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Palladium Complexes

Phosphido-Bridged Di- and Trinuclear Palladium Complexes from Electron-Poor Phosphanes R_2PH (R = C_2F_5, C_6F_5, $(CF_3)_2C_6H_3$)

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Abstract: Electron-withdrawing substituents R in complexes [L_n M(PR_2)] influence the P–M bond length due to a decreased σ-donation and enhanced π-back-bonding, leading to an increased Lewis acidity of the metal ion and therefore strengthening the M–L bond to electron-rich ligands L. This influences the Lewis acidity and the redox behavior of corresponding transition-metal complexes, which is important for the design of optimized catalytic systems. To investigate this effect, the electron-poor phosphanes R_2PH with R = C_2F_5, C_6F_5, 2,4-$(CF_3)_2C_6H_3$ were treated with Pd(F_6acac)$_2$ (F_6acac = hexafluoroacetylacetonato) and Pd(acac)$_2$ (acac = acetylacetonato). While the reaction of the phosphanes with Pd(F_6acac)$_2$ in all cases yielded the corresponding phosphido-bridged dinuclear palladium complexes [{(F_6acac)Pd[μ-(PR_2)]}$_2$], the compounds obtained in the reaction with Pd(acac)$_2$ were structurally more diverse. For R = C_2F_5, the dinuclear palladium complex [{(acac)Pd{μ-[P(C_2F_5)$_2$]}}$_2$] was obtained, while the reaction with $(C_6F_5)_2PH$ yielded a trinuclear palladium complex bridged by four phosphido units. All complexes were fully characterized, including X-ray crystallography.

Introduction

The structural motif of 1,3-diphospha-2,4-dimetallacyclobutane rings is well-known in transition-metal complexes. Phosphido bridges decorated by perfluoroalkyl- or –aryl groups, however, are rare. A few iron complexes with CF_3 substituents at the phosphorus atom are reported by Grobe et al.,[1] Dobbie et al.[2] and Clegg,[3] other examples comprise metals of groups 6,[4] 7,[5] 9[6] and 10[7].

While complexes with μ-diphenylphosphido ligands are well-characterized, only three compounds are described for their perfluorinated counterpart C_6F_5: [{(CO)$_3$Fe{μ-[P(C_6F_5)$_2$]}}$_2$],[8] [{(CO)$_3$Ru{μ-[P(C_6F_5)$_2$]}}$_2$],[8] and $Pd_2(C_6F_5)_2$[μ-P(C_6F_5)CH_2CH_2P(C_6F_5)$_2$]$_2$.[9] Of these, only the palladium complex has been structurally characterized. In fact, it is the only known palladium complex with a Pd(μ-P)$_2$Pd four-membered ring in which the phosphorus atoms bear perfluorinated substituents. No such example with CF_3 substituents or even alkyl substituents bearing a fluorine atom at the α-carbon atom is documented; only one heavier homologue, the platinum complex [{Cl(PEt_3)Pt{μ-[P(CF_3)H]}}$_2$],[7] is known. And while a handful of neutral Pd^{II} complexes with bridging dialkylphosphido units have been reported in the literature,[10] no X-ray structural data are available.

The most conducive and feasible procedure to synthesize dinuclear palladium(II) complexes with bridging phosphido units was devised by Shmidt, Belykh and Goremyka.[11] They precisely describe the reaction of Ph_2PH with Pd(acac)$_2$ (acac = acetylacetonato) which led to di- and trinuclear palladium complexes bridged by diphenylphosphido units. A related complex featuring chelating F_6acac ligands (F_6acac = hexafluoroacetylacetonato), albeit synthesized differently, was published by Röschenthaler et al. including an X-ray structural investigation.[12]

Perfluoroalkyl and -aryl groups distinctly influence the electronic properties of phosphane ligands. The HOMO, which correlates with the negative ionization energy, as well as the LUMO, which correlates with the negative electron affinity, of the fluorinated phosphane derivatives are lowered (Figure 1, left), which is expressed in a decreased nucleophilicity of the

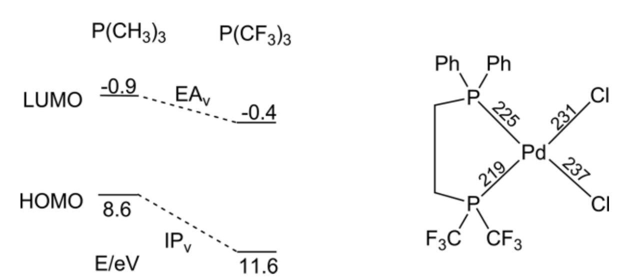

Figure 1. Left: schematic depiction of frontier orbital energies with calculated (B3LYP/6-311G(d,p))[16] ionization potential (IP_V ≈ –HOMO) and electron affinity (EA_V ≈ –LUMO) of trimethylphosphane and tris(trifluoromethyl)phosphane. Right: [$PdCl_2${$Ph_2PCH_2CH_2P(CF_3)_2$}] with bond lengths.[17]

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lone pair (i.e. decreased σ-bonding) and an increased Lewis acidity (i.e. enhanced π-back-bonding).[13] One means to measure this effect is the Tolman electronic parameter. In accordance with Tolman's concept, the carbonyl vibration bands of the nickel complexes $[Ni(CO)_3PR_3]$ (R = CF_3, C_2F_5, C_6F_5) are shifted by 22–49 cm^{-1} towards higher wave numbers in comparison to their non-fluorinated counterparts.[14,15]

Muir et al. documented the influence of electron-withdrawing substituents by means of the molecular structure of the complex $[PdCl_2\{Ph_2PCH_2CH_2P(CF_3)_2\}]$ (Figure 1, right).[17] The higher Lewis acidity of the $P(CF_3)_2$ unit in comparison to the PPh_2 unit manifests itself in a shortened Pd–$P(CF_3)_2$ bond as a result of an increased π-back-bonding from the Pd atom. Thus, the electron-withdrawing substituents at the phosphorus ligands induce an increased Lewis acidic behavior of the central metal ion. Correspondingly, the Pd–Cl bond length to the Cl atom *trans* to the $P(CF_3)_2$ unit is shortened by about 6 pm in comparison to the Cl atom *trans* to the PPh_2 unit.

The increased electron-withdrawing character of perfluoroorganyl groups was successfully employed by our group for the development of highly active catalysts for the Suzuki coupling. These complexes were synthesized via the treatment of phosphinous acids R_2POH with different palladium precursors.[18]

To access a broader range of finely tunable palladium complexes, we investigated the reaction of secondary phosphanes R_2PH with palladium acetylacetonato derivatives.

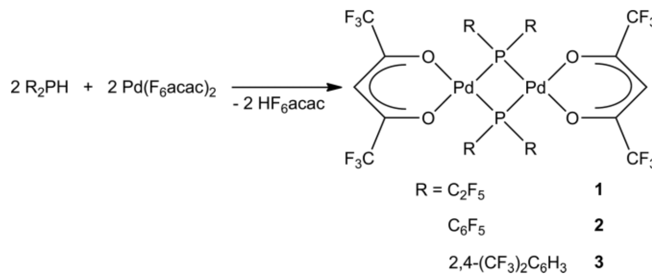
Fluorinated secondary phosphanes R_2PH exhibit an increased Brønsted acidity. Deprotonation results in the corresponding phosphanides $[PR_2]^-$ (R = CF_3, C_2F_5, C_6F_5) that were isolated either as ligands in transition-metal complexes[15,19] or even as the phosphanide salt $[K[18]crown\text{-}6][P(CF_3)_2]$.[20]

In this paper we will give an account on the synthesis and characterization of the products obtained from the reaction between $Pd(F_6acac)_2$ or $Pd(acac)_2$ and the electron-poor phosphanes R_2PH (R = CF_3, C_2F_5, C_6F_5, 2,4-$(CF_3)_2C_6H_3$) and discuss the influence of electron-withdrawing substituents.

Results and Discussion

^{31}P NMR spectroscopic monitoring of the reaction of $(CF_3)_2PH$ with $Pd(F_6acac)_2$ (F_6acac = hexafluoroacetylacetonato) discloses a broadening of the phosphane resonance. A second resonance at –8.6 ppm is assigned to the diphosphane $(CF_3)_2PP(CF_3)_2$[21] as the result of a reductive elimination.

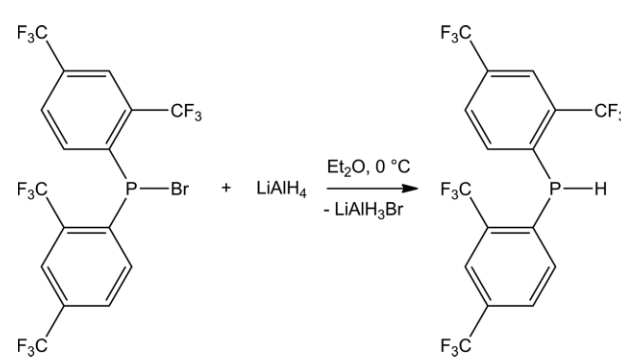
The reaction of the heavier homologue $(C_2F_5)_2PH$ with $Pd(F_6acac)_2$, however, selectively gives rise to the formation of $[\{(F_6acac)Pd\{\mu\text{-}[P(C_2F_5)_2]\}\}_2]$, **1** (Scheme 1). NMR spectroscopy, usually a highly valuable tool for compounds featuring a perfluoroalkyl- or –aryl phosphorus unit, failed for a satisfactory characterization of the complexes described in this paper. The molecular structures could not be derived from NMR experiments alone and had to be elucidated by an X-ray crystal structure analysis (see below). In the ^{31}P NMR spectrum of **1** the phosphorus atom gives rise to a multiplet at $\delta(^{31}P)$ = –98.8 ppm which is observed as a sharp singlet upon ^{19}F decoupling. This resonance is markedly shielded in comparison to the one of $(C_2F_5)_2PH$ ($\delta(^{31}P)$ = –50.8 ppm).[15] The ^{19}F NMR spectrum exhibits one set of signals for the CF_3 and CF_2 units. The resonance of the CF_3 units is observed as a singlet at –80.2 ppm, while the CF_2 units gave a multiplet of higher order at –97.6 ppm with a $^2J(PF)$ coupling constant of about 35 Hz, which is comparatively small for bis(pentafluoroethyl)phosphane derivatives. ^{31}P decoupling again leads to a sharp singlet. Additionally, the resonance for the CF_3 groups of the F_6acac ligand is observed at –75.1 ppm in the typical range for one F_6acac ligand chelating a palladium atom.



Scheme 1. Synthesis of palladium complexes **1**, **2** and **3**.

The reaction of $(C_6F_5)_2PH$ with $Pd(F_6acac)_2$ proceeds analogously to **1**, with a selective formation of $[\{(F_6acac)Pd\{\mu\text{-}[P(C_6F_5)_2]\}\}_2]$, **2** (Scheme 1). **2** is only poorly soluble which impeded meaningful ^{13}C NMR spectra. The ^{31}P NMR spectrum shows a multiplet at –175.8 ppm which, upon ^{19}F decoupling, turns into a sharp singlet. The resonances for the F_6acac ligand and the C_6F_5 rings in the ^{19}F NMR spectrum are observed in the expected range and their integrals are consistent with the proposed structure.

In contrast to many functionalized bis[2,4-bis(trifluoromethyl)phenyl]phosphane derivatives, bis[2,4-bis(trifluoromethyl)phenyl]phosphane, $[(CF_3)_2C_6H_3]_2PH$, has not been described in the literature before. The corresponding aminophosphane $[(CF_3)_2C_6H_3]_2PNEt_2$[22] was chosen as a conducive precursor which upon treatment with two equivalents of gaseous HBr selectively afforded the corresponding bromophosphane as a colorless solid in an 84 % yield. Its NMR data agree with the ones reported by Dillon et al.[23] Similar to the synthesis of $(C_6F_5)_2PH$ described by Schmutzler et al.,[24] the bromophosphane was treated with a 1 M solution of $LiAlH_4$ in diethyl ether. The mixture was subsequently quenched with aqueous HCl. After the removal of all volatile compounds in vacuo and recrystallization of the residue from *n*-pentane, $[(CF_3)_2C_6H_3]_2PH$ was obtained as a colorless solid in a 67 % yield (Scheme 2).

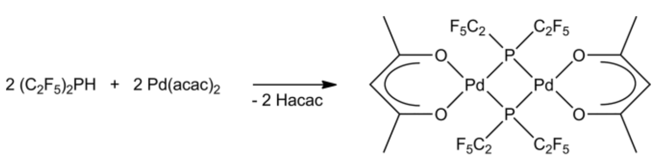


Scheme 2. Synthesis of bis[2,4-bis(trifluoromethyl)phenyl]phosphane.

Its ^{31}P NMR spectrum exhibits a doublet of septets at –49.8 ppm with a ^{1}J(PH) coupling constant of 232 Hz which is comparable to the C_2F_5 derivative (^{1}J(PH)=230 Hz)[15] as well as the C_6F_5 (^{1}J(PH)=218 Hz)[24] and Ph derivative (^{1}J(PH)=214 Hz).[25] The ^{4}J(PF) coupling constant of 38 Hz is rather small compared to other bis[2,4-bis(trifluoromethyl)phenyl]phosphane derivatives which usually are found in the range of 55–65 Hz.[22,23,26,27]

The reaction of the phosphane $[(CF_3)_2C_6H_3]_2PH$ with Pd(F_6acac)$_2$, analogously, selectively furnished the dinuclear palladium complex [{(F_6acac)Pd{μ-{P[$C_6H_3(CF_3)_2]_2$}}}$_2$], **3** (Scheme 1). The ^{31}P NMR resonance is shifted about 30 ppm to higher field and is observed at –80.6 ppm as a broad multiplet. The ^{19}F NMR spectrum displays two broad signals for the ortho-CF_3 groups in a ratio of 1.3:1. This is probably due to a hindered rotation of one ortho-CF_3 group per P[$C_6H_3(CF_3)_2]_2$ unit, as in the solid-state structure of **3** an F···P contact was observed (see below). The ^{1}H NMR spectrum exhibits resonances for the aromatic protons that also point at a hindered rotation.

Treating $(CF_3)_2$PH with the non-fluorinated palladium precursor Pd(acac)$_2$ (acac = acetylacetonato) again results in a broadening of the resonance in the ^{31}P NMR spectrum without any significant shifts in the ^{31}P or ^{19}F NMR spectrum, as well as in the formation of the diphosphane $(F_3C)_2PP(CF_3)_2$.



4

Scheme 3. Synthesis of palladium complex **4**.

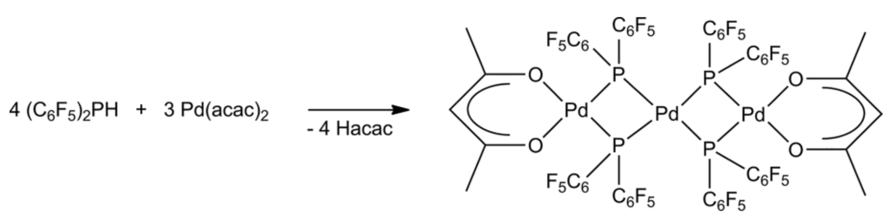
The reaction of Pd(acac)$_2$ with $(C_2F_5)_2$PH in diethyl ether selectively gives rise to the formation of [{(acac)Pd{μ-[P($C_2F_5)_2$]}}$_2$], **4** (Scheme 3).

The resonance in the ^{31}P NMR spectrum is detected as a multiplet of higher order at $\delta(^{31}P)$ = –88.6 ppm. ^{19}F decoupling leads to a sharp singlet. The ^{19}F NMR spectrum is similar to that of the F_6acac complex, with a singlet at –80.2 ppm for the CF_3 units and a higher-order multiplet at –98.8 for the CF_2 units with a ^{2}J(PF) coupling constant of about 30 Hz. The ^{1}H NMR spectrum displays signals for the acetylacetonato ligand at 5.4 and 2.2 ppm with corresponding signals in the ^{13}C NMR spectrum at 26.5 for the CH_3 groups, 99.1 for the CH unit and 185.8 for the oxygen-bound carbon atom. The latter resonance as well as the resonance for the CH_3 groups are split into triplets with coupling constants of ^{3}J(PC) = 2 and ^{4}J(PC) = 6 Hz, respectively. After removal of all volatile compounds, the compound remained as a red powder.

At a first glance, the reaction of $(C_6F_5)_2$PH with Pd(acac)$_2$ seems to proceed analogously to that with Pd(F_6acac)$_2$. The ^{31}P{^{19}F} NMR spectrum reveals a sharp singlet at –177.0 ppm. But contrary to the complexes discussed above, complex **5** (Scheme 4) is obtained as a trinuclear palladium complex with four bridging bis(pentafluorophenyl)phosphido units and two chelating acac ligands, as confirmed by an X-ray analysis (see below).

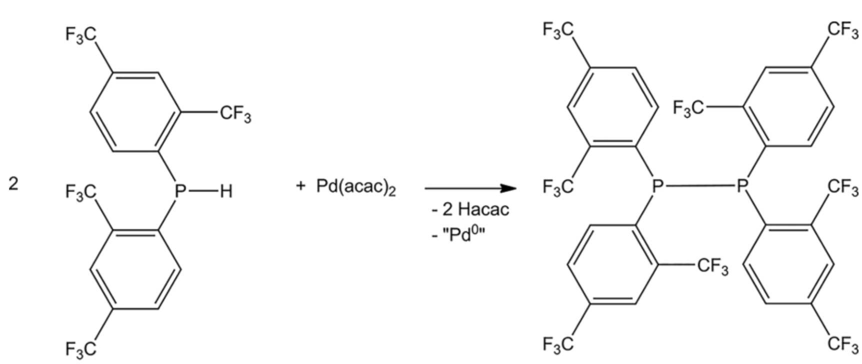
The resonances of the C_6F_5 rings in the ^{19}F NMR spectrum are comparable to those of **2**.

Surprisingly, the reaction of [2,4-$(CF_3)_2C_6H_3]_2$PH with Pd(acac)$_2$ affords tetrakis[2,4-bis(trifluoromethyl)phenyl]diphosphane, **6**, which was isolated as a colorless solid in a 56 % yield (Scheme 5). Until now, this diphosphane has been an elusive species. A common reaction, the treatment of a bis[2,4-bis(tri-



5

Scheme 4. Synthesis of the trinuclear palladium complex **5**.



6

Scheme 5. Synthesis of tetrakis[2,4-bis(trifluoromethyl)phenyl]diphosphane, **6**.

fluoromethyl)phenyl]halogenophosphane with elemental mercury or antimony powder, does not yield any conversion at all, not even at elevated temperatures.

The ^{31}P NMR spectrum is characterized by a broad multiplet of higher order at –27.8 ppm. Proton-decoupling shows a slightly decreased linewidth, while fluorine-decoupling leads to a broad singlet with shoulders. The ^{19}F NMR spectrum exhibits two signals: the resonance of the para CF_3 groups is observed as a singlet at –63.5 ppm, while the ortho CF_3 groups give rise to a multiplet (formally an $[[A_3]_2X]_2$ spin system; A = ^{19}F, X = ^{31}P) at –57.6 ppm which on ^{31}P decoupling is observed as a singlet.

X-ray Structural Investigation

Compound **1** crystallizes in the monoclinic space group $P2_1$ with two molecules per unit cell (Figure 2); two of the six C_2F_5 groups are disordered. The overall structure is quite similar to that of [{(F_6acac)Pd[*μ*-(PPh_2)]}$_2$] described by Röschenthaler et al.[12] The only striking difference concerns the averaged Pd–O distance of 204.8 pm which is about 6 pm shorter than in the Ph derivative [{(F_6acac)Pd[*μ*-(PPh_2)]}$_2$].[12] The P–Pd bond lengths of **1**, however, are with d_{av} = 223.9 pm comparable to those of the Ph derivative (d_{av} = 223.6 pm). While the π-back-bonding from the metal in **1** clearly compensates for the reduced σ-basicity which results in comparable Pd–P bond lengths of the C_2F_5 and Ph derivative, the increased Lewis acidity at the metal atom in **1** leads to shortened Pd–O bond lengths.

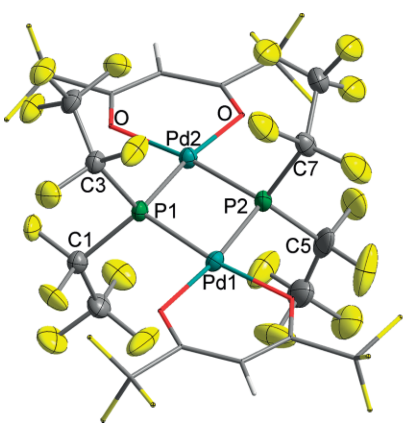


Figure 2. Molecular structure of [{(F_6acac)Pd{*μ*-[P(C_2F_5)$_2$]}}$_2$] (**1**). Thermal ellipsoids are shown at the 50 % probability level. For clarity, F_6acac ligands are displayed in a wires/sticks model and the minor occupied parts of the disorder (ratio 57:43) are omitted.

The Pd–P–Pd bond angles are 104.45(6) and 104.67(6)° and the P–Pd–P bond angles amount to only 75.20(5) and 75.17(5)°. This results in a Pd1–Pd2 distance of 354.23(6) pm and a short P1–P2 distance of 273.2(2) pm, which is about 100 pm shorter than the sum of the van-der-Waals radii. These structural features are also observed in many neutral Pd^{II} complexes with a Pd(μ-P)$_2$Pd four-membered ring, although especially the P–P distance of **1** is rather short compared to the average P–P distance of about 280 pm.[9,12,28] The C-P–C angles amount to 101.6(3) and 106.6(5)°.

2 crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell (Figure 3). The distances and angles are largely comparable to **1** and are summarized in Table 1.

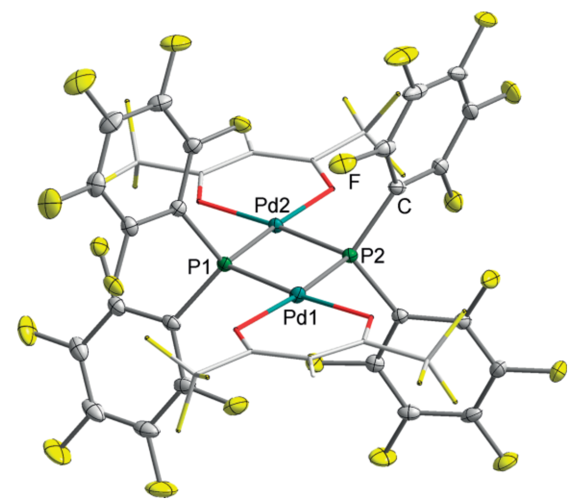


Figure 3. Molecular structure of [{(F_6acac)Pd{*μ*-[P(C_6F_5)$_2$]}}$_2$] (**2**). Thermal ellipsoids are shown at the 50 % probability level. For clarity, F_6acac ligands are displayed in a wires/sticks model. Disorder of one CF_3 group (F_6acac) (ratio 56:44).

3 crystallizes in the monoclinic space group $P2_1/n$ with one solvent molecule (diethyl ether) per formula unit (Figure 4). One CF_3 group is disoredered (ratio 73:27). The average Pd–O distance of 208.18 pm is slightly longer than in complexes **1** (204.8 pm) or **2** (207.1 pm), indicating a decreased Lewis acidity

Table 1. Comparison of selected structural parameters of [{(F_6acac)Pd{*μ*-[P(C_2F_5)$_2$]}}$_2$] (**1**), [{(F_6acac)Pd{*μ*-[P(C_6F_5)$_2$]}}$_2$] (**2**), [{(F_6acac)Pd{*μ*-{P[C_6H_3(CF_3)$_2$]$_2$}}}$_2$] (**3**)·Et_2O, [{(acac)Pd{*μ*-[P(C_2F_5)$_2$]}}$_2$] (**4**), and [Pd{{*μ*-[P(C_6F_5)$_2$]$_2$}Pd(acac)}$_2$] (**5**)·2PhCl.

	1	2	3	4	5
d_{av}(Pd–P) / pm	223.9	223.8	225.4	225.2	225.2[a] 234.8[b]
d_{av}(Pd–O) / pm	204.8	207.11	208.18	202.60	204.50
d(P–P) / pm	273.19	275.15	274.77	278.36	283.14[c]
d(Pd–Pd) / pm	354.23	353.16	339.82	354.12	354.65 (1–2) 341.07 (2–3)
$<_{av}$(P–Pd–P') / °	75.19	75.84	75.10	76.34	77.91[a] 74.17[b]
$<_{av}$(Pd–P–Pd') / °	104.56	104.16	97.84	103.660	98.29
$<_{av}$(C-P–C') / °	104.14	106.65	109.70	87.993	106.38

[a] acacPd(*μ*-P)$_2$. [b] Pd(*μ*-P)$_4$. [c] Average.

of the $P[C_6H_3(CF_3)_2]_2$ unit in comparison with the $P(C_2F_5)$ unit. The four-membered ring $Pd(\mu\text{-}P)_2Pd$ is highly bent with an angle of 143.90(3)°, which results in a shortened Pd–Pd distance of 339.82(3) pm and a Pd–P–Pd angle of only 97.84°. F18 and F19 display weak F···P contacts of 295.24(18) and 294.02(16) pm and are nearly linearly aligned with the opposite atoms (F18–P1–C6 = 175.38(9) and F19–P2–Pd1 = 176.82(4)°).

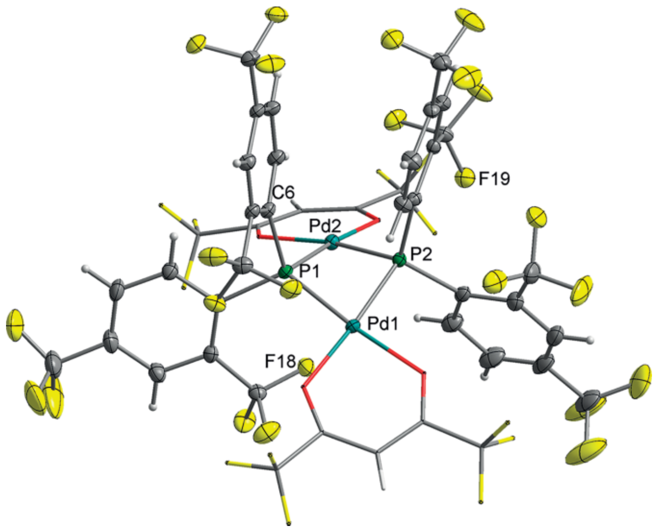


Figure 4. Molecular structure of $[\{(F_6acac)Pd\{\mu\text{-}\{P[C_6H_3(CF_3)_2]_2\}\}\}_2]$ (**3**)·Et_2O. Thermal ellipsoids are shown at the 50 % probability level. For clarity, F_6acac ligands are displayed in a wires/sticks model and the solvent molecule and the minor occupied CF_3 group were omitted.

4 crystallizes in the triclinic space group $P\bar{1}$ at a center of inversion (Figure 5) with disordered C_2F_5 groups. Due to a decomposition of the crystal at low temperatures, the measurement was performed at 250 K which led to large thermal ellipsoids. The bond lengths and angles are generally comparable to its F_6acac counterpart **1**, with a slightly longer P–P distance of 278.36(2) pm.

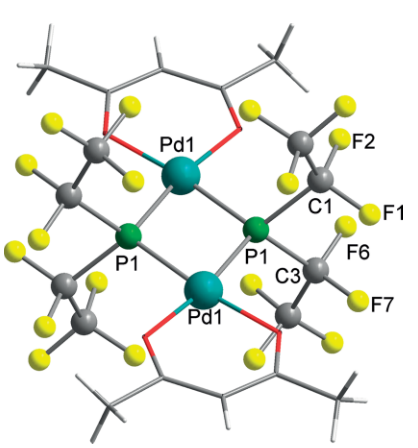


Figure 5. Molecular structure of $[\{(acac)Pd\{\mu\text{-}[P(C_2F_5)_2]\}\}_2]$ (**4**). For clarity, acac ligands are displayed in a wires/sticks model; only major occupied parts are shown.

5 crystallizes in the triclinic space group $P\bar{1}$ with two chlorobenzene molecules, which served as a solvent, per formula unit (Figure 6). The two four-membered rings $(Pd(\mu\text{-}P)_2Pd)$ deviate significantly from planarity with fold angles of 23.55(2)° resp. 39.59(2)° along the P–P line and 29.11(2)° resp. 47.02(2)° along Pd–Pd. This results in considerably shortened Pd–Pd distances of 354.65(1) pm (Pd1–Pd2) and 341.07(1) pm (Pd2–Pd3). The mean P–Pd–P angle of the $(acac)Pd(\mu\text{-}P)_2$ unit (77.91°) is slightly widened compared to its counterpart in the $Pd(\mu\text{-}P)_4$ unit (74.17°). These units also exhibit significantly differing Pd–P bond lengths: The mean Pd–P bond length in the $(acac)Pd(\mu\text{-}P)_2$ units of 225.2 pm is comparable with those obtained in complexes **1–4**, while the average Pd2–P bond length of the central $Pd(\mu\text{-}P)_4$ unit of 234.8 pm is significantly longer. A similar observation has been made by Mathey and Le Floch for their trinuclear bis(diphosphaferrocene) palladium complex in which the Pd–P bonds of 243.05(7) and 251.60(7) pm of the central $Pd(\mu\text{-}P)_4$ unit are between 20 and 30 pm longer than those in the outer $L_2Pd(\mu\text{-}P)_2$ units.[29]

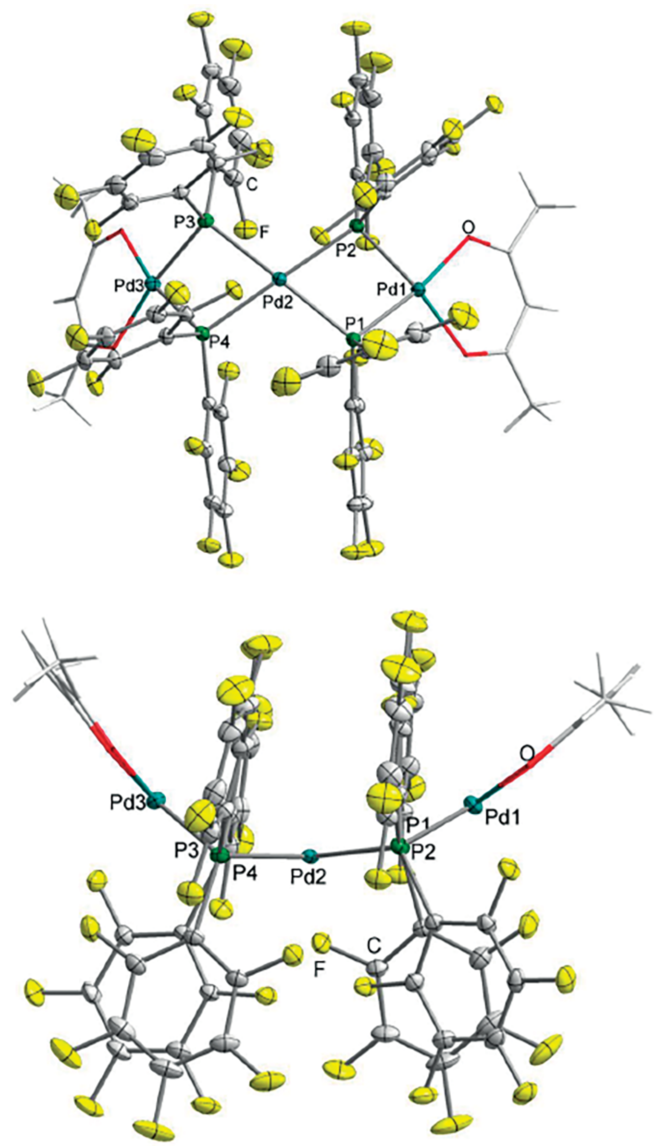


Figure 6. Molecular structure of $[Pd\{\{\mu\text{-}[P(C_6F_5)_2]_2\}Pd(acac)\}_2]$ (**5**)·2PhCl. Thermal ellipsoids are shown at the 50 % probability level. For clarity, acac ligands are displayed in a wires/sticks model and solvent molecules were omitted.

6 crystallizes in the monoclinic space group *C*2/*c* at a two-fold axis with four formula units per unit cell (Figure 7) and heavily disordered solvent molecules. The P–P′ distance of 223.15(5) pm fits well into the range of P–P bonds in diphosphanes $R_2P–PR_2$, for example 221.7 for R = Ph,[30] 224.6 for R = CF_3,[31] 224.8 for R = C_6F_5[32] and 226.0 for R = Mes.[33] The C-P–C angle of 101.12(4)° is well comparable to the ones observed in solid-state structures of other bis[2,4-bis(trifluoromethyl)phenyl)phosphane derivatives.[22,23,26] Like these examples, **6** also exhibits weak P···F contacts between ortho-CF_3 fluorine atoms and the phosphorus atom in a range of 307–313 pm.

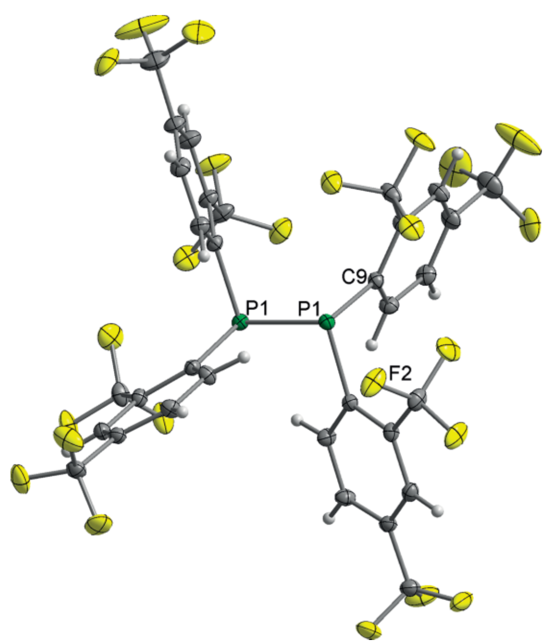


Figure 7. Molecular structure of $[(CF_3)_2C_6H_3]_2PP[C_6H_3(CF_3)_2]$ (**6**). Thermal ellipsoids are shown at the 50 % probability level. Disorder of one CF_3 group (ratio 58:42); only major occupied part is shown.

Conclusions

We investigated the influence of electron-withdrawing substituents R in the palladium complexes [{(L)Pd{*μ*-[PR_2]}}$_2$]. The corresponding complexes were obtained by the reaction of the phosphanes R_2PH (R = CF_3, C_2F_5, C_6F_5, $(CF_3)_2C_6H_3$) with Pd(F_6acac)$_2$ and Pd(acac)$_2$. A synthetic protocol for the so far unknown $[(CF_3)_2C_6H_3]_2PH$ was devised. The reaction of the phosphanes with Pd(F_6acac)$_2$ yielded the corresponding phosphido-bridged dinuclear palladium complexes [{(F_6acac)Pd-[*μ*-(PR_2)]}$_2$], which exhibit shortened Pd–O bond lengths in comparison with the non-fluorinated Ph derivative. This can be rationalized by an increased Lewis acidity of the Pd atom, induced via the electron-withdrawing effect of the substituents R at the phosphorus atoms. The compounds obtained in the reaction with Pd(acac)$_2$ were structurally more diverse. For R = C_2F_5, the dinuclear palladium complex [{(acac)Pd{*μ*-[P(C_2F_5)$_2$]}}$_2$] was obtained, while the reaction with $(C_6F_5)_2PH$ yielded a trinuclear palladium complex bridged by four phosphido units. The reaction with $[(CF_3)_2C_6H_3]_2PH$ yielded the diphosphane $[(CF_3)_2C_6H_3]_2PP[C_6H_3(CF_3)_2]_2$ as the main product.

Experimental Section

$(C_2F_5)_2PH$,[15] $(C_6F_5)_2PH$[24] and $[2,4-(CF_3)_2C_6H_3]_2PNEt_2$[22] were synthesized following literature procedures. All other chemicals were obtained from commercial sources and used without further purification. Standard high-vacuum techniques were employed for all preparative procedures. Non-volatile compounds were handled in a dry N_2 atmosphere using Schlenk techniques. NMR spectra were recorded with a Bruker Avance III 300 (^{1}H: 300.13 MHz; ^{13}C: 75.47 MHz; ^{19}F: 282.40 MHz; ^{31}P: 111.92 MHz) and a Bruker Avance III 500 HD spectrometer (^{1}H: 500.20 MHz; ^{13}C: 125.79 MHz; ^{19}F: 470.61 MHz; ^{31}P: 202.48 MHz) with positive shifts being downfield from the external standards [85 % orthophosphoric acid (^{31}P), CCl_3F (^{19}F) and TMS (^{1}H, ^{13}C)]. IR spectra were recorded on an ALPHA-FT-IR spectrometer (Bruker Daltonik GmbH, Bremen, Germany) using an ATR unit with a diamond crystal for liquids and solids. Melting and visible decomposition points were determined using a Mettler Toledo MP70-Melting Point System. Elemental analyses were carried out with a HEKAtech Euro EA 3000. Crystal data were collected with a Rigaku Supernova diffractometer with $Mo_{K\alpha}$ (λ=71.073 pm) radiation at 100.0 K except for **4** which was measured at 250 K. Using Olex2,[34] the structures were solved with the ShelXS[35] structure solution program using Direct Methods and refined with the ShelXL[36 refinement package using Least Squares minimization. Crystals of **6** contained heavily disordered diethyl ether molecules that could not be refined reasonably, so a solvent mask was applied. Details of the X-ray investigation are given in Table 2.

CCDC 1937087 (for **1**), 1937088 (for **2**), 1937089 (for **3**), 1937090 (for **4**), 1937091 (for **5**), and 193092 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of [{(F_6acac)Pd{*μ*-[P(C_2F_5)$_2$]}}$_2$] (1): $(C_2F_5)_2PH$ (1.0 mmol) was condensed onto a solution of Pd(F_6acac)$_2$ (0.381 g, 0.732 mmol) in diethyl ether. The reaction mixture was stirred at room temperature for 24 h, during which the solution turned orange-red and an off-white solid precipitated. After filtration and washing of the solid with diethyl ether, the solid was dried in vacuo (0.413 g, 97 %). Single crystals were obtained by combining $(C_2F_5)_2PH$ and Pd(F_6acac)$_2$ in diethyl ether without stirring and storage of the mixture for three days. M.p. 171–176 °C. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 6.4 ppm (s, br, 1H, F_6acac); ^{19}F NMR ($CDCl_3$, 282.40 MHz): δ = –75.1 (s, 6F, **F$_6$**acac), –80.2 (s, 6F, CF_2**CF_3**), –97.6 ppm (m, ^2J(PF)~35 Hz, 4F, CF_2); ^{31}P NMR ($CDCl_3$, 111.92 MHz): δ = –98.8 ppm (m); ^{31}P{^{19}F} NMR ($CDCl_3$, 111.92 MHz): δ = –98.8 ppm (s); IR (ATR): $\tilde{\nu}$ = 2923 (vw), 2853 (vw), 1632 (w), 1610 (m), 1579 (vw), 1559 (vw), 1532 (vw), 1443 (w), 1305 (w), 1254 (m), 1204 (vs), 1145 (vs), 1103 (vs), 952 (s), 809 (m), 749 (s), 685 (m), 630 (w), 593 (m), 513 (w), 481 (m), 443 (w), 424 (w), 407 (vw) cm^{-1}; elemental analysis calcd. (%) for $C_{18}H_2F_{32}O_4P_2Pd_2$: C 18.56, H 0.17; found C 17.92, H 0.10.

Synthesis of [{(F_6acac)Pd{*μ*-[P(C_6F_5)$_2$]}}$_2$] (2): $(C_6F_5)_2PH$ (0.269 g, 0.735 mmol) was dissolved in diethyl ether (10 mL) and treated with solid Pd(F_6acac)$_2$ (0.381 g, 0.732 mmol). The yellow solution was stirred for 10 min whereupon a yellow solid precipitated. It was filtered off, washed with diethyl ether (5 mL) and dried in vacuo. [{(F_6acac)Pd{*μ*-[P(C_6F_5)$_2$]}}$_2$] remained as a yellow solid (0.400 g, 80 %). Single crystals were obtained from acetone by slow evaporation of the solvent. M.p. 209–211 °C. ^{19}F NMR ([D$_6$]acetone, 470.61 MHz): δ = –75.1 (s, 6F, **F$_6$**acac), –125.7 (d, m, ^3J(FF)=21 Hz, 4F, ortho-F), –146.4 (t, m, ^3J(FF)=21 Hz, 2F, para-F), –160.4 ppm (t,

Table 2. Structure and refinement data for [{(F_6acac)Pd{μ-[P(C_2F_5)$_2$]}}$_2$] (**1**), [{(F_6acac)Pd{μ-[P(C_6F_5)$_2$]}}$_2$] (**2**), [{(F_6acac)Pd{μ-{P[C_6H_3(CF_3)$_2$]$_2$}}}$_2$] (**3**)·Et_2O, [{(acac)Pd{μ-[P(C_2F_5)$_2$]}}$_2$] (**4**), [Pd{{μ-[P(C_6F_5)$_2$]$_2$}Pd(acac)}$_2$] (**5**)·2PhCl, and [(CF_3)$_2C_6H_3$]$_2$PP[C_6H_3(CF_3)$_2$]$_2$ (**6**).

	1	2	3	4	5	6
Empirical formula	$C_{18}H_2F_{32}O_4P_2Pd_2$	$C_{34}H_2F_{32}O_4P_2Pd_2$	$C_{46}H_{24}F_{36}O_5P_2Pd_2$	$C_{18}H_{14}F_{20}O_4P_2Pd_2$	$C_{70}H_{24}Cl_2F_{40}O_4P_4Pd_3$	$C_{32}H_{12}F_{24}P_2$
Formula weight / g mol^{-1}	1164.94	1357.10	1615.39	949.03	2202.87	914.36
Crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a / Å	9.7326(2)	9.59065(17)	15.97470(10)	8.0934(3)	12.29780(12)	7.74570(10)
b / Å	15.9713(3)	12.2578(3)	14.09430(10)	10.4552(4)	13.71540(13)	24.3118(3)
c / Å	10.6702(3)	17.7907(4)	25.3792(2)	10.5046(4)	23.23519(19)	20.0956(3)
α / °	90	81.5690(18)	90	115.693(4)	87.1821(7)	90
β / °	108.172(3)	84.7168(17)	96.0150(10)	102.072(4)	87.9762(7)	95.4820(10)
γ / °	90	79.6801(16)	90	100.240(3)	70.4764(9)	90
V / Å^3	1575.89(7)	2030.76(7)	5682.72(7)	746.05(6)	3688.52(6)	3766.93(9)
Z	2	2	4	1	2	4
ρ_{calc} / g cm^{-3}	2.455	2.219	1.888	2.112	1.983	1.612
μ / mm^{-1}	1.463	1.153	0.852	1.463	1.035	0.258
F(000)	1104.0	1296.0	3144.0	456.0	2136.0	1800.0
Crystal size / mm^{-3}	0.27 × 0.14 × 0.01	0.50 × 0.32 × 0.24	0.27 × 0.19 × 0.15	0.32 × 0.19 × 0.09	0.38 × 0.28 × 0.22	0.38 × 0.26 × 0.19
2Θ range for data collection /°	4.0 to 60.0	3.4 to 60.1	3.2 to 60.2	5.9 to 60.0	3.2 to 60.1	3.4 to 64.4
Index ranges	$-13 \le h \le 13$, $-22 \le k \le 22$, $-15 \le l \le 15$	$-13 \le h \le 13$, $-17 \le k \le 17$, $-25 \le l \le 25$	$-22 \le h \le 22$, $-19 \le k \le 19$, $-35 \le l \le 35$	$-11 \le h \le 11$, $-14 \le k \le 14$, $-14 \le l \le 14$	$-17 \le h \le 17$, $-19 \le k \le 19$, $-32 \le l \le 32$	$-11 \le h \le 11$, $-35 \le k \le 34$, $-30 \le l \le 29$
Reflections collected	30878	118854	322462	14371	214741	61378
Data/restraints/parameters	9172/1/534	11864/15/662	16697/0/829	4357/0/195	21590/1/1133	6330/0/314
Goodness-of-fit on F^2	1.053	1.056	1.291	1.059	1.063	1.089
R_1/wR_2 [$I > 2\sigma(I)$]	R_1 = 0.0359, wR_2 = 0.0853	R_1 = 0.0251, wR_2 = 0.0585	R_1 = 0.0416, wR_2 = 0.0816	R_1 = 0.0500, wR_2 = 0.1495	R_1 = 0.0218, wR_2 = 0.0554	R_1 = 0.0341, wR_2 = 0.0864
R_1/wR_2 (all data)	R_1 = 0.0393, wR_2 = 0.0875	R_1 = 0.0264, wR_2 = 0.0592	R_1 = 0.0444, wR_2 = 0.0826	R_1 = 0.0605, wR_2 = 0.1611	R_1 = 0.0242, wR_2 = 0.0566	R_1 = 0.0368, wR_2 = 0.0877
Largest diff. peak/hole /e Å^{-3}	0.93/–0.73	0.93/–0.75	1.15/–1.03	0.75/–0.68	0.57/–0.49	0.48/–0.29
CCDC number	1937087	1937088	1937089	1937090	1937091	1937092

m, ^3J(FF)=21 Hz, 4F, meta-F); ^{31}P{^{19}F} NMR ([D$_6$]acetone, 202.48 MHz): δ = –175.8 ppm (s); IR (ATR): $\tilde{\nu}$ = 1629 (m), 1605 (w), 1556 (vw), 1517 (m), 1475 (vs), 1460 (m), 1389 (w), 1345 (vw), 1298 (w), 1258 (m), 1210 (s), 1144 (vs), 1092 (vs), 1018 (vw), 975 (vs), 857 (w), 844 (vw), 817 (vw), 802 (m), 765 (vw), 746 (vw), 724 (vw), 682 (m), 630 (w), 590 (w), 518 (w), 509 (w), 494 (m), 446 (w), 435 (m), 412 (w) cm^{-1}; elemental analysis calcd. (%) for $C_{34}H_2F_{32}O_4P_2Pd_2$: C 30.09, H 0.15; found 30.10, H 0.25.

Synthesis of [2,4-(CF_3)$_2C_6H_3$]$_2$PBr: A solution of [2,4-(CF_3)$_2C_6H_3$]$_2$PNEt$_2$ (4.361 g, 8.239 mmol) in diethyl ether (50 mL) was cooled to –15 °C and stirred in an atmosphere of gaseous HBr (23 mmol) until the pressure was stable. Stirring of the mixture was continued for 30 min at room temperature. The precipitate was filtered off and washed with diethyl ether (20 mL). The combined organic phases were dried in vacuo. The remaining yellowish oil was dissolved in *n*-pentane and stored overnight at –28 °C. The supernatant was separated and the colorless solid dried in vacuo. [2,4-(CF_3)$_2C_6H_3$]$_2$PBr remained as a colorless solid (3.701 g, 84 %). The NMR data agree with the ones reported by Dillon et al.[22] Elemental analysis calcd. (%) for $C_{16}H_6BrF_{12}P$: C 35.78, H 1.13; found C 35.57, H 1.00.

Synthesis of [2,4-(CF_3)$_2C_6H_3$]$_2$PH: A solution of $LiAlH_4$ in diethyl ether (1 M, 3.7 mL, 3.7 mmol) was added at 0 °C to a solution of [2,4-(CF_3)$_2C_6H_3$]$_2$PBr (1.66 g, 3.10 mmol) in diethyl ether. After stirring the mixture for 10 min, aqueous HCl (0.1 M, 5 mL) was added at 0 °C. The aqueous phase was separated, and the organic phase was freed from the solvent in vacuo. The remaining colorless oil was redissolved in *n*-pentane and stored overnight at –28 °C. The supernatant solution was separated and the remaining solid dried in vacuo. [2,4-(CF_3)$_2C_6H_3$]$_2$PH remained as a colorless solid (0.96 g, 67 %). ^{1}H NMR (CDCl$_3$, 300.13 MHz): δ = 5.7 (d, quin, ^1J(PH)=232, ^5J(FH)=3 Hz, 1H, PH), 7.5 (d, d, ^3J(HH)=8, J(PH)=5 Hz, 2H, H6), 7.7 (d, ^3J(HH)=8 Hz, 2H, H5), 8.0 ppm (s, 2H, H3); ^{13}C{^{1}H} NMR (CDCl$_3$, 75.47 MHz): δ = 123.1 (quar, ^1J(CF)=273 Hz, para-CF$_3$), 123.4 (quar, ^1J(CF)=275 Hz, ortho-CF$_3$), 123.7 (m, C3), 128.5 (m, C5), 131.7 (pseudo-d, J=34 Hz), 137.8 ppm (d, J=7 Hz, C6); ^{13}C{^{19}F}DEPT45 NMR (CDCl$_3$, 75.47 MHz): δ = 123.0 (t, d, ^3J(CH)=5, ^5J(PC)=1 Hz, para-CF$_3$), 123.4 ppm (d, t, ^3J(PC)=5, J=1 Hz, ortho-CF$_3$); ^{19}F NMR (CDCl$_3$, 282.40 MHz): δ = –59.5 (d, d, ^4J(PF)=37, ^5J(FH)=3 Hz, 3F, ortho-CF$_3$), –63.2 ppm (s, 3F, para-CF$_3$); ^{31}P NMR (CDCl$_3$, 111.92 MHz): δ = –49.8 ppm (d, sept(br), ^1J(PH)=232, ^4J(PF)=38 Hz); ^{31}P{^{19}F} NMR (CDCl$_3$, 111.92 MHz): δ = –49.8 ppm (d, pseudo-sept, ^1J(PH)=232, $^{3/4}J$(PH)=3 Hz); IR (ATR): $\tilde{\nu}$ = 2922 (vw), 2853 (vw), 2374 (vw), 1619 (vw), 1571 (vw), 1339 (w), 1296 (w), 1277 (s), 1261 (m), 1172 (s), 1119 (vs), 1073 (s), 1036 (m), 943 (w), 912 (m), 842 (m), 808 (w), 747 (w), 730 (w), 698 (m), 662 (m), 609 (vw), 572 (w), 522 (vw), 474 (w) cm^{-1}.

Synthesis of [{(F_6acac)Pd{μ-{P[C_6H_3(CF_3)$_2$]$_2$}}}$_2$] (3): A solution of [(CF_3)$_2C_6H_3$]$_2$PH (0.313 g, 0.683 mmol) in diethyl ether (10 mL) was treated with solid Pd(F_6acac)$_2$ ((0.355 g, 0.682 mmol). The red solution was stirred for 2 h and the solvents evaporated to dryness. The remaining red oil was redissolved in a diethyl ether/*n*-pentane mixture (1:4) and stored overnight at –28 °C. The red supernatant was separated and the yellow residue dried in vacuo to give [{(F_6acac)Pd{μ-{P[C_6H_3(CF_3)$_2$]$_2$}}}$_2$] as a yellow solid (0.464 g, 90 %). M.p. 188–191 °C. ^{1}H NMR (CDCl$_3$, 500.20 MHz): δ = 6.1 (s (br), 1H, F_6acac), 7.6 (d, J(HH)=8 Hz, 2H, H5), 8.0 (m, 2H, H3/6), 8.4 ppm (m, 2H, H3/6); ^{13}C{^{1}H} NMR (CDCl$_3$, 125.79 MHz): δ = 90.5 (m, F$_3$CC(O)**C**H), 117.2 (quar, ^1J(CF)=286 Hz, F$_3$**C**C(O)CH), 122.4 (quar, ^1J(CF)=273 Hz, para-CF$_3$), 122.8 (quar, m, ^1J(CF)=276 Hz, ortho-CF$_3$), 124.4/7 (m, C3), 127.3/5 (m, C5), 129.9 (t, J=11 Hz, C1), 134.1 (quar, ^2J(CF)=35 Hz, C2/4), 139.4/6 (m, C6), 175.5 ppm (quar, ^2J(CF)=35 Hz,

$CF_3\mathbf{C}(O)CH$); $^{13}C\{^{19}F\}$DEPT135 NMR ($CDCl_3$, 125.79 MHz): δ = 117.2 (t, J=4 Hz, $F_3\mathbf{C}C(O)CH$), 122.4 (t, J=4 Hz, para-CF_3), 175.5 ppm (s, $CF_3\mathbf{C}(O)CH$); ^{19}F NMR ($CDCl_3$, 470.61 MHz): δ = –56.5 (s (br), 3F, ortho-CF_3), –57.1 (s (br), 3F, ortho-CF_3), –63.8 (s, ^1J(CF)=273 Hz, 6F, para-CF_3), –75.7 ppm (s, ^1J(CF)=284 Hz, 6F, F_6acac); ^{31}P NMR ($CDCl_3$, 202.48 MHz): δ = –80.6 ppm (m (br)); IR (ATR): $\tilde{\nu}$ = 1632 (w), 1608 (vw), 1556 (vw), 1528 (vw), 1469 (vw), 1459 (vw), 1341 (m), 1294 (w), 1281 (m), 1256 (s), 1222 (w), 1177 (m), 1130 (vs), 1099 (s), 1073 (vs), 1036 (m), 914 (w), 846 (w), 803 (w), 751 (w), 706 (w), 680 (w), 662 (w), 615 (vw), 591 (vw), 574 (w), 526 (w), 496 (vw), 475 (vw), 461 (vw), 442 (vw) cm^{-1}; elemental analysis calcd. (%) for $C_{42}H_{14}F_{36}O_4P_2Pd_2$: C 32.72, H 0.92; found C 32.42, H 0.91.

Synthesis of [{(acac)Pd{μ-[P(C_2F_5)$_2$]}}$_2$] (4): $(C_2F_5)_2PH$ (1.5 mmol) was condensed onto a suspension of Pd(acac)$_2$ (0.178 g, 0.584 mmol) in diethyl ether. The reaction mixture was stirred for 24 h at room temperature, during which the solution turned brown-red. All volatile compounds were removed in vacuo. The remaining red solid was redissolved in diethyl ether and stored for 2 days at –28 °C. The red supernatant was removed from the brown-beige solid which was dried in vacuo. [{(acac)Pd{μ-[P(C_2F_5)$_2$]}}$_2$] remained as a brown-beige solid (0.187 g, 70 %). ^1H NMR ($CDCl_3$, 300.13 MHz): δ = 2.0 (s, 6H, CH_3), 5.4 ppm (s, 1H, CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 26.5 (t, ^4J(PC)=6 Hz, CH_3), 99.1 (s, CH), 185.8 ppm (t, ^3J(PC)=2 Hz, **C**=O); $^{13}C\{^{19}F\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 113.4 (s, CF_2), 118.3 ppm (t, J=10 Hz, CF_3); ^{19}F NMR ($CDCl_3$, 282.40 MHz): δ = –80.2 (m, 3F, CF_3), –98.8 (m, ^2J(PF) ca. 30 Hz, CF_2); ^{31}P NMR ($CDCl_3$, 111.92 MHz): δ = –88.6 (m, ^2J(PF)=31 Hz); IR (ATR): $\tilde{\nu}$ = 1576 (w), 1557 (m), 1521 (m), 1433 (vw), 1372 (w), 1300 (m), 1273 (w), 1251 (s), 1201 (vs), 1125 (s), 1105 (s), 1024 (w), 952 (vs), 784 (w), 749 (s), 686 (vw), 663 (vw), 626 (w), 594 (w), 546 (vw), 519 (w), 480 (m), 448 (s), 415 (m) cm^{-1}.

Synthesis of [Pd{{μ-[P(C_6F_5)$_2$]$_2$}Pd(acac)}$_2$] (5): Pd(acac)$_2$ (0.280 g, 0.919 mmol) and $(C_6F_5)_2PH$ (0.450 g, 1.23 mmol) were dissolved in diethyl ether and the reaction mixture was stirred for 10 min. The red solution was dried in vacuo. The remaining dark red solid was redissolved in acetonitrile and extracted with *n*-pentane. The combined *n*-pentane phases were dried in vacuo. [Pd{{μ-[P(C_6F_5)$_2$]$_2$}-Pd(acac)}$_2$] remained as a light red solid (0.328 g, 62 %). Single-crystals were obtained by storing a PhCl solution at –28 °C. ^1H NMR ($CDCl_3$, 300.13 MHz): δ = 1.7 (s, 6H, CH_3), 5.2 ppm (s, 1H, CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 26.9 (s, CH_3), 99.7 (s, CH), 137.1 (d, m, ^1J(CF)=261 Hz, meta-CF), 142.3 (d, m, ^1J(CF)=260 Hz, para-CF), 147.4 (d, m, ^1J(CF)=250 Hz, ortho-CF), 186.2 ppm (s, C=O); $^{13}C\{^{19}F\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 137.1 (meta-CF), 142.3 (para-CF), 147.5 ppm (ortho-CF); ^{19}F NMR ($CDCl_3$, 282.40 MHz): δ = –124.9 (d, m, J=12 Hz, 2F, ortho-F), –148.2 (t, ^3J(FF)=20 Hz, 1F, para-F), –160.4 ppm (t(br), ^3J(FF)=20 Hz, 2F, meta-F); $^{31}P\{^{19}F\}$ NMR ($CDCl_3$, 111.92 MHz): δ = –179.9 ppm (s); IR (ATR): $\tilde{\nu}$ = 2923 (vw), 2853 (vw), 1640 (vw), 1575 (w), 1514 (s), 1467 (vs), 1384 (m), 1293 (w), 1265 (vw), 1200 (vw), 1147 (vw), 1089 (s), 1019 (w), 973 (vs), 932 (vw), 848 (vw), 835 (vw), 803 (vw), 776 (vw), 764 (vw), 753 (vw),721 (vw), 680 (vw), 623 (w), 589 (vw), 518 (w), 507 (vw), 461 (vw), 430 (m), 418 (m) cm^{-1}.

Synthesis of tetrakis[2,4-bis(trifluoromethyl)phenyl]diphosphane (6): A solution of [2,4-$(CF_3)_2C_6H_3$]$_2$PH (0.258 g, 0.563 mmol) in diethyl ether (10 mL) was treated with solid Pd(acac)$_2$ (0.170 g, 0.558 mmol). The intense red solution was stirred for 1 h and most of the solvent was evaporated. The remaining solution was stored at –28 °C for 3 days. The supernatant solution was separated and the remaining solid dried in vacuo. [2,4-$(CF_3)_2C_6H_3$]$_2$PP[C_6H_3-2,4-$(CF_3)_2$] remained as a colorless solid (0.144 g, 56 %). ^1H NMR ($CDCl_3$, 500.20 MHz): δ = 7.8 (d(br), ^3J(HH)=8 Hz, 1H, H5), 7.9 (s(br), 1H, H3), 8.2 ppm (d(br), ^3J(HH)=8 Hz, 1H, H6); $^1H\{^{19}F\}$ NMR ($CDCl_3$, 500.20 MHz): δ = 7.8 (d, d, ^3J(HH)=8, J=2 Hz, 1H, H5), 7.9 (quar, J= 2 Hz, 1H, H3), 8.2 ppm (d, ^3J(HH)=8, 1H, H6); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.79 MHz): δ = 122.7 (quar, ^1J(CF)=276 Hz, ortho-CF_3), 122.8 (quar, ^1J(CF)=273 Hz, para-CF_3), 124.2 (s(br), C3), 128.4 (quar, ^3J(CF)=3 Hz, C5), 132.8 (quar, ^2J(CF)=35 Hz, C4), 135.5 (m, C1, C2), 137.9 ppm (m, J=18 Hz, C6); $^{13}C\{^{19}F\}$DEPT135 NMR ($CDCl_3$, 125.79 MHz): δ = 122.7 (d(br), ^3J(CH)=5 Hz, ortho-CF_3), 122.8 (t, d, ^3J(CH)=4, ^4J(CH)=1 Hz, para-CF_3), 132.8 (d, ^3J(CH)=8 Hz, C4), 135.6 ppm (d, t, m, J=9, J= 6 Hz, C1, C2); ^{19}F NMR ($CDCl_3$, 470.61 MHz): δ = –57.6 (m, 3F, ortho-CF_3), –63.5 ppm (s, 3F, para-CF_3); $^{19}F\{^{31}P\}$ NMR ($CDCl_3$, 470.61 MHz): δ = –57.6 (s, 3F, ortho-CF_3), –63.5 ppm (s, ^1J(FC)=273 Hz, para-CF_3); ^{31}P NMR ($CDCl_3$, 202.48 MHz): δ = –27.8 ppm (m); $^{31}P\{^{19}F\}$ NMR ($CDCl_3$, 202.48 MHz): δ = –27.8 ppm (s(br)); IR (ATR): $\tilde{\nu}$ = 2921 (vw), 1618 (vw), 1572 (vw), 1339 (w), 1280 (m), 1259 (m), 1169 (m), 1127 (vs), 1072 (s), 1035 (m), 915 (w), 842 (w), 750 (vw), 699 (m), 672 (w), 663 (w), 575 (w), 524 (vw), 499 (vw), 472 (vw), 407 (vw) cm^{-1}; elemental analysis calcd. (%) for $C_{32}H_{12}F_{24}P_2$: C 42.04, H 1.32; found C 42.80, H 1.95.

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[1] J. Grobe, *Z. Anorg. Allg. Chem.* **1968**, *361*, 47–57.
[2] R. C. Dobbie, M. J. Hopkinson, D. Whittaker, *J. Chem. Soc., Dalton Trans.* **1972**, *10*, 1030.
[3] W. Clegg, *Inorg. Chem.* **2002**, *15*, 2928–2931.
[4] a) R. C. Dobbie, *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 191–193; b) J. Grobe, R. Haubold, *Z. Anorg. Allg. Chem.* **1985**, *522*, 159–170; c) J. Grobe, R. Haubold, *Z. Anorg. Allg. Chem.* **1986**, *534*, 121–136.
[5] a) J. Grobe, R. Rau, *J. Organomet. Chem.* **1978**, *157*, 281–297; b) J. Grobe, W. Mohr, *J. Fluorine Chem.* **1976**, *8*, 145–164.
[6] a) G. Beysel, J. Grobe, W. Mohr, *J. Organomet. Chem.* **1979**, *170*, 319–336; b) R. C. Dobbie, D. Whittaker, *J. Chem. Soc., Dalton Trans.* **1973**, 2427; c) J. Grobe, H. Stierand, *Z. Anorg. Allg. Chem.* **1969**, *371*, 99–105.
[7] H. Eshtiagh-Hosseini, H. W. Kroto, J. F. Nixon, M. J. Maah, M. J. Taylor, *J. Chem. Soc., Chem. Commun.* **1981**, *4*, 199.
[8] M. Cooke, M. Green, D. Kirkpatrick, *J. Chem. Soc. A* **1968**, 1507.
[9] R. H. Heyn, C. H. Görbitz, *Organometallics* **2002**, *21*, 2781–2784.
[10] a) R. G. Hayter, *Nature* **1962**, *193*, 872; b) R. G. Hayter, F. S. Humiec, *Inorg. Chem.* **1963**, *2*, 306-312; c) R. G. Hayter, *Inorg. Chem.* **1964**, *3*, 301–302; d) H. Goldwhite, A. S. Hirschon, *Trans. Met. Chem.* **1977**, *2*, 144–149; e) J. B. Brandon, K. R. Dixon, *Can. J. Chem.* **1981**, *59*, 1188–1200; f) A. S. Berenblyum, A. P. Aeeva, L. I. Lakhman, I. I. Moiseev, *J. Organomet. Chem.* **1982**, *234*, 237–248.
[11] a) F. K. Shmidt, L. B. Belykh, T. V. Goremyka, *Russ. J. Coord. Chem.* **2002**, *28*, 92–103; b) L. B. Belykh, T. V. Goremyka, S. V. Zinchenko, A. V. Rokhin, G. V. Ratovskii, F. K. Schmidt, *Russ. J. Coord. Chem.* **2002**, *28*, 664–670.
[12] G. Bekiaris, G. V. Röschenthaler, U. Behrens, *Z. Anorg. Allg. Chem.* **1992**, *618*, 153–157.
[13] M. Wiesemann, B. Hoge, *Chem. Eur. J.* **2018**, *24*, 16457–16471.
[14] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.
[15] A. V. Zakharov, Y. V. Vishnevskiy, N. Allefeld, J. Bader, B. Kurscheid, S. Steinhauer, B. Hoge, B. Neumann, H.-G. Stammler, R. J. F. Berger, N. W. Mitzel, *Eur. J. Inorg. Chem.* **2013**, 3392–3404.
[16] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Na-

katsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, **2013***.

[17] L. Manojlović-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, W. E. Hill, J. V. Quagliano, L. M. Vallarino, *J. Chem. Soc., Chem. Commun.* **1974**, 999–1000.

[18] For example: a) B. Hoge, J. Bader, B. Kurscheid, N. Ignat'ev, E. F. Aust, WO **2010**/009818 A1, **2010,** Merck Patent GmbH, Darmstadt; b) B. Kurscheid, L. Belkoura, B. Hoge, *Organometallics* **2011**, *31*, 1329–1334; c) B. Kurscheid, B. Neumann, H.-G. Stammler, B. Hoge, *Chem. Eur. J.* **2011**, *17*, 14935–14941.

[19] a) B. Hoge, C. Thösen, T. Herrmann, I. Pantenburg, *Inorg. Chem.* **2003**, *42*, 3633–3641; b) B. Hoge, T. Herrmann, C. Thösen, I. Pantenburg, *Inorg. Chem.* **2003**, *42*, 5422–5428; c) B. Hoge, C. Thösen, T. Herrmann, P. Panne, I. Pantenburg, *J. Fluorine Chem.* **2004**, *125*, 831–851.

[20] B. Hoge, C. Thösen, *Inorg. Chem.* **2001**, *40*, 3113–3116.

[21] A. B. Burg, *Inorg. Chem.* **2002**, *17*, 2322–2324.

[22] B. Hoge, B. Kurscheid, S. Peuker, W. Tyrra, H. T. M. Fischer, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1679–1685.

[23] A. S. Batsanov, S. M. Cornet, K. B. Dillon, A. E. Goeta, P. Hazendonk, A. L. Thompson, *J. Chem. Soc., Dalton Trans.* **2002**, *24*, 4622–4628.

[24] J. R. Goerlich, V. Plack, R. Schmutzler, *J. Fluorine Chem.* **1996**, *76*, 29–35.

[25] K. Moedritzer, L. Maier, L. C. D. Groenweghe, *J. Chem. Eng. Data* **1962**, *7*, 307–310.

[26] B. Hoge, B. Kurscheid, *Angew. Chem. Int. Ed.* **2008**, *47*, 6814–6816; *Angew. Chem.* **2008**, *120*, 6920.

[27] a) L. Heuer, P. G. Jones, R. Schmutzler, *J. Fluorine Chem.* **1990**, *46*, 243–254; b) B. Kurscheid, Dissertation, Universität Bielefeld, **2011**.

[28] a) M. J. Ray, M. Bühl, L. J. Taylor, K. S. Athukorala Arachchige, A. M. Z. Slawin, P. Kilian, *Inorg. Chem.* **2014**, *53*, 8538–8547; b) M. C. MacInnis, R. McDonald, L. Turculet, *Organometallics* **2011**, *30*, 6408–6415; c) A. T. Ekubo, M. R. J. Elsegood, A. J. Lake, M. B. Smith, *Inorg. Chem.* **2010**, *49*, 3703–3705; d) L. Chahen, B. Therrien, G. Süss-Fink, *Acta Crystallogr., Sect. E* **2007**, *63*, m1989–m1989; e) L. Boubekeur, L. Ricard, P. Le Floch, N. Mézailles, *Organometallics* **2005**, *24*, 3856–3863; f) W.-K. Wong, H. Liang, M.-Y. Yung, J.-P. Guo, K.-F. Yung, W.-T. Wong, P. G. Edwards, *Inorg. Chem. Commun.* **2004**, *7*, 737–740; g) H. Brunner, S. Dormeier, I. Grau, M. Zabel, *Eur. J. Inorg. Chem.* **2002**, *2002*, 2603–2613; h) M. A. Zhuravel, J. R. Moncarz, D. S. Glueck, K.-C. Lam, A. L. Rheingold, *Organometallics* **2000**, *19*, 3447–3454; i) T. Gebauer, G. Frenzen, K. Dehnicke, *Z. Naturforsch. B* **1992**, *47*, 1505–1512.

[29] M. Melaimi, L. Ricard, F. Mathey, P. Le Floch, *J. Organomet. Chem.* **2003**, *684*, 189–193.

[30] A. Dashti-Mommertz, B. Neumüller, *Z. Anorg. Allg. Chem.* **1999**, *625*, 954–960.

[31] G. Becker, W. Golla, J. Grobe, K. W. Klinkhammer, D. Le Van, A. H. Maulitz, O. Mundt, H. Oberhammer, M. Sachs, *Inorg. Chem.* **1999**, *38*, 1099–1107.

[32] M. Kuprat, M. Lehmann, A. Schulz, A. Villinger, *Inorg. Chem.* **2011**, *50*, 5784–5792.

[33] S. G. Baxter, A. H. Cowley, R. E. Davis, P. E. Riley, *J. Am. Chem. Soc.* **1981**, *103*, 1699–1702.

[34] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339–341.

[35] G. M. Sheldrick, *Acta Cryst. A* **2015**, *71*, 3–8.

[36] G. M. Sheldrick, *Acta Cryst. C* **2015**, *71*, 3–8.

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