(C_4H_8O)$ |
| $a$ [pm] | 1326.68(6) | 1766.65(3) | 1091.83(3) |
| $b$ [pm] | 1700.49(7) | 1420.81(4) | 1110.30(3) |
| $c$ [pm] | 1373.85(6) | 2029.02(4) | 1165.85(2) |
| $\alpha$ [°] | – | – | 93.3222(2) |
| $\beta$ [°] | 99.058(2) | 97.840(2) | 115.626(2) |
| $\gamma$ [°] | – | – | 117.907(2) |
| $V$ [$10^6$ pm$^3$] | 3060.8(2) | 5045.4(2) | 1064.29(4) |
| $Z$ | 4 | 4 | 1 |
| $\rho_x$ [g cm$^{-3}$] | 2.092 | 1.727 | 2.113 |
| crystal system | monoclinic | monoclinic | triclinic |
| space group | $P2_1/n$ (no. 14) | $P2_1/n$ (no. 14) | $P\bar{1}$ (no. 2) |
| color | colorless | colorless | colorless |
| crystal size [mm$^3$] | 0.13×0.11×0.11 | 0.52×0.33×0.14 | 0.13×0.07×0.07 |
| diffractometer | Bruker Kappa APEX II | SuperNova, Single source at offset, Eos | |
| radiation | $Mo_{K\alpha}$ ($\lambda$ = 71.073 pm) | | |
| $T$ [K] | 100(2) | 100.0(1) | 100.0(2) |
| $\theta$ range [°] | 3.38/28.50 | 2.62/32.36 | 2.62/32.4255 |
| index range | $-17 \le h \le 17$<br>$-22 \le k \le 22$<br>$-18 \le l \le 18$ | $-24 \le h \le 22$<br>$-18 \le k \le 19$<br>$-28 \le l \le 28$ | $-15 \le h \le 15$<br>$-15 \le k \le 15$<br>$-16 \le l \le 16$ |
| total data collected | 140095 | 51147 | 81610 |
| unique data | 7731 | 14686 | 6200 |
| $R$(int)/$R(\sigma)$ | 0.0772 | 0.0324 | 0.0273 |
| observed data ($I > 2\sigma$) | 6216 | 12159 | 5954 |
| $\mu$ [mm$^{-1}$] (numerical) | 1.671 | 0.673 | 1.264 |
| $T$ min/max | 0.8058/0.8427 | 0.777/2.111 | 0.938/1.041 |
| $R_1$/w$R_2$ [$I > 2\sigma(I)$] | 0.0343/0.0837 | 0.0421/0.0816 | 0.0160/0.0384 |
| $R_1$/w$R_2$ (all data) | 0.0525/0.0994 | 0.0555/0.0870 | 0.0169/0.0388 |
| goodness of fit ($S_{all}$) | 1.194 | 1.092 | 1.037 |
| $\Delta\rho_{max/min}$ [$10^6$ e pm$^{-3}$] | 1.789/−1.095 | 0.63/−0.90 | 0.45/−0.50 |
| F(000) | 1888 | 2628 | 660 |
| CCDC number | 1016499 | 1016500 | 1016501 |

[a] Using SIR-97 and ShelXL-97.[8] [b] Using Olex2,[9] the structure was dissolved with the ShelXS[8] structure solution program using Direct Methods and refined with the ShelXL[8] refinement package using Least Squares minimization.

(ATR): $\tilde{\nu}$ = 430 (m), 449 (m), 483 (s), 548 (m), 580 (m), 592 (m), 625 (m), 667 (m), 748 (m), 769 (m), 826 (m), 923 (s), 976 (s), 1055 (m), 1117 (s), 1203 (s), 1307 (m), 1390 (w), 1453 (w), 2860 (w), 2930 cm$^{-1}$ (w).

**Synthesis of $2[C_{14}H_{19}N_2]^+[Pt\{P(C_2F_5)(OH)O\}_4]^{2-}$, 4**: Solid $PtCl_2$ (0.12 g, 0.45 mmol), suspended in dichloromethane (6 mL), was treated with $(C_2F_5)P(O)(OH)H$ (0.37 g, 2.00 mmol) and stirred at room temperature for 10 days. The reaction mixture was concentrated in vacuo. The residue was taken up in diethyl ether and filtered. Addition of a solution of 1,8-bis(dimethylamino)naphthalene (0.18 g, 0.84 mmol) in diethyl ether resulted in the precipitation of a colorless solid. The suspension was stirred for 12 h before removal of the solvent. The residue was repeatedly washed with diethyl ether and dried in vacuo yielding 0.48 g (0.35 mmol, 78%) of colorless solid **4**. $^1$H NMR ([D$_3$]acetonitrile, RT): $\delta$ = 3.2 (d, $J$ = 3 Hz, $^1J$(C,H) = 141 Hz, 12H, N(C***H***$_3$)$_2$), 7.7 (t, $^3J$(H,H) = 8 Hz, 2H, *meta*-C***H***), 8.0 (d, $^3J$(H,H) = 8 Hz, 2H, *ortho*-C***H***), 8.1 (d, $^3J$(H,H) = 8 Hz, 2H, *para*-C***H***), 16.5 (s, 2H, O***H***), 18.7 ppm (s, 1H, N···***H***···N); $^{13}$C{$^1$H} NMR ([D]acetonitrile, RT): $\delta$ = 45.8 (s, ***C***H$_3$), 119.2 (s, *meta*-***C***), 121.7 (s, *ortho*-***C***H), 127.1 (s, *meta*-***C***H), 129.2 (s, *para*-***C***H), 135.4 (s, *ortho*-***C***), 144.5 ppm (s, ***C***N); $^{13}$C{$^{19}$F} NMR ([D$_3$]acetonitrile, RT): $\delta$ = 113.3 (m, ***C***F$_2$), 120.1 ppm (m, ***C***F$_3$); $^{19}$F NMR ([D$_3$]acetonitrile, RT): $\delta$ = −124.3 (m, 2F, C***F***$_2$), −80.3 ppm (s, $^4J$(Pt,F) = 13 Hz, 3F, C***F***$_3$); $^{31}$P NMR ([D$_3$]acetonitrile, RT): $\delta$ = 85.9 ppm (m, $^1J$(Pt,P) = 2751 Hz, ***P***); $^{195}$Pt NMR ([D$_3$]acetonitrile, RT): $\delta$ = −5191.1 ppm (quint, m, $^1J$(Pt,P) = 2747 Hz, ***Pt***); IR (ATR): $\tilde{\nu}$ = 418 (s), 439 (s), 467 (s), 488 (s), 543 (m), 590 (m), 634 (m), 744 (m), 772 (s), 836 (m), 975 (s), 1003 (s), 1029 (s), 1074 (m), 1105 (s), 1138 (m), 1194 (s), 1263 (w), 1302 (m), 1380 (w), 1415 (w), 1461 (w), 1476 (w), 1517 (w), 1665 (w), 2982 cm$^{-1}$ (w).

**Synthesis of $[Pd\{P(C_2F_5)(OH)O\}_2\{P(C_2F_5)(OH)_2\}_2]$ (5)**: Treatment of a slurry of $[Pd(acac)_2]$ (0.08 g, 0.26 mmol) in diethyl ether (4 mL) with $(C_2F_5)P(O)(OH)H$ (0.22 g, 1.20 mmol) at room temperature yielded a colorless solution. The solution was filtered and all volatile compounds were removed in vacuo. Recrystallization from dichloromethane yielded 0.16 g (0.19 mmol, 73%) of colorless crystalline **5**. $^1$H NMR (Et$_2$O, RT): $\delta$ = 13.4 ppm (s, ***H***); $^{13}$C{$^{19}$F} NMR (Et$_2$O, RT): $\delta$ = 110.9 (d, $^1J$(C,P) = 91 Hz, ***C***F$_2$), 119.3 ppm (t, $J$ = 7 Hz, ***C***F$_3$); $^{19}$F NMR (Et$_2$O, RT): $\delta$ = −121.9 (d, m, $^2J$(P,F) = 106 Hz, 2F, C***F***$_2$), −79.7 ppm (s, 3 F, C***F***$_3$); $^{31}$P NMR (Et$_2$O, RT): $\delta$ = 80.0 ppm (m, ***P***); IR (ATR): $\tilde{\nu}$ = 471 (s), 548 (m), 593 (m), 629 (m), 749 (m), 873 (s), 977 (s), 1083 (s), 1116 (s), 1200 (s), 1306 cm$^{-1}$ (m).

**Synthesis of $2[C_{14}H_{19}N_2]^+[Pd\{P(C_2F_5)(OH)O\}_4]^{2-}$ (6)**: $(C_2F_5)P(O)(OH)H$ (0.33 g, 1.78 mmol) was added to a suspension of $[Pd(acac)_2]$ (0.14 g, 0.44 mmol) in 5 mL of diethyl ether and stirred at room temperature resulting in a light-yellow solution. A solution of 1,8-bis(dimethylamino)naphthalene (0.19 g, 0.89 mmol) in diethyl ether was slowly added. The precipitate was filtered and washed with diethyl ether. The residue was dissolved in acetonitrile and all volatile compounds were removed in vacuo yielding a colorless solid **6** (0.54 g; 0.42 mmol, 95%). $^1$H NMR ([D$_3$]acetonitrile, RT): $\delta$ = 3.1 (d, $J$ = 3 Hz, 12H, N(C***H***$_3$)$_2$), 7.7 (t, $^3J$(H,H) = 8 Hz, 2H, *meta*-C***H***), 7.9 (d, $^3J$(H,H) = 8 Hz, 2H, *ortho*-C***H***), 8.0 (d, $^3J$(H,H) = 8 Hz, 2H, *para*-C***H***), 12.3 (s, 2H, O***H***), 18.7 ppm (s, 1H, N···***H***···N); $^{13}$C{$^1$H} NMR ([D$_3$]acetonitrile, RT): $\delta$ = 45.8 (s, ***C***H$_3$), 119.2 (s, *meta*-***C***), 121.6 (s, *ortho*-***C***H), 127.1 (s, *meta*-***C***H), 129.3 (s, *para*-***C***H), 135.4 (s, *ortho*-***C***), 144.3 ppm (s, ***C***N); $^{13}$C{$^{19}$F} NMR ([D$_3$]acetonitrile, RT): $\delta$ = 112.9 (m, ***C***F$_2$), 119.9 ppm (m, ***C***F$_3$); $^{19}$F NMR ([D$_3$]acetonitrile, RT): $\delta$ = −124.7 (m, 2F, C***F***$_2$), −80.2 ppm (s, 3F, C***F***$_3$); $^{31}$P NMR ([D$_3$]acetonitrile, RT): $\delta$ = 97.7 ppm (m, ***P***); IR (ATR): $\tilde{\nu}$ = 378 (m), 399 (m), 419 (m), 436 (m), 463 (s), 481 (s), 543 (m), 590 (m), 744 (m), 769 (s), 834 (m), 972 (s), 1015 (s), 1099 (s), 1135 (m), 1198 (s), 1300 (m), 1340 (w), 1376 (w), 1417 (w), 1463 (w), 1477 cm$^{-1}$ (w); elemental analysis calcd (%) for $C_{36}H_{42}F_{20}N_4O_8P_4Pd$: C 34.07, H 3.33, N 4.42; found: C 34.35, H 3.56, N 4.76.

**Synthesis of $[Pd_2(\mu\text{-}Cl)_2\{[P(C_2F_5)(OH)O]_2H\}_2]$ (8a)**: The reaction mixture of $PdCl_2$ (0.11 g, 0.63 mmol) and $(C_2F_5)P(O)(OH)H$ (0.23 g, 1.26 mmol) in dichloromethane (5 mL) during 11 d led to the precipitation of a colorless solid. All volatile compounds were removed in vacuo and excess $(C_2F_5)P(O)(OH)H$ was distilled off. The residue was dissolved in diethyl ether and filtered. All volatile compounds were removed in vacuo yielding 0.30 g (0.30 mmol, 95%)

of light-yellow solid **8a**. $^{1}$H NMR (dioxane, RT): $\delta = 13.1$ ppm (s, ***H***); $^{13}$C{$^{19}$F} NMR (dioxane, RT): $\delta = 110.6$ (d, $^{1}J$(C,P) = 88 Hz, ***C***$F_2$), 119.1 ppm (t, $J = 7$ Hz, ***C***$F_3$); $^{19}$F NMR (dioxane, RT): $\delta = -122.2$ (d, m, $^{2}J$(P,F) = 105 Hz, 2F, C***F***$_2$), $-79.6$ ppm (s, 3 F, C***F***$_3$); $^{31}$P NMR (dioxane, RT): $\delta = 79.5$ ppm (m, ***P***); IR (ATR): $\tilde{\nu} = 419$ (m), 447 (m), 473 (m), 503 (m), 528 (m), 549 (m), 593 (w), 630 (w), 749 (m), 834 (m), 912 (m), 948 (m), 983 (m), 1028 (m), 1118 (s), 1200 (s), 1302 cm$^{-1}$ (m).

**Synthesis of $[Pd_2(\mu\text{-}Cl)_2\{[P(CF_3)(OH)O]_2H\}_2]$ (8b)**: $(CF_3)P(O)(OH)H$ (0.22 g, 1.64 mmol) was dissolved in diethyl ether and two drops of water were added. After the addition of $PdCl_2$ (0.105 g, 0.60 mmol) in diethyl ether (5 mL) the reaction mixture was stirred at ambient temperature for 3 h. The colorless reaction mixture was filtered and all volatile compounds were removed in vacuo yielding 0.24 g (0.29 mmol, 97%) of light-yellow solid **8b**. $^{1}$H NMR ($Et_2O$, RT): $\delta = 13.5$ ppm (s, ***H***); $^{19}$F NMR ($Et_2O$, RT): $\delta = -73.2$ ppm (d, m, $^{2}J$(P,F) = 112 Hz, C***F***$_3$); $^{31}$P NMR ($Et_2O$, RT): $\delta = 74.8$ ppm (m, ***P***); IR (ATR): $\tilde{\nu} = 475$ (s), 500 (s), 555 (s), 579 (m), 743 (m), 828 (m), 909 (m), 939 (m), 1042 (m), 1123 (s), 1193 (m), 1387 (w), 1444 (w), 1503 (w), 1685 (w), 2267 (w), 2852 (w), 2922 (w), 2995 cm$^{-1}$ (w).

**Synthesis of $[Pd_2(\mu\text{-}Cl)_2\{[P(C_6F_5)(OH)O]_2H\}_2]$ (8c)**: $(C_6F_5)P(O)(OH)H$ (0.58 g, 2.52 mmol) was added to a slurry of $PdCl_2$ (0.11 g, 0.63 mmol) in dichloromethane (5 mL) and stirred at room temperature for 3 days. The suspension was filtered and washed with dichloromethane. The colorless residue was dissolved in diethyl ether and filtered. The solvent was removed in vacuo yielding 0.31 g (0.26 mmol, 83%) of colorless solid **8c**. $^{1}$H NMR ($Et_2O$, RT): $\delta = 11.3$ ppm (s, ***H***); $^{13}$C{$^{19}$F} NMR ($Et_2O$, RT): $\delta = 137.8$ (m, *meta*-C), 143.6 (s, *para*-C), 147.0 ppm (s, *ortho*-C); $^{19}$F NMR ($Et_2O$, RT): $\delta = -162.7$ (m, 2F, *meta*-F), $-150.9$ (t, $^{3}J$(F,F) = 20 Hz, 1F, *para*-F), $-132.3$ (m, 2F, *ortho*-F); $^{31}$P NMR ($Et_2O$, RT): $\delta = 73.2$ ppm (s, ***P***); IR (ATR): $\tilde{\nu} = 431$ (m), 455 (m), 475 (s), 507 (m), 524 (s), 543 (m), 586 (w), 636 (m), 655 (w), 727 (m), 761 (w), 791 (m), 832 (m), 911 (s), 951 (s), 979 (s), 1059 (m), 1094 (s), 1155 (w), 1235 (w), 1297 (w), 1385 (w), 1475 (s), 1517 (m), 1643 (w), 2300 (w), 2737 (w), 2880 (w), 2986 cm$^{-1}$ (w).

## Acknowledgements

Merck KGaA (Darmstadt, Germany) is acknowledged for financial support. We are grateful to the Solvay GmbH (Hannover, Germany) for providing chemicals. We thank Dr. Julia Bader and Prof. Dr. Lothar Weber for helpful discussions.

**Keywords:** coordination modes · cross-coupling · fluorine · palladium · phosphorus · platinum

[1] N. V. Dubrovina, A. Börner, *Angew. Chem.* **2004**, *116*, 6007 – 6010.
[2] L. Ackermann, *Synthesis* **2006**, 1557 – 1571.
[3] J. Chatt, B. T. Heaton, *J. Chem. Soc. A* **1968**, 2745 – 2757.
[4] a) C. King, D. M. Roundhill, F. R. Fronczek, *Inorg. Chem.* **1987**, *26*, 4288 – 4290; b) M. Sokolov, E. Chubarova, A. Virovets, R. Llusar, V. Fedin, *J. Cluster Sci.* **2003**, *14*, 227 – 235; c) M. N. Sokolov, R. Hernandez-Molina, W. Clegg, V. P. Fedin, A. Mederos, *Chem. Commun.* **2003**, 140 – 141; d) M. N. Sokolov, E. V. Chubarova, K. A. Kovalenko, I. V. Mironov, A. V. Virovets, E. V. Peresypkina, V. P. Fedin, *Russ. Chem. Bull.* **2005**, *54*, 615 – 622; e) D. N. Akbayeva, M. Di Vaira, S. Seniori Costantini, M. Peruzzini, P. Stoppioni, *Dalton Trans.* **2006**, 389 – 395; f) R. Hernández Molina, I. Kalinina, M. Sokolov, M. Clausen, J. Gonzalez Platas, C. Vicent, R. Llusar, *Dalton Trans.* **2007**, 550 – 557; g) A. G. Algarra, M. G. Basallote, M. J. Fernandez-Trujillo, R. Hernandez-Molina, V. S. Safont, *Chem. Commun.* **2007**, 3071.
[5] B. Kurscheid, H.-G. Stammler, B. Neumann, B. Hoge, *Z. Anorg. Allg. Chem.* **2012**, *638*, 534 – 542.
[6] N. Allefeld, J. Bader, B. Neumann, H.-G. Stammler, N. Ignatiev, B. Hoge, **2015**: DOI: 10.1021/acs.inorgchem.5b01038.
[7] B. Kurscheid, L. Belkoura, B. Hoge, *Organometallics* **2012**, *31*, 1329 – 1334.
[8] G. M. Sheldrick, *Acta Cryst.* **2008**, *64*, 112 – 122.
[9] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339 – 341.

Received: May 20, 2015
Published online on August 6, 2015