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Routes to unique palladium A-frame complexes with a bridging fluoro-ligand

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Treatment of a toluene solution of $[PdMe_2(Cy_2PCH_2PCy_2)]$ (**1**) with pentafluoropyridine in the presence of traces of water affords the generation of the A-frame complexes $[(PdMe)_2\{\mu\text{-}\kappa^2(P,P)Cy_2PCH_2PCy_2\}_2(\mu\text{-}F)][SiMeF_4]$ (**2a**) and $[(PdMe)_2\{\mu\text{-}\kappa^2(P,P)Cy_2PCH_2PCy_2\}_2(\mu\text{-}F)][OC_5NF_4]$ (**2b**). If the reaction is performed in an NMR tube equipped with a PFA inliner, complex **2b** is produced, only. Treatment of **1** with pentafluoropyridine in the presence of an excess water yields the pyridyloxy complex $[PdMe(OC_5NF_4)(Cy_2PCH_2PCy_2)]$ (**3**). Compound $[(PdMe)_2\{\mu\text{-}\kappa^2(P,P)Cy_2PCH_2PCy_2\}_2(\mu\text{-}F)][FHF]$ (**2c**) bearing a bifluoride anion instead of $SiMeF_4^-$ or $OC_5NF_4^-$ can be generated by reaction of **1** with substoichiometric amounts of $Et_3N{\cdot}3HF$. The analogous complex $[(PdMe)_2\{\mu\text{-}\kappa^2(P,P)Ph_2PCH_2PPh_2\}_2(\mu\text{-}F)][FHF]$ (**5c**) has been synthesized by addition of $Ph_2PCH_2PPh_2$ to a solution of $[PdMe_2(Me_2NCH_2CH_2NMe_2)]$ (**4**) in THF and subsequent treatment of the reaction mixture with $Et_3N{\cdot}3HF$. The structure of the A-frame complex **5c** has been determined by X-ray crystallography.

Introduction

The combination of soft metals and hard ligands is known to lead often to complexes with unique properties and therefore an interesting synthetic chemistry.[1] In particular, transition-metal fluoro complexes reveal intriguing features, because the characteristics of fluorine impart an unusual reactivity to the metal–fluorine bond which can be exploited in preparative organometallic chemistry or in catalysis.[2–8] The nature of the metal–fluorine bond has been discussed controversely.[2,4,5,7–13] Thus, it has been reasoned that fluorine is a better π-donor than iodine or other halogen ligands.[4,10] At square-planar transition d^8 metal complexes this can lead to a destabilisation, because of a M–F d_π–p_π filled/filled interaction. This model has been questioned by several research groups, who suggest that fluorine is a very poor π-donor, but the properties of the transition-metal fluorine bond can be explained by its ionic component.[4,11,13] At square-planar d^8 complexes electrostatic interactions lead to a raise in energy of the metal based orbitals.[13] In either case a stabilisation can be achieved by a push/pull interaction induced by a π-acceptor ligand in the *trans*-position to the fluoride.[4,10,13] An alternative way to stabilise a late transition-metal fluoro moiety is to alleviate electron density from the fluorine. This can be achieved by a bridging mode of the fluoro ligand between two metal atoms or by a hydrogen bond, for example from the metal-bound fluorine to H_2O, to a CH unit, or to HF like in platinum-metal bifluoride complexes.[5,14–21]

There are a number of methods of introduction of fluorine at late transition-metal centres,[14–30] some of which have been surveyed in several reviews.[5,22] We found that palladium fluorides are accessible by oxidative addition of fluorinated aromatics.[21–23] As an alternative palladium iodides can be treated with AgF.[8,19,24,25] It has been shown by Grushin and Marshall that the latter method also led to the binuclear complexes $[PdPh(\mu\text{-}F)(PR_3)]_2$ (R = Cy, *i*Pr) bearing a bridging fluoride.[17] XeF_2 has been employed by Vigalok and co-workers to prepare palladium fluoro complexes by treatment of Pd(II) dimethyl phosphine compounds.[25]

Late transition-metal fluorides have also been synthesised by treatment of suitable precursors with $Et_3N{\cdot}3HF$, which is a mild source of HF.[15,16,18,19,26,28] However, this route often leads to the formation of bifluorides. Thus, palladium hydroxo complexes can be converted into palladium fluorides or bifluorides on treatment with $Et_3N{\cdot}3HF$, depending on the stoichiometry.[19,24] Note that at rhodium hydroxides or methoxides can be used in a comparable fashion to prepare rhodium fluorides.[28] We found that treatment of the hydrido compound $[HRh(PEt_3)_3]$ with $Et_3N{\cdot}3HF$ yields the fluoro complex $[RhF(PEt_3)_3]$.[18,26] Perutz and co-workers used ruthenium hydride precursors, some of which give by reaction with $Et_3N{\cdot}3HF$ the fluoride-bridged ruthenium complexes $[Ru_2(\mu\text{-}F)_3(PR_3)_6][F(HF)_n]$ (R = Et, Pr, Bu; $n \approx 3$).[15,16]

In this paper we describe the generation of cationic palladium complexes, which exhibit an A-frame structure and a bridging fluoro ligand. The compounds can be synthesised *via* two routes: (i) by treatment of a palladium(II) dimethyl complex with pentafluoropyridine in the presence of small amounts of water; or (ii) by reactions of palladium(II) dimethyl precursors with $Et_3N{\cdot}3HF$.

Results

Pentafluoropyridine as fluoride source

Treatment of a toluene solution of $[PdMe_2(Cy_2PCH_2PCy_2)]$ (**1**) with pentafluoropyridine at room temperature in a glass NMR tube affords after 7 d the generation of the binuclear palladium complex $[(PdMe)_2\{\mu\text{-}\kappa^2(P,P)Cy_2PCH_2PCy_2\}_2(\mu\text{-}F)][SiMeF_4]$ (**2a**) as a low-soluble white powder (Scheme 1). An NMR investigation of the reaction solution reveals the presence of small amounts of $[(PdMe)_2\{\mu\text{-}\kappa^2(P,P)Cy_2PCH_2PCy_2\}_2(\mu\text{-}F)][OC_5NF_4]$ (**2b**). The addition of Et_3N as a base has no influence on the product distribution. A reaction of **1** with 2,4,6-trifluoropyrimidine also yields **2a**, but a variety of additional organic products could not be further identified.

The NMR data of **2a** suggest the existence of a binuclear cation with A-frame configuration and the phosphines and one fluoro ligand in bridging positions.[31] The bridging fluoro ligand in **2a** appears in the ^{19}F NMR spectrum as a broad signal at high field at δ −387.[15,17] The resonance resolves to a quintet ($J_{PF} = 14.7$ Hz) in the proton decoupled spectrum. The ^{31}P NMR spectrum reveals only one signal at δ 19.7 with a characteristic doublet splitting ($J_{PF} = 16.2$ Hz) for the equivalent phosphorus nuclei. The protons at the CH_2 groups in the phosphines are prochiral, which results in a signal at δ 3.68 in the ^1H NMR spectrum. A COSY NMR spectrum confirms that the second

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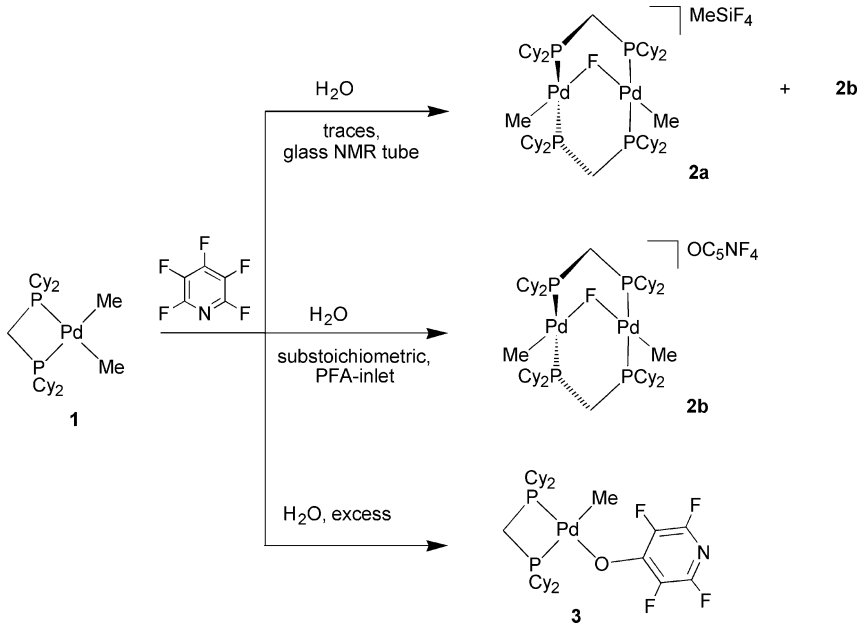


Scheme 1 Reactivity of **1** towards pentafluoropyridinepyridine and water.

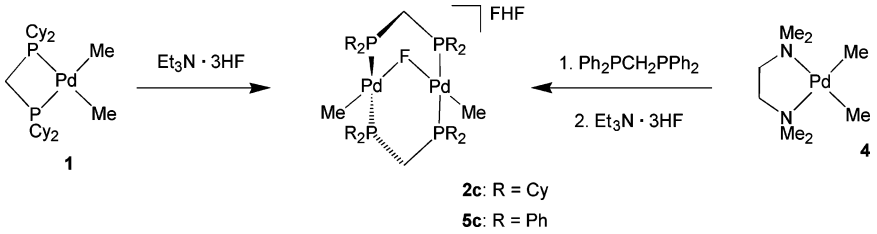
resonance at δ 1.9 is covered by the signals of the cyclohexyl group. A quartet ($J_{FH} = 5$ Hz) with ^{29}Si satellites ($J_{SiF} = 216$ Hz) at δ −111 ppm in the ^{19}F NMR spectrum and a quintet at δ 0.01 ppm ($J_{HF} = 5.0$ Hz) in the ^{1}H NMR spectrum can be assigned to the $SiMeF_4^-$ anion.[32] The NMR data of **2b** suggest a similar cationic A-frame structure as it has been found for **2a**. Two signals in the ^{19}F NMR spectrum at δ −101.7 and δ −171.1 reveal the presence of a tetrafluoropyridyloxy anion, which has been identified by comparison of its ^{19}F NMR data with these of its sodium salt.[33]

The presence of $SiMeF_4^-$ evidently arises from HF or fluoride attack at the glass tubes.[20,29,34] Sources of the fluoride anions can be fluoro complexes such as [Pd(F)(Me)($Cy_2PCH_2PCy_2$)] (**I**), [{(Pd(F)(Me)}$_2${μ-κ^2(*P*,*P*)$Cy_2PCH_2PCy_2$}$_2$] (**II**) or [(PdMe)$_2$-{μ-κ^2(*P*,*P*)$Cy_2PCH_2PCy_2$}$_2$(μ-F)]F (**III**). Especially an intermediate such as **III**, which exhibits an outer-sphere anion as a source for a "naked fluoride" seems to be precedented for the formation of an $SiMeF_4^-$ anion.[34] Compounds **I–III** are presumably intermediates for the formation of **2a** and are produced by reaction of **1** with HF. HF itself could be generated in a palladium-mediated process from pentafluoropyridine in presence of adventitious water, as it has been shown before.[35] Note, that for the synthesis of **1** water has been used in the work-up process.[36] Therefore, we performed the reactions in an NMR tube equipped with a PFA inliner using batches of **1**, which had been recrystallised several times. After treatment of **1** with pentafluoropyridine only tiny amounts of **2b** were formed and no **2a** was generated. Deliberate addition of small amounts of water to the reaction mixture gave immediately **2b**, confirming the assumption that a reaction of pentafluoropyridine with water is the source of the pyrdyloxy anion. Note that neither **1** reacts with water without the presence of the pentafluoropyridine, nor does the heterocycle react with water at room temperature without the presence of **1**.

Treatment of **1** with pentafluoropyridine in the presence of an excess water yields the pyridyloxy complex [PdMe(OC_5NF_4)($Cy_2PCH_2PCy_2$)] (**3**) (Scheme 1). Alternatively **3** can also be synthesised from **1** and 4-hydroxytetrafluoropyridine. The ^{1}H NMR spectrum of **3** reveals, apart for the signals of the metal bound phosphine ligand, a resonance at δ 0.26 for the methyl ligand at palladium. The ^{19}F NMR spectrum displays two multiplets at δ −97.9 and −167.2 for the tetrafluoropyridyloxy group. These chemical shifts are comparable to these found for [PdMe(OC_5NF_4)($Me_2NCH_2CH_2NMe_2$)], but distinctively different from the values obtained for a tetrafluoropyridyl ligand, which is directly connected to a metal centre at the 4-position.[21,35,38]

Synthesis of palladium A-frame complexes with $Et_3N{\cdot}3HF$ as fluorinating agent

In an alternative procedure to the C–F activation reactions described above, compound [(PdMe)$_2${μ-κ^2(*P*,*P*)-$Cy_2PCH_2PCy_2$}$_2$(μ-F)][FHF] (**2c**) bearing a bifluoride anion instead of $SiMeF_4^-$ or $OC_5NF_4^-$ can be generated by reaction of **1** with substoichiometric amounts of $Et_3N{\cdot}3HF$ (Scheme 2). The NMR data for the cation in **2c** are the same as these for **2a** or **2b**. However, instead of the signals for the silicate anion or pyridyloxy anion a new resonance at δ −155 ppm appears in the ^{19}F NMR spectrum. This observation and a broad signal in the ^{1}H NMR spectrum at δ 16.2 suggest the presence of bifluoride anion.[16,39] Low-temperature NMR data of **2c** at 193 K indeed reveal the expected triplet ($J_{HF} = 123$ Hz) in the ^{1}H NMR spectrum and the corresponding doublet in the ^{19}F NMR spectrum. The broadness of the signals at room temperature can be attributed to a dynamic behaviour involving the bifluoride anion. The exact nature of the fluoxionality is not clear, but variable-temperature NMR experiments reveal neither



Scheme 2 Formation of cationic complexes with A-frame structure.

a broadening of the signals for the methyl or methylene group in the ^{1}H NMR spectrum nor a shift of the resonance for the bridging fluoride in the ^{19}F NMR spectrum. This suggests that the A-frame geometry stays intact and indicates that a process in which a face-to-face dimer is formed is not involved.[15–17,40] We speculate that HF exchange between FHF^- and small amounts of polyfluoride anions $[F(HF)_x]^-$ might be the reason for the broadening.[15]

Because a complex analogous to the starting compound **1** bearing $Ph_2PCH_2PPh_2$ instead of $Cy_2PCH_2PCy_2$ can not be prepared,[37] complex $[(PdMe)_2\{\mu\text{-}\kappa^2(P,P)Ph_2PCH_2PPh_2\}_2(\mu\text{-}F)][FHF]$ (**5c**) has been synthesised by addition of $Ph_2PCH_2PPh_2$ to a solution of $[PdMe_2(Me_2NCH_2CH_2NMe_2)]$ (**4**) in THF and subsequent treatment of the reaction mixture with $Et_3N{\cdot}3HF$ (Scheme 2). The ^{1}H NMR spectroscopic data of the reaction solution reveal that the conversion is accompanied by the formation of methane and $[(Pd_3(\mu\text{-}\kappa^2(P,P)\text{-}Ph_2PCH_2PPh_2)_3]$.[37] However, **5c** can be isolated in a yield of 16%, because of its low solubility in THF. The ^{19}F and ^{31}P NMR spectroscopic data **5c** resemble the data found for **2c**.

The IR spectra of **2c** and **5c** exhibit a broad absorption band between 1600 and 1800 cm^{-1}, which is compatible with a free bifluoride anion.[16,41] Conductivity measurements of solutions in CH_2Cl_2 are also in accordance with the presence of an ionic compound.[39,40] A reaction of **5c** with Me_3SiCl affords Me_3SiF and the binuclear palladium complex $[(PdClMe)_2\{\mu\text{-}\kappa^2(P,P)\text{-}Ph_2PCH_2PPh_2\}_2]$ (**6**), which has been described before.[31]

Structure of 5c in the solid state

The colourless complex **5c** was crystallized at 20 °C from a solution in THF. The crystal structure was determined by X-ray diffraction at 100 K. The structure of the cation $[(PdMe)_2\text{-}\{\mu\text{-}\kappa^2(P,P)Ph_2PCH_2PPh_2\}_2(\mu\text{-}F)]^+$ is depicted in Fig. 1. Selected bond lengths and angles are summarised in Table 1. The cation exhibits an approximately square-planar geometry about each palladium atom, with the two planes inclined towards each other through the bridging fluoride. The Pd–F–Pd angle at the fluoro ligand of 87.92(5)° is smaller than the comparable angle in $[PdPh(\mu\text{-}F)(P\textit{i}Pr_3)]_2$ of 101.26°, possibly because of the phosphine brace in **5c**.[17] The Pd–Pd separation is 2.9956(2) Å. Complex **5c** has C_2 symmetry. The eight-membered $Pd_2P_4C_2$ ring adopts a twisted boat conformation, such that the CH_2 groups are oriented towards the bridging fluorine (Fig. 2). Along the Pd–Pd vector the cation exhibits a chiral axis defined by a torsion angle P–Pd–Pd–P of 19.1°. Similar distorted A-frame boat conformations with the halogen atom and the CH_2 groups on the same face of the Pd_2P_4 plane have been determined for other palladium complexes with a bridging chloride, iodide or bromide.[31,42] Only in one case a boat conformation with the CH_2 groups and the bridging halogen lying on opposite faces of the Pd_2P_4 plane has been observed.[43] The palladium fluoride bond of 2.1578(10) Å is longer than the Pd–F separation in mononuclear palladium fluoro complexes, and also longer than the comparable distances found in $[PdPh(\mu\text{-}F)(P\textit{i}Pr_3)]_2$ [2.098(1), 2.118(1) Å].[12,17,21,24,25] The F–F distance in the bifluoride anion of 2.29 Å is comparable to those found in other bifluoride salts.[41]

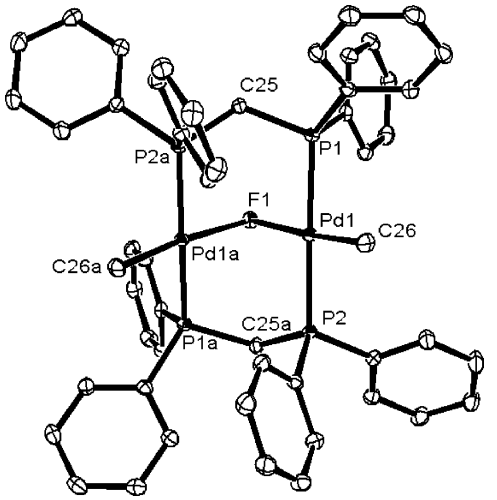


Fig. 1 Structure of the cation in **5c**.

Table 1 Selected bond lengths (Å) and angles (°) of $[(PdMe)_2\text{-}\{\mu\text{-}\kappa^2(P,P)Ph_2PCH_2PPh_2\}_2(\mu\text{-}F)][FHF]$ (**5c**) with the estimated standard deviations in parentheses

Pd(1)–F(1)	2.1578(10)	Pd(1)–Pd(1)	2.9956(2)
Pd(1)–P(1)	2.3066(4)	P(1)–C(25)	1.8387(15)
Pd(1)–P(2)	2.3025(4)	P(2a)–C(25)	1.8405(16)
Pd(1)–C(26)	2.0407(16)	F(2)–C(H2a)	1.452(10)
C(26)–Pd(1)–F(1)	174.11(5)	F(1)–Pd(1)–P(2)	92.038(11)
P(2)–Pd(1)–P(1)	171.997(15)	F(1)–Pd(1)–P(1)	82.906(12)
C(26)–Pd(1)–P(1)	92.80(5)	Pd(1)–F(1)–Pd(1a)	87.92(5)
C(26)–Pd(1)–P(2)	92.66(5)	P(1)–C(25)–P(2a)	116.32(8)

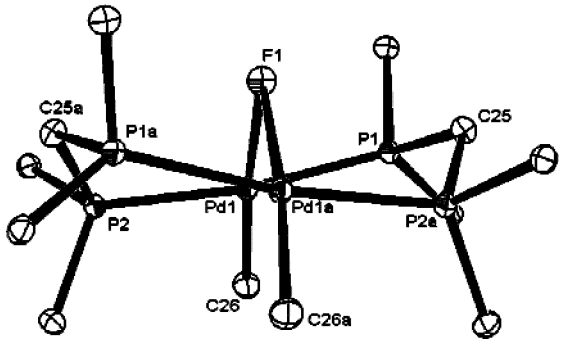
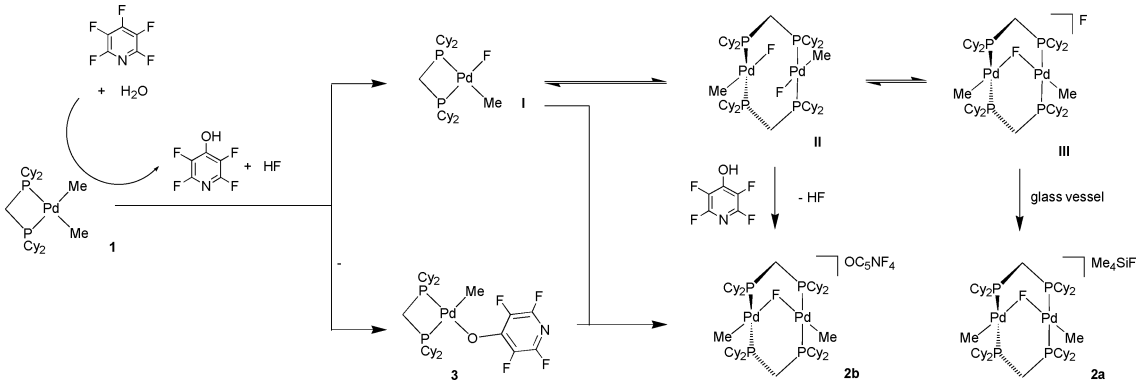


Fig. 2 Structure of the cation in **5c**; The phenyl groups are omitted for clarity.

Discussion

The syntheses of the A-frame complexes **2a–2c** and **5c** using pentafluoropyridine–water or $Et_3N{\cdot}3HF$ as sources of HF are shown in the Schemes 1 and 2. Mechanistically either an initial protonation at the metal—followed by reductive elimination of methane—or a protonation of the methyl ligand yielding methane and $[Pd(F)(Me)(Cy_2PCH_2PCy_2]$ (**I**) are conceivable.[18] In the presence of $Et_3N{\cdot}3HF$ two molecules of **I** rearrange to give the binuclear A-frame structures **2c** or **5c** and the bifluoride anion (Scheme 2).

Concerning the reaction pathway for the formation of **2a** and **2b**, there is some evidence that HF and 4-hydroxytetrafluoropyridine can be produced as intermediates from pentafluoropyridine and water in the presence of **1**. Note that it has been suggested before that $[PdMe_2(Me_2NCH_2CH_2NMe_2)]$ (**4**) can induce a substitution of fluorine by a hydroxy group in pentafluoropyridine to give HF and 4-hydroxytetrafluoropyridine from water.[35] We speculate about a similar transformation. Both compounds HF and intermediate 4-hydroxytetrafluoropyridine could react with **1** to afford $[Pd(F)(Me)(Cy_2PCH_2PCy_2)]$ (**I**) and $[PdMe(OC_5NF_4)(Cy_2PCH_2PCy_2)]$ (**3**), respectively (Scheme 3). In particular, the latter conversion might benefit from the fact that 4-hydroxytetrafluoropyridine, is already present in the coordination sphere of **1**. It also has been confirmed by an independent experiment that treatment of **1** with 4-hydroxytetrafluoropyridine yields complex **3**. From a mixture of **I** and **3** the A-frame complex **2b** can be furnished. Alternatively, binuclear complexes such as $[\{(Pd(F)(Me)\}_2\{\mu\text{-}\kappa^2(P,P)Cy_2PCH_2PCy_2\}_2]$ (**II**) or $[(PdMe)_2\text{-}\{\mu\text{-}\kappa^2(P,P)Cy_2PCH_2PCy_2\}_2(\mu\text{-}F)]F$ (**III**) might react with intermediate 4-hydroxytetrafluoropyridine to yield **2b** and HF (Scheme 3). However, although **1** does not react with water



Scheme 3 Possible reaction pathways for the formation of **2a** and **2b**.

without the presence of the heterocycle, we can not entirely exclude that under the reaction conditions an intermediate hydroxo complex is generated (*e.g.* from a palladium fluoride), which could react with pentafluoropyridine to give HF and $[PdMe(OC_5NF_4)(Cy_2PCH_2PCy_2)]$ (**3**). We were not able to identify any hydroxo complex or other intermediate by low-temperature NMR experiments.

It has been indicated in the introduction, that a strong π-acceptor ligand *trans* to the fluoride can stabilise a metal–fluorine interaction by diminishing the d_π–p_π filled/filled repulsion or the ionic character of the metal–fluorine bond. The instability of an intermediate such as $[Pd(F)(Me)(Cy_2PCH_2PCy_2)]$ (**I**) could therefore be attributed to a less favourable *trans*-position of the fluoride and the phosphine, which leads to the lability of the fluoro ligand (Scheme 3). On the other hand, Vigalok and co-workers described recently the square-planar palladium fluoro complexes $[PdF_2(L_2)]$ (L_2 = diisopropylphosphinopropane, dicyclohexylphosphinopropane) with a phosphine unit in the *trans*-position to the fluoride.[25] The existence of square-planar trisphosphine rhodium fluoro complexes also indicates that a phosphine ligand in the *trans* position to the fluoride might be sufficient.[18,26,28] Therefore, the formation of an A-frame structure might rather be attributed to the small bite angle of $R_2PCH_2PR_2$ (R = Cy, Ph) at palladium and the tendency of $R_2PCH_2PR_2$ to adopt a bridging coordination mode initially resulting in the binuclear complex $[\{(Pd(F)(Me)\}_2\{\mu\text{-}\kappa^2(P,P)Cy_2PCH_2PCy_2\}_2]$ (**II**).[31,40] The *trans* arrangement of fluoride and the methyl ligand in a complex such as **II** would be strongly disfavoured resulting in the A-frame geometry, in which a bridging mode of the fluoro ligand stabilises the transition-metal fluoro moiety.[15] Note that the molecular structure of the chloro compound $[(PdClMe)_2\{\mu\text{-}\kappa^2(P,P)Ph_2PCH_2PPh_2\}_2]$ has been reported. In this case, the complex exhibits a binuclear face-to-face geometry with bridging phosphines.[31]

Conclusions

In conclusion several routes to cationic palladium complexes with a bridging fluoro ligand have been elaborated. The reactions result in binuclear compounds with a distorted A-frame structure. So far, only two palladium complexes with a fluorine ligand in the bridging position have been reported.[17] The studies underline that late transition-metal fluoro complexes can be stabilised by a bridging coordination mode of the fluoro ligand.[15]

Experimental

The synthetic work was carried out on a Schlenk line or a nitrogen-filled glove box with oxygen levels below 10 ppm. All solvents were purified and dried by conventional methods and distilled under argon before use. $Et_3N{\cdot}3HF$ and pentafluoropyridine were obtained from Aldrich and ABCR, respectively. $[PdMe_2(Cy_2PCH_2PCy_2)]$ (**1**),[37] $[PdMe_2(Me_2NCH_2CH_2NMe_2)]$ (**4**)[36] and $Ph_2PCH_2PPh_2$[44] were prepared according to the literature.

The NMR spectra were recorded on a Bruker DRX 500 (^1H, $^{31}P\{^1H\}$ and ^{19}F NMR spectra) or a Bruker Avance 600 ($^{19}F\{^1H\}$ NMR spectra) spectrometer. The ^1H NMR chemical shifts were referenced to residual $CHDCl_2$ at δ 5.3 or C_6H_5D at δ 7.15. The $^{31}P\{^1H\}$ NMR spectra are reported downfield of an external solution of H_3PO_4 (85%). The ^{19}F NMR spectra were referenced to external C_6F_6 at δ −162.9. The infrared spectra were recorded on a Bruker IFS-66 spectrometer.

Synthesis of $[(PdMe)_2\{\mu\text{-}\kappa^2(P,P)Cy_2PCH_2PCy_2\}_2\text{-}(\mu\text{-}F)][SiMeF_4]$ (2a)

Complex $[PdMe_2(Cy_2PCH_2PCy_2)]$ (**1**) (422 mg, 0.77 mmol) was suspended in toluene (20 mL), and pentafluoropyridine (100 µL, 0.92 mmol) was added. The yellow reaction mixture was stirred for 7 days at room temperature and the orange solution was filtered through a cannula. The ^{19}F NMR spectra confirmed that the filtrate contains small amounts of $[(PdMe)_2\{\mu\text{-}\kappa^2(P,P)Cy_2PCH_2PCy_2\}_2(\mu\text{-}F)][OC_5NF_4]$ (**2b**). The remaining solid was washed with toluene (5 mL) and dried in the vacuum giving a colourless powder. Yield (**2a**) 114 mg (34%) (Found: C, 58.48; H, 9.18. $C_{53}H_{101}F_5P_4PdSi$ requires C, 58.31; H, 9.32%). ^1H NMR (500 MHz, CD_2Cl_2): δ 3.68 (m, 2H, CH_AH_B), 1.14–2.01 (m, 92 H, Cy, CH_AH_B), 0.39 (m, d in $^1H\{^{31}P\}$ NMR, J_{FH} = 1.5 Hz, 6 H, $PdCH_3$), 0.01 (qnt, 3H, J_{HF} = 5.0 Hz, $SiMeF_4^-$). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2): δ 19.7 (d, J_{PF} = 16.2 Hz). ^{19}F NMR (470.4 MHz, CD_2Cl_2): δ −111.2 (q with ^{29}Si satellites, J_{FH} = 5, J_{SiF} = 216 Hz, $SiMeF_4^-$), −387 (s, br, qnt in $^{19}F\{^1H\}$ NMR, J_{PF} = 14.7 Hz, PdF). NMR spectroscopic data for **2b**: δ 3.68 (m, 2H, CH_AH_B), 1.14–2.01 (m, 92 H, Cy, CH_AH_B), 0.39 (m, 6 H, $PdCH_3$). $^{31}P\{^1H\}$ NMR (202.5 MHz, C_6D_6): δ 19.7 (d, J_{PF} = 17.1 Hz). ^{19}F NMR (470.4 MHz, C_6D_6): δ −101.7 (s, br, 2F, CF), −171.1 (s, br, 2F, CF), −387 (s, br, qnt in $^{19}F\{^1H\}$ NMR, J_{PF} = 14.7 Hz, PdF).

Synthesis of $[PdMe(OC_5NF_4)(Cy_2PCH_2PCy_2)]$ (3)

166 mg (0.30 mmol) of **1** were dissolved in 5 ml THF at −30 °C and treated with a solution of 44 mg (0.26 mmol) 4-hydroxytetrafluoropyridine in 5 ml THF. After stirring the yellow reaction mixture for 2 h at 0 °C, the volatiles were removed *in vacuo* and the residue was washed twice with 3 mL toluene. A pale yellow substance remained. Yield 154 mg (85%) (Found: C, 53.70; H, 7.34; N 1.69. $C_{31}H_{49}F_4NOP_2Pd$ requires C, 53.50; H, 7.05; N 2.01%). ^1H NMR (500 MHz, CD_2Cl_2): δ 2.58 (dd, J_{PH} = 10.0, J_{PH} = 6.9 Hz, 2H, PCH_2), 1.70–2.10 (m, 22 H, Cy), 0.26 (d, J_{PH} = 8.8 Hz, 3 H, $PdCH_3$). $^{31}P\{^1H\}$ NMR (202.5 MHz, C_6D_6): δ 14.3 (d, J_{PP} = 59.7 Hz), −21.0 (d, J_{PP} = 59.7 Hz). ^{19}F NMR (470.4 MHz, C_6D_6): δ −97.9 (s, br, 2F), −167.2 (s, br, 2F).

Synthesis of [(PdMe)$_2${μ-κ^2(*P*,*P*)Cy$_2$PCH$_2$PCy$_2$}$_2$(μ-F)][FHF] (2c)

A solution of [PdMe$_2$(Cy$_2$PCH$_2$PCy$_2$)] (**1**) (291 mg, 0.53 mmol) in toluene (20 mL) was treated with a solution of Et$_3$N·3HF in THF (180 μL, 0.18 mmol). After 3 h stirring at room temperature, the yellow suspension was filtered. The colourless residue was washed twice with toluene (5 mL) and dried under vacuum. Yield 102 mg (35%) (Found: C, 61.59; H, 9.38. $C_{52}H_{99}F_3P_4Pd$ requires C, 61.74; H, 9.86%). The NMR spectroscopic data of the cation are similar to the data obtained for **2a**. Molar conductivity (Λ_M/S cm^2 mol^{-1}) = 42. The anion has been identified by comparison of the NMR and IR data with these in the literature.[16,39,41]

Synthesis of [(PdMe)$_2${μ-κ^2(*P*,*P*)Ph$_2$PCH$_2$PPh$_2$}$_2$(μ-F)][FHF] (5c)

A solution of [PdMe$_2$(Me$_2$NCH$_2$CH$_2$NMe$_2$)] (**4**) (273 mg, 1.08 mmol) in THF (7 mL) was treated with Ph$_2$PCH$_2$PPh$_2$ (436 mg, 1.13 mmol). The solution was stirred for 5 min and a solution of Et$_3$N·3HF in THF (55 μL, 0.54 mmol) was added. After 2 h stirring at room temperature, the yellow suspension was filtered. The colourless residue was washed twice with THF (5 mL) and dried under vacuum. Yield 191 mg (16%) (Found: C, 64.68; H, 5.23. $C_{52}H_{51}F_3P_4Pd$ requires C, 64.84; H, 5.34%). NMR spectroscopic data of the cation: ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.42–7.24 (m, 40 H, Ph), 3.86 (m, d in ^{31}P{^{1}H}, J_{HH} = 13.4 Hz, 2H, CH_AH$_B$), 3.36 (m, 2H, d in ^{31}P{^{1}H}, J_{HH} = 13.4 Hz, CH$_A$$H_B$), 0.43 (m, 6 H, PdCH$_3$). ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): δ 13.8 (d, J_{PF} = 15.4 Hz). ^{19}F NMR (470.4 MHz, CD_2Cl_2): δ −377 (m, br, PdF). Molar conductivity (Λ_M/S cm^2 mol^{-1}) = 38. The anion has been identified by comparison of the NMR and IR data with these in the literature.[16,39,41]

Formation of [(PdClMe)$_2${μ-κ^2(*P*,*P*)Ph$_2$PCH$_2$PPh$_2$}$_2$] (6)

A solution of **5c** (12 mg, 0.01 mmol) in CD_2Cl_2 (0.6 mL) was treated with Me$_3$SiCl (23 μL, 0.12 mmol). The NMR spectroscopic data reveal the formation of **6**.[31]

Structure determination for complex 5c·2THF

Colourless crystals of **5c**·2THF were obtained at 20 °C from a solution in THF. Diffraction data were collected for a fragment with the dimensions 0.20 × 0.10 × 0.07 mm on a Nonius KappaCCD diffractometer.

Crystal data. $C_{60}H_{67}F_3O_2P_4Pd_2$, M = 1213.82, monoclinic, space group $C2/c$, a = 24.6810(3), b = 9.23800(10), c = 25.2280(3) Å, β = 108.8150(6)°, V = 5444.70(11) Å^3, T = 100(2) K, Z = 4, μ(Mo-Kα) = 0.831 mm^{-1}, 57348 reflections measured, 7922 unique (R_{int} = 0.042). The structure was solved by direct methods (SHELXTL PLUS) and refined with the full matrix least squares methods on F^2 (SHELX-97).[45] Final R_1, wR_2 values on all data: 0.0327, 0.0633. R_1, wR_2 values for 6861 reflections with $I_o > 2\sigma(I_o)$: 0.0259, 0.0607. Hydrogen atoms were placed at calculated positions and refined using a riding model except for H(2A), which was refined isotropically. The symmetry generated atoms are related to those in the asymmetric unit by the $-x + 1, y, -z + 1/2$ symmetry operation.

CCDC reference number 276221.

See http://dx.doi.org/10.1039/b509032f for crystallographic data in CIF or other electronic format.

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