



A terminal palladium fluoride complex supported by an anionic PNP pincer ligand

Rafael Huacuja^a, David E. Herbert^a, Claudia M. Fafard^b, Oleg V. Ozerov^{a,*}

^a Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, TX 77842, USA

^b Department of Chemistry, Brandeis University, 415 South Street, Waltham, MA 02454, USA

ARTICLE INFO

Article history:

Received 18 June 2010

Received in revised form 8 July 2010

Accepted 19 July 2010

Available online 24 July 2010

Keywords:

Palladium

Pincer

PNP

Phosphine

Fluoride

ABSTRACT

A terminal palladium (II) fluoride complex (^FPNP)PdF (where ^FPNP is an anionic fluoro-substituted diarylamido/bis(phosphine) pincer ligand) has been prepared and characterized spectroscopically and structurally. An X-ray diffraction study revealed an approximately square-planar environment about Pd and a short Pd–F bond distance. (^FPNP)PdF reacted with silanes containing electron-withdrawing groups on Si by exchange of fluoride with one of the substituents on Si. An analysis of the ¹⁹F chemical shifts of both the Pd-bound fluoride and of the fluorines on the backbone of the ^FPNP ligand is provided.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Well-defined molecular transition-metal fluoride complexes have been attracting attention of synthetic chemists for a number of years [1]. The chemistry of Pd fluoride complexes has seen particular development over the last decade. Palladium fluoride complexes appear to be somewhat more synthetically challenging to access and some are more prone to decomposition compared to the Pd complexes of heavier halides. This is especially true for complexes with phosphine ligands and for difluoride complexes. Only comparatively recently, the work of Grushin [2,3] and Vigalok and co-workers [4] has yielded isolable palladium fluoride complexes with phosphine donors and palladium difluoride complexes. The interest in palladium fluoride complexes is partly guided by the quest for aryl-fluorine reductive elimination at Pd [5,6], an essential step of the highly desirable catalytic C–F bond formation. Although many other aryl-heteroatom reductive eliminations from Pd(II) are well known [7], unambiguous aryl-fluorine reductive elimination from Pd(II) in a catalytic cycle was first achieved only in 2009 by Buchwald and co-workers [8]. At the same time, an alternative aryl-fluorine bond formation relying on reductive elimination from Pd(IV) complexes has been studied by the groups of Sanford and co-workers [9], Yu and co-workers [10], and Ritter and co-workers [11,12].

Our group has studied complexes of the diarylamido/bis(phosphine) PNP ligands [13], versatile members of the pincer class

[14]. Against the backdrop of interest in Pd fluoride complexes, we surmised that a square-planar Pd monofluoride complex supported by a PNP ligand should be accessible and robust. Sanford et al. reported a stable fluoropalladium complex supported by the NCN pincer ligand in 2010 [15]. We also wanted to test whether our fluoride complex may prove to be a convenient precursor to other (PNP)PdX complexes through F/X metathesis with silane reagents. We have chosen to use the fluoro-substituted ^FPNP ligand (Fig. 1) instead of, for example, the ^{Me}PNP ligand because of the extra convenience of the ¹⁹F NMR spectroscopic handle built into the pincer ligand. Here we report the synthesis of (^FPNP)PdF, its structural and spectroscopic characterization, as well a discussion of the ¹⁹F NMR chemical shifts in ^FPNP complexes.

2. Results and discussion

2.1. Synthesis of (^FPNP)PdF and its reactivity with Si reagents

Treatment of the previously reported (^FPNP)PdOTf [16] with CsF in toluene for 2 days with vigorous stirring resulted in the formation of (^FPNP)PdF, which was isolated as a red crystalline powder in 64% yield upon workup. The NMR resonances corresponding to the ^FPNP ligand in (^FPNP)PdF are generally typical for (^FPNP)Pd–X complexes. C_{2v} symmetry was observed on the NMR time scale. For example, two resonances for the inequivalent Me groups and a single CH resonance from the diisopropylphosphine arms were detected by ¹H and ¹³C NMR. Consistent with this symmetry, only a single ¹⁹F and a single ³¹P resonance were detected for the ^FPNP ligand.

* Corresponding author.

E-mail address: ozеров@chem.tamu.edu (O.V. Ozerov).

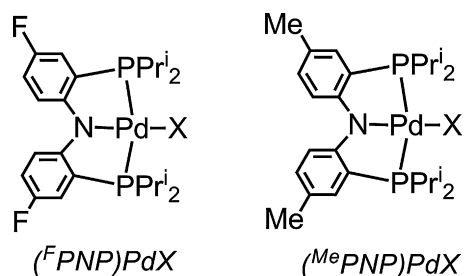
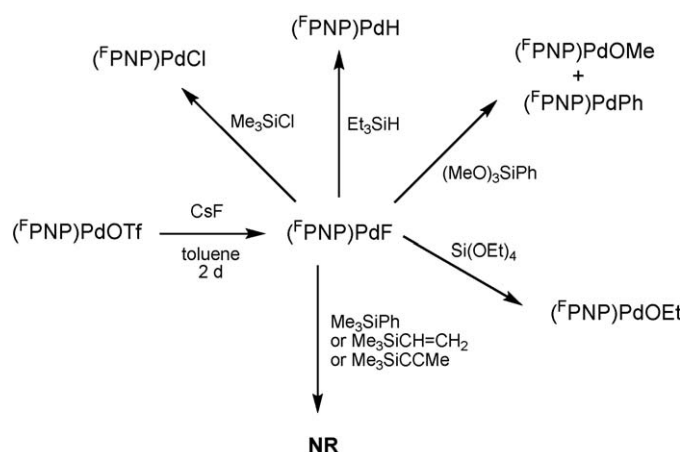


Fig. 1. Illustrative depiction of square-planar complexes of the general type $(^{\text{F}}\text{PNP})\text{PdX}$ and $(^{\text{Me}}\text{PNP})\text{PdX}$.

The Pd-bound fluoride resonated at -414.3 ppm in the ^{19}F NMR spectrum. This value of the chemical shift appears to be at the upfield end of the range of chemical shifts for metal fluorides [1]. There are relatively few examples of the ^{19}F NMR chemical shifts upfield of -400 ppm [17,18]. For square-planar Pd(II) complexes, it appears there is some correlation between the ^{19}F NMR chemical shift and the nature of the ligand *trans* to the fluoride. The more negative chemical shifts are observed when fluoride is *trans* to a hard, weak *trans*-influence ligand. Grushin's *trans*-(py) $_2$ PdF $_2$ (where py = pyridine or 4-*t*-butylpyridine) resonate at δ ca. -390 ppm (F *trans* to F) [3] and Sanford's (tBu-bpy)PdF $_2$ resonates at δ -354 ppm (F *trans* to N of bipyridine) [15]. In contrast, when F is *trans* to an aryl ligand, the ^{19}F NMR chemical shift is considerably more downfield, as in (Ph $_3$ P) $_2$ Pd(Ph)(F) (δ -274 ppm) [19], or (NCN)PdF (δ -244 ppm) [15]. In [(Et $_3$ P) $_3$ PdF] $^+$, the fluoride resonated at δ -253 ppm when *trans* to a phosphine [20].

$(^{\text{F}}\text{PNP})\text{PdF}$ reacted cleanly at ambient temperature in C $_6$ D $_6$ with Me $_3$ SiCl and with Et $_3$ SiH to produce the known compounds $(^{\text{F}}\text{PNP})\text{PdCl}$ and $(^{\text{F}}\text{PNP})\text{PdH}$, respectively (Scheme 1). The reaction of $(^{\text{F}}\text{PNP})\text{PdF}$ with (MeO) $_3$ SiPh under analogous conditions produced an 83:17 mixture of $(^{\text{F}}\text{PNP})\text{PdOMe}$ and $(^{\text{F}}\text{PNP})\text{PdPh}$. The observation of the transfer of the phenyl group to Pd from Si is not surprising given the use of trialkoxyarylsilanes as aryl transfer agents in the Pd-catalyzed Hiyama coupling [21]. The reaction of $(^{\text{F}}\text{PNP})\text{PdF}$ with Si(OEt) $_4$ in C $_6$ D $_6$ resulted in the formation of 80% $(^{\text{F}}\text{PNP})\text{PdOEt}$ in 1 h, along with 20% of other, unidentified products. On the other hand, no reaction took place between $(^{\text{F}}\text{PNP})\text{PdF}$ and Me $_3$ SiPh or Me $_3$ SiCH=CH $_2$ or Me $_3$ SiC \equiv CMe in C $_6$ D $_6$. Ostensibly, the transfer of a substituent from Si to Pd is facilitated by the presence of electronegative substituents on Si.



Scheme 1.

2.2. Solid-state structure of $(^{\text{F}}\text{PNP})\text{PdF}$

An X-ray diffraction study on a suitable single crystal of $(^{\text{F}}\text{PNP})\text{PdF}$ revealed a molecular structure that is closely related to other (PNP)PdX compounds (Fig. 2). The coordination environment about the Pd center is approximately square-planar. The main deviation arises from the constraint of the $^{\text{F}}\text{PNP}$ ligand: the P1–Pd–P2 angle is $167.14(6)^\circ$. This value is similar to the P–Pd–P angles $(^{\text{F}}\text{PNP})\text{PdOAc}$ ($168.16(6)^\circ$) [22] and $(^{\text{Me}}\text{PNP})\text{PdCl}$ ($163.54(2)^\circ$) [23]. The Pd–P distances in $(^{\text{F}}\text{PNP})\text{PdF}$ are also unremarkable and fall within the 2.27–2.29 Å range for $(^{\text{F}}\text{PNP})\text{PdOAc}$ and $(^{\text{Me}}\text{PNP})\text{PdCl}$. The Pd–N distance of 1.996(5) Å in $(^{\text{F}}\text{PNP})\text{PdF}$ is among the shortest we have observed in any structurally analyzed (PNP)PdX complex; for comparison, the Pd–N distance is 2.015(5) Å in both $(^{\text{F}}\text{PNP})\text{PdOAc}$ [22] and $(^{\text{Me}}\text{PNP})\text{PdCl}$ [23]. The Pd–N distance is affected by the *trans*-influence of the ligand *trans* to it, as we discussed in a previous publication [24]. Fluoride is a weak *trans*-influence ligand and a short Pd–N distance *trans* to it is expected. The Pd–F distance in $(^{\text{F}}\text{PNP})\text{PdF}$ is 1.981(4) Å. This is only slightly longer (by $>3\sigma$) than the Pd–F distances of ca. 1.95 Å in *trans*-(py) $_2$ PdF $_2$ reported by Grushin and Marshall in 2008 to be the shortest Pd–F distances for Pd(II) [3]. The short Pd–F distances *trans* to either N $_{\text{PNP}}$ or another fluoride are to be expected, from our point of view, given that both diarylamido N and F are weak *trans*-influence ligands [25]. The Pd–F distance *trans*

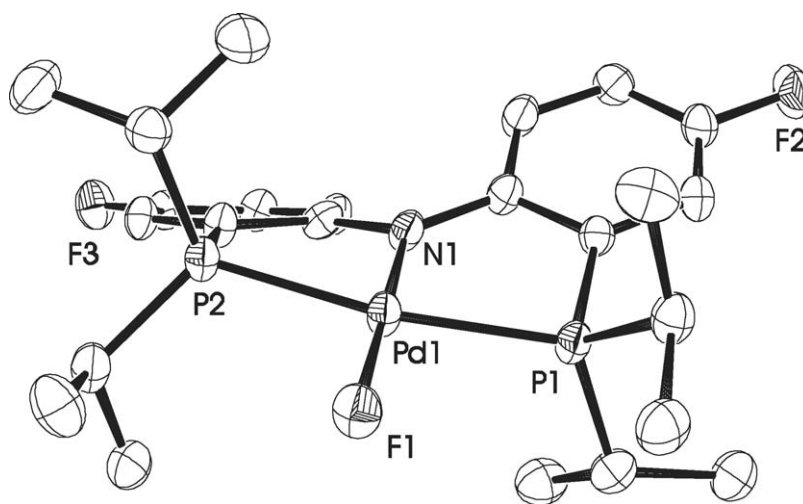


Fig. 2. ORTEP [32] drawing (50% thermal ellipsoids) of $(^{\text{F}}\text{PNP})\text{PdF}$ showing selected atom labeling. Hydrogen atoms and the toluene solvent molecule are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$) follow: Pd1–N1, 1.996(5); Pd1–F1, 1.981(4); Pd1–P1, 2.279(4); Pd1–P2, 2.288(4); F1–Pd1–N1, 179.12(15); F1–Pd1–P1, 96.77(10); N1–Pd1–P1, 83.47(13); F1–Pd1–P2, 96.04(12); N1–Pd1–P2, 83.74(14); P1–Pd1–P2, 167.14(6).

Table 1

^{31}P and ^{19}F NMR chemical shifts arising from the $^{\text{F}}\text{PNP}$ ligand in a series of $(^{\text{F}}\text{PNP})\text{PdX}$ compounds [16,22,33–35], collected in C_6D_6 solutions. The chemical shifts should be considered with up to 0.1 ppm uncertainty in measurement.

#	X	δ , ^{31}P NMR	δ , ^{19}F NMR	Reference
1	OTf	52.9	–126.5	[16]
2	NH_3^+	53.3 ^a	–126.9 ^a	[33]
3	Cl	47.4	–128.0	[34]
4	OAc	38.0	–128.1	[22]
5	F	43.1	–128.4	This work
6	OEt	38.6	–129.2	[16]
7	OPr^i	38.7	–129.3	[16]
8	OH	40.4	–129.3	[16]
9	NH_2	41.1	–129.8	[33]
10	Ph	39.2	–130.5	[16]
11	Me	40.9	–130.8	[34]
12	CH_2Ph	38.4	–130.9	[16]
13	$\text{Pd}(^{\text{F}}\text{PNP})$	46.5	–130.9	[33]
14	Et	37.1	–131.0	[16]
15	$^n\text{C}_8\text{H}_{17}$	37.3	–131.0	[33]
16	^nBu	37.3	–131.1	[16]
17	H	59.1	–131.3	[34]
18	$\text{ZnPd}(^{\text{F}}\text{PNP})$	53.9	–131.9	[35]

^a Collected in acetone- d_6 .

to N of a neutral donor in Sanford's [15] (tBu-bpy)PdF₂ of 1.999(4) is also comparable. Grushin and Marshall [3] paid significant attention to the π -effects on Pd–F bond distances, but considering that Pd(II) is a weak π -base, π - π repulsion with fluoride or N_{PNP} is likely insignificant. Notably, Ritter et al. [12] and Sanford et al. [26] reported two Pd(IV) complexes containing Pd–F bonds *trans* to N of sulfonamide ligands, and these Pd–F distances are quite short at 1.955(3) and 1.927(2) Å.

2.3. Analysis of the ^{19}F NMR chemical shifts in $^{\text{F}}\text{PNP}$ complexes

The two equivalent fluorines of the $^{\text{F}}\text{PNP}$ ligand in $(^{\text{F}}\text{PNP})\text{PdF}$ resonated at –128.4 ppm. While the ^{19}F NMR resonances of the Pd complexes of the $^{\text{F}}\text{PNP}$ ligand in its amido form fall within a fairly narrow chemical shift range, close examination reveals a dependence of the chemical shift on the identity of the fourth ligand (X) in $(^{\text{F}}\text{PNP})\text{PdX}$. We do not endeavor to extract any quantitative relationship here, but there does exist a correlation between the increasing donicity or *trans*-influence of X and the increasingly negative ^{19}F chemical shift (Table 1). The most downfield (least negative) chemical shift is found for $(^{\text{F}}\text{PNP})\text{PdOTf}$ and triflate is certainly the least donating or *trans*-influencing X in Table 1. The most upfield chemical shifts are found for compounds where X is most strongly donating: a hydride or a metal or an alkyl. The chemical shift for X=F falls close to X=Cl and X=OAc, as may be expected. On the other hand, no correlation between the donicity of X and the ^{31}P chemical shifts can be discerned.

The ^{19}F chemical shifts of the complexes of the $^{\text{F}}\text{PNP}$ ligand (amido–N) of other late transition metals (Table 2, entries 3–11)

Table 2

^{31}P and ^{19}F NMR chemical shifts arising from the $^{\text{F}}\text{PNP}$ ligand in a series of $^{\text{F}}\text{PNP}$ complexes [22,34,36,37], collected in C_6D_6 solutions.

#	Compound	δ , ^{31}P NMR	δ , ^{19}F NMR	Reference
1	$[(^{\text{F}}\text{PN}(\text{Me})\text{P})\text{PdCl}]^+$	43.6	–110.8	[22]
2	$(^{\text{F}}\text{PN}(\text{Me})\text{P})\text{RhCl}$	32.8	–116.3	[36]
3	$(^{\text{F}}\text{PNP})\text{PtCl}$	40.7	–127.8	[34]
4	$(^{\text{F}}\text{PNP})\text{NiCl}$	33.6	–128.1	[34]
5	$(^{\text{F}}\text{PNP})\text{Rh}(\text{Me})(\text{Cl})$	36.5	–128.3	[36]
6	$(^{\text{F}}\text{PNP})\text{Rh}(\text{CO})$	61.5	–129.7	[37]
7	$(^{\text{F}}\text{PNP})\text{RhH}_2$	63.8	–130.1	[37]
8	$(^{\text{F}}\text{PNP})\text{PtH}$	58.8	–130.2	[34]
9	$(^{\text{F}}\text{PNP})\text{PtMe}$	40.9	–130.3	[34]
10	$(^{\text{F}}\text{PNP})\text{NiMe}$	35.4	–130.4	[34]
11	$(^{\text{F}}\text{PNP})\text{NiH}$	56.0	–130.5	[34]

are generally within the –127 to –132 ppm range found in Pd complexes. In contrast, complexes of the N-methylated $^{\text{F}}\text{PNP}$ ligand (amine–N, entries 1 and 2 in Table 2) display chemical shifts that are different enough to be clearly distinguishable from the amido– $^{\text{F}}\text{PNP}$ complexes.

The chemical shift of the ^{19}F nucleus attached to an aromatic ring can generally be correlated to how electron rich the aromatic ring is. This has been used for the analysis of substituent effects in organic chemistry [27]. For the $^{\text{F}}\text{PNP}$ complexes, the increased donicity of the X ligand in $(^{\text{F}}\text{PNP})\text{PdX}$ increases the electron density on the diarylamido backbone and results in the upfield shift of the ^{19}F NMR resonance. N-methylation removes the lone pair of N from conjugation with the aromatic rings and thus causes a dramatic decrease in electron density and a consequent downfield shift of the ^{19}F NMR resonance. All in all, the ^{19}F NMR resonance of the $^{\text{F}}\text{PNP}$ ligand provides a spectroscopic handle that can be quite informative about the formal charge of the ligand and, to a useful degree, about the nature of the substituents on the metal.

Some of our previous publications have reported ^{19}F NMR chemical shifts referenced to 1 M CF_3COOH in CDCl_3 . In this work, we convert all the ^{19}F NMR chemical shifts to the scale that is referenced to 99% CF_3COOH at –78.5 ppm. This latter scale more properly corresponds to the chemical shift of 0 ppm for CFCl_3 . The difference between the ^{19}F chemical shifts of 1 M CF_3COOH in CDCl_3 and of 99% CF_3COOH is ca. 2.3 ppm.

3. Conclusion

In summary, we have prepared and characterized a terminal palladium fluoride complex $(^{\text{F}}\text{PNP})\text{PdF}$ supported by a diarylamido-based PNP pincer ligand. This complex displays square-planar geometry about the Pd center and a short Pd–F distance owing to the weak *trans*-influence of the amido ligand *trans* to F. $(^{\text{F}}\text{PNP})\text{PdF}$ reacted with some Si reagents by metathesis of the fluoride, however, the reaction appeared to proceed only in the case of silanes bearing electron-withdrawing groups on silicon. We have also analyzed the ^{19}F NMR chemical shifts arising from the fluorines on the backbone of the $^{\text{F}}\text{PNP}$ ligand and demonstrated their relationship with the nature of ligand X in $(^{\text{F}}\text{PNP})\text{PdX}$ complexes.

4. Experimental

4.1. General considerations

Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Toluene was dried over $\text{NaK}/\text{Ph}_2\text{CO}/18$ -crown-6, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glovebox. Trimethoxyphenylsilane and trimethylethoxysilane were used as received from commercial vendors. Tetraethoxysilane, triethylsilane, trimethylsilyl chloride, tetraethoxysilane, trimethylphenylsilane, trimethyl(vinyl)silane and trimethylsilylpropyne were distilled under reduced pressure. All reactions were run using a 0.050 M solution of $(^{\text{F}}\text{PNP})\text{PdF}$ in C_6D_6 . Compounds $(^{\text{F}}\text{PNP})\text{PdOTf}$ [16], $(^{\text{F}}\text{PNP})\text{PdH}$ [34], $(^{\text{F}}\text{PNP})\text{PdCl}$ [34], $(^{\text{F}}\text{PNP})\text{PdPh}$ [16], $(^{\text{F}}\text{PNP})\text{PdOMe}$ [16], $(^{\text{F}}\text{PNP})\text{PdOEt}$ [16] have been previously synthesized via other methods. NMR spectra were recorded on a NMRS 500 (^1H NMR, 499.703 MHz; ^{13}C NMR, 125.697 MHz; ^{31}P NMR, 202.289 MHz; ^{19}F NMR, 470.069 MHz) spectrometer. Chemical shifts are reported in δ ppm. For ^1H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ (0 ppm). ^{19}F NMR spectra were referenced externally using 99% $\text{CF}_3\text{CO}_2\text{H}$ at –78.5 ppm. Elemental analysis was performed by CALI Labs, Parsippany, NJ, USA.

4.2. Synthesis of (^FPNP)PdF

(^FPNP)PdOTf (145 mg, 0.21 mmol) was dissolved in 2.0 mL of toluene in a 10 mL Schlenk flask and was treated with CsF (90 mg, 0.59 mmol) at RT for 2 days. The mixture was then filtered through a pad of celite and the volatiles were removed from the filtrate under vacuum. The solid was redissolved in a minimum amount toluene and layered with pentane. The solution was placed in a freezer overnight at –35 °C. The reaction yielded 75 mg (64%) of a red crystalline powder of (^FPNP)PdF. ¹H NMR (C₆D₆): δ 7.23 (m, 2H, Ar–H), 6.67 (m, 2H, Ar–H), 6.60 (td, 2H), 1.96 (m, 4H, CHMe₂), 1.33 (app. quartet (dvt), 12 H, *J* = 9 Hz, PCHMe₂), 1.00 (app. quartet (dvt), 12H, *J* = 8 Hz, PCHMe₂); ¹³C{¹H} NMR (C₆D₆): δ 161.4 (t, *J*_{CP} = 11 Hz, C–N), 155.3 (dvt, *J*_{CF} = 239 Hz, *J*_{CP} = 5 Hz, C–F), 121.0 (vtd, *J*_{CP} = 18 Hz, *J*_{CF} = 5 Hz), 119.2 (d, *J*_{CF} = 22.5 Hz), 119.1 (d, *J*_{CF} = 21 Hz), 117.1 (app. q, 7 Hz), 25.0 (t, *J*_{CP} = 13 Hz, CHMe₂), 19.0 (br s, CHMe₂), 18.4 (s, CHMe₂). ³¹P{¹H} NMR (C₆D₆): δ 43.5. ¹⁹F NMR (C₆D₆): δ –128.7 (m, C–F), –414.3 (br s, Pd–F). Anal. Calcd (Found) for C₂₄H₃₄F₃NP₂Pd, C, 51.30 (51.27); H, 6.10 (5.94).

4.3. Reaction of (^FPNP)PdF with Et₃SiH

In a J. Young tube, Et₃SiH (40 μL, 0.25 mmol) was added to a solution of (^FPNP)PdF (0.50 mL of 0.050 M solution in C₆D₆, 0.025 mmol). After 20 h the reaction yielded an equimolar amount of (^FPNP)PdH and Et₃SiF.

4.4. Reaction of (^FPNP)PdF with Me₃SiCl

In a J. Young tube, Me₃SiCl (32 μL, 0.25 mmol) was added to a solution of (^FPNP)PdF (0.50 mL of 0.050 M solution in C₆D₆, 0.025 mmol). After 1 h the reaction yielded an equimolar amount of (^FPNP)PdCl and Me₃SiF.

4.5. Reaction of (^FPNP)PdF and (MeO)₃SiPh

In a J. Young tube, (MeO)₃SiPh (35 μL, 0.19 mmol) was added to a solution of (^FPNP)PdF (0.50 mL of 0.050 M solution in C₆D₆, 0.025 mmol). After 1 h the reaction yielded a mixture of (^FPNP)PdOMe (83%) and (^FPNP)Pd(C₆H₅) (17%).

4.6. Reaction of (^FPNP)PdF and (EtO)₄Si

In a J. Young tube, (EtO)₄Si (35 μL, 0.16 mmol) was added to a solution of (^FPNP)PdF (0.50 mL of 0.050 M solution in C₆D₆, 0.025 mmol). The solution was allowed to react at RT for 1 h. The reaction yielded (^FPNP)PdOEt (80%) and two unknown products (20%).

4.7. Attempted reactions of (^FPNP)PdF with Me₃SiPh, Me₃SiCH=CH₂, Me₃SiOEt, and Me₃SiC≡CMe

In four J. Young tubes, 0.19 mmol of Me₃SiPh (25 μL), Me₃SiCH=CH₂ (28 μL), Me₃SiOEt (30 μL), Me₃SiC≡CMe (35 μL) were each added to a separate solution of (^FPNP)PdF (0.50 mL of 0.050 M solution in C₆D₆, 0.025 mmol). After 20 h there was no observable change by NMR. The reactions with Me₃SiCH=CH₂ and Me₃SiOEt were additionally placed into a 100 °C oil bath for 20 h, with no change by NMR spectroscopy after these thermolyses.

4.8. X-ray data collection, solution, and refinement for (^FPNP)PdF

A red, multi-faceted crystal of suitable size (0.2 mm × 0.1 mm × 0.1 mm) and quality was selected from a representative sample of crystals of the same habit using an optical microscope, mounted onto a nylon loop and placed in a cold stream of nitrogen (110 K). Low-temperature X-ray data were obtained on a Bruker APEXII

CCD based diffractometer (Mo sealed X-ray tube, *K*_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker Apex2 software [28]. An absorption correction was applied using SADABS [29]. The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on *F*². No obvious missed symmetry was reported by PLATON [30]. The structure was solved in the triclinic *P*-1 space group using XS [31] (incorporated in SHELXTL). All non-hydrogen atoms were refined with anisotropic thermal parameters. The Hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on *F*²) to convergence.

Acknowledgements

We are grateful to the US National Science Foundation (grant CHE-08002907 for the “Powering the Planet” Center for Chemical Innovation), the Dreyfus foundation (Teacher-Scholar Award to O.V.O.), and the Alfred P. Sloan Foundation (Research Fellowship to O.V.O.) for the support of this research. We thank Prof. A. Vigalok for helpful suggestions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.07.010.

References

- [1] (a) N.M. Doherty, N.W. Hoffmann, *Chem. Rev.* 91 (1991) 553–573; (b) E.F. Murphy, R. Murugavel, H.W. Roesky, *Chem. Rev.* 97 (1997) 3425–3468; (c) V.V. Grushin, *Chem. Eur. J.* 8 (2002) 1006–1014; (d) A. Vigalok, *Chem. Eur. J.* 14 (2008) 5102–5108.
- [2] (a) V.V. Grushin, *Organometallics* 19 (2000) 1888–1900; (b) V.V. Grushin, W.J. Marshall, *Angew. Chem. Int. Ed.* 41 (2002) 4476–4479.
- [3] V.V. Grushin, W.J. Marshall, *J. Am. Chem. Soc.* 131 (2009) 918–919.
- [4] (a) A.W. Kaspi, A. Yahav-Levi, I. Goldberg, A. Vigalok, *Inorg. Chem.* 47 (2008) 5–7; (b) A. Yahav, I. Goldberg, A. Vigalok, *J. Am. Chem. Soc.* 125 (2003) 13634–13635.
- [5] D.V. Yandulov, N.T. Tran, *J. Am. Chem. Soc.* 129 (2007) 1342–1358.
- [6] V.V. Grushin, *Acc. Chem. Res.* 43 (2010) 160–171.
- [7] (a) E.I. Negishi (Ed.), *Handbook of Organopalladium Chemistry for Organic Synthesis*, Wiley-Interscience, New York, 2002; (b) J.F. Hartwig, *Organotransition Metal Chemistry*, University Science Books, Sausalito, CA, 2002, Chapter 19.
- [8] D.A. Watson, M. Su, G. Teverovskiy, Y. Zhang, J. García-Fortanet, T. Kinzel, S.L. Buchwald, *Science* 325 (2009) 1661–1664.
- [9] K.L. Hull, W.Q. Anani, M.S. Sanford, *J. Am. Chem. Soc.* 128 (2006) 7134–7135.
- [10] X. Wang, T.-S. Mei, J.Q. Yu, *J. Am. Chem. Soc.* 131 (2009) 7520–7521.
- [11] (a) F.T. Furuya, H.M. Kaiser, T. Ritter, *Chem. Rev.* 47 (2008) 5993–5996; (b) T. Furuya, T. Ritter, *J. Am. Chem. Soc.* 130 (2008) 10060–10061.
- [12] T. Furuya, D. Benitez, E. Tkatchouk, A.E. Strom, P. Tang, W.A. Goddard, T. Ritter III, *J. Am. Chem. Soc.* 132 (2010) 3793–3807.
- [13] For reviews on the diarylamido-based PNP complexes, see: (a) L.-C. Liang, *Coord. Chem. Rev.* 250 (2006) 1152–1177; (b) O.V. Ozerov, in: D. Morales-Morales, C.M. Jensen (Eds.), *The Chemistry of Pincer Compounds*, Elsevier, Amsterdam, 2007.
- [14] (a) D. Morales-Morales, C.M. Jensen (Eds.), *The Chemistry of Pincer Compounds*, Elsevier, Amsterdam, 2007; (b) M.E. van der Boom, D. Milstein, *Chem. Rev.* 103 (2003) 1759–1792.
- [15] N.D. Ball, J.W. Kampf, M.S. Sanford, *Dalton Trans.* 39 (2010) 632–640.
- [16] C.M. Fafard, O.V. Ozerov, *Inorg. Chim. Acta* 360 (2007) 286–292.
- [17] (a) S.R. Caskey, M.L.H. Stewart, M.J.A. Ahn, M.L.H. Johnson, J.L.C. Rowsell, J.W. Kampf, *Organometallics* 26 (2007) 1912–1923; (b) C.J. Bourgeois, S.A. Garratt, R.P. Hughes, R.B. Larichev, J.M. Smith, A.J. Ward, S. Willemsen, D. Zhang, A.G. DiPasquale, L.N. Zakharov, A.L. Rheingold, *Organometallics* 25 (2006) 3474–3480; (c) S.K. Agbossou, C. Roger, A. Igau, J.A. Gladysz, *Inorg. Chem.* 31 (1992) 419–424; (d) J.E. Veltheer, P. Burger, R.G. Bergman, *J. Am. Chem. Soc.* 117 (1995) 12478–12488; (e) S.A. Brewer, J.H. Holloway, E.G. Hope, P.G. Watson, *J. Chem. Soc. Chem. Commun.* (1992) 1577–1578.
- [18] A. Yahav, I. Goldberg, A. Vigalok, *Inorg. Chem.* 44 (2005) 1547–1553.
- [19] S.L. Fraser, M.Y. Antipin, V.N. Khroustalyov, V.V. Grushin, *J. Am. Chem. Soc.* 119 (1997) 4769–4770.

- [20] K.R. Dixon, J.J. McFarland, J. Chem. Soc. Chem. Commun. (1972) 1274–1275.
- [21] T. Hiyama, J. Organomet. Chem. 653 (2002) 58–61.
- [22] L. Fan, L. Yang, C. Guo, B.M. Foxman, O.V. Ozerov, Organometallics 23 (2004) 4778–4787.
- [23] L. Fan, B.M. Foxman, O.V. Ozerov, Organometallics 23 (2004) 326–328.
- [24] L.C. Gregor, C.-H. Chen, C.M. Fafard, L. Fan, C. Guo, B.M. Foxman, D.G. Gusev, O.V. Ozerov, Dalton Trans 39 (2010) 3195–3202.
- [25] We have previously [30] analyzed the relative trans-influence of the diarylamido N in our PNP ligands using $^1J_{Pt-H}$ values in various trans-(R₃P)₂PtHX complexes. Based on this criterion, it appears to be markedly weaker than that of H or Ph, comparable to PhO, and somewhat stronger than that of Cl.
- [26] N.D. Ball, J.W. Kampf, M.S. Sanford, J. Am. Chem. Soc. 132 (2010) 2878–2879.
- [27] ORTEP plots were created using Ortep-3 for Windows.
(a) L.J. Farugia, Appl. Crystallogr. 30 (1997) 565.
- [28] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (1991) 165–195.
- [29] C.M. Fafard, D. Adhikari, B.M. Foxman, D.J. Mindiola, O.V. Ozerov, J. Am. Chem. Soc. 129 (2007) 10318–10319.
- [30] O.V. Ozerov, C. Guo, L. Fan, B.M. Foxman, Organometallics 23 (2004) 5573–5580.
- [31] C.M. Fafard, C.H. Chen, B.M. Foxman, O.V. Ozerov, Chem. Commun. (2007) 4465–4467.
- [32] W. Weng, C. Guo, C.P. Moura, L. Yang, B.M. Foxman, O.V. Ozerov, Organometallics 24 (2005) 3487–3499.
- [33] W. Weng, C. Guo, R. Çelenligil-Çetin, B.M. Foxman, O.V. Ozerov, Chem. Commun. (2006) 197–199.
- [34] APEX2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June 2006.
- [35] G.M. Sheldrick, SADABS (version 2008/1): Program for Absorption Correction for Data from Area Detector Frames, University of Göttingen, 2008.
- [36] A.L. Spek, (2006) PLATON—A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, A.L. Spek, Acta Cryst. A 46 (1990) C34.
- [37] G.M. Sheldrick, Acta Cryst. A 64 (2008) 112–122.