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

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ABSTRACT

A terminal palladium (II) fluoride complex (^{F}PNP)PdF (where ^{F}PNP is a 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. (^{F}PNP)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 ^{19}F chemical shifts of both the Pd-bound fluoride and of the fluorines on the backbone of the ^{F}PNP ligand is provided.

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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 ^{F}PNP ligand (Fig. 1) instead of, for example, the ^{Me}PNP ligand because of the extra convenience of the ^{19}F NMR spectroscopic handle built into the pincer ligand. Here we report the synthesis of (^{F}PNP)PdF, its structural and spectroscopic characterization, as well a discussion of the ^{19}F NMR chemical shifts in ^{F}PNP complexes.

2. Results and discussion

2.1. Synthesis of (^{F}PNP)PdF and its reactivity with Si reagents

Treatment of the previously reported (^{F}PNP)PdOTf [16] with CsF in toluene for 2 days with vigorous stirring resulted in the formation of (^{F}PNP)PdF, which was isolated as a red crystalline powder in 64% yield upon workup. The NMR resonances corresponding to the ^{F}PNP ligand in (^{F}PNP)PdF are generally typical for (^{F}PNP)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 ^{1}H and ^{13}C NMR. Consistent with this symmetry, only a single ^{19}F and a single ^{31}P resonance were detected for the ^{F}PNP ligand.

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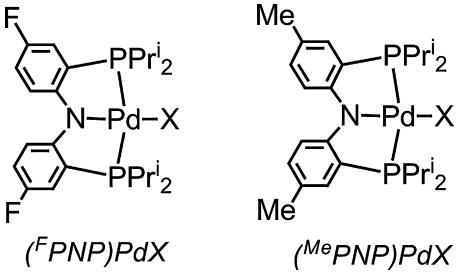
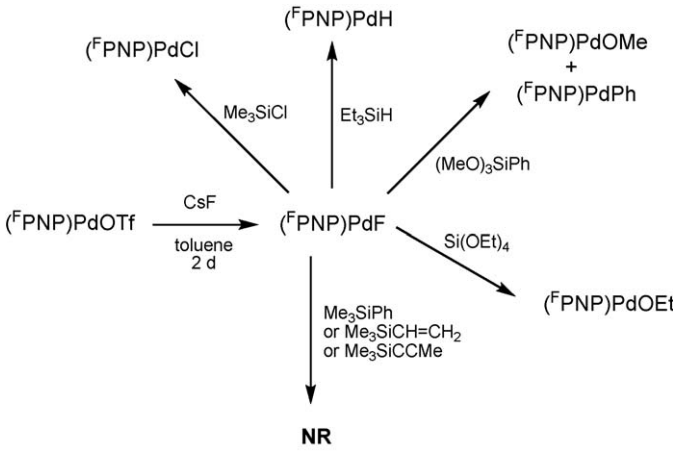


Fig. 1. Illustrative depiction of square–planar complexes of the general type (^{F}PNP)PdX and (^{Me}PNP)PdX.

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*-$(py)_2PdF_2$ (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 $(Ph_3P)_2Pd(Ph)(F)$ (δ −274 ppm) [19], or (NCN)PdF (δ −244 ppm) [15]. In $[(Et_3P)_3PdF]^+$, the fluoride resonated at δ −253 ppm when *trans* to a phosphine [20].

(^{F}PNP)PdF reacted cleanly at ambient temperature in C_6D_6 with Me_3SiCl and with Et_3SiH to produce the known compounds (^{F}PNP)PdCl and (^{F}PNP)PdH, respectively (Scheme 1). The reaction of (^{F}PNP)PdF with $(MeO)_3SiPh$ under analogous conditions produced an 83:17 mixture of (^{F}PNP)PdOMe and (^{F}PNP)PdPh. The observation of the transfer of the phenyl group to Pd from Si is not surpising given the use of trialkoxyarylsilanes as aryl transfer agents in the Pd-catalyzed Hiyama coupling [21]. The reaction of (^{F}PNP)PdF with $Si(OEt)_4$ in C_6D_6 resulted in the formation of 80% (^{F}PNP)PdOEt in 1 h, along with 20% of other, unidentified products. On the other hand, no reaction took place between (^{F}PNP)PdF and Me_3SiPh or $Me_3SiCH{=}CH_2$ or $Me_3SiC{\equiv}CMe$ in C_6D_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 (^{F}PNP)PdF

An X-ray diffraction study on a suitable single crystal of (^{F}PNP)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 ^{F}PNP ligand: the P1–Pd–P2 angle is 167.14(6)°. This value is similar to the P–Pd–P angles (^{F}PNP)PdOAc (168.16(6)°) [22] and (^{Me}PNP)PdCl (163.54(2)°) [23]. The Pd–P distances in (^{F}PNP)PdF are also unremarkable and fall within the 2.27–2.29 Å range for (^{F}PNP)PdOAc and (^{Me}PNP)PdCl. The Pd–N distance of 1.996(5) Å in (^{F}PNP)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 (^{F}PNP)PdOAc [22] and (^{Me}PNP)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 (^{F}PNP)PdF is 1.981(4) Å. This is only slightly longer (by >3σ) than the Pd–F distances of ca. 1.95 Å in *trans*-$(py)_2PdF_2$ 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_{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*

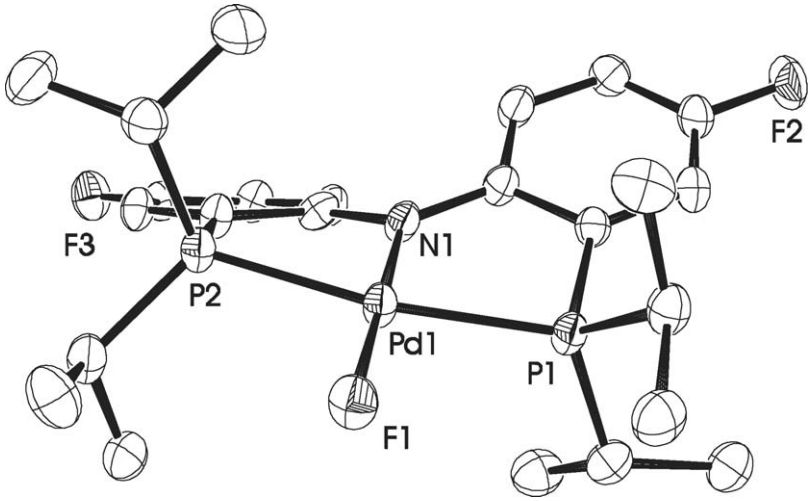


Fig. 2. ORTEP [32] drawing (50% thermal ellipsoids) of (^{F}PNP)PdF showing selected atom labeling. Hydrogen atoms and the toluene solvent molecule are omitted for clarity. Selected bond distances (Å) and angles (°) follow: Pd1–N1, 1.996(5); Pd1–F1, 1.981(4); Pd1–P1, 2.279(4); Pd1–P2, 2.288(4); F1–Pd1–N1, 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 ^{F}PNP ligand in a series of (^{F}PNP)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	Pd(^{F}PNP)	46.5	−130.9	[33]
14	Et	37.1	−131.0	[16]
15	$^{n}C_8H_{17}$	37.3	−131.0	[33]
16	^{n}Bu	37.3	−131.1	[16]
17	H	59.1	−131.3	[34]
18	ZnPd(^{F}PNP)	53.9	−131.9	[35]

[a] Collected in acetone-d_6.

to N of a neutral donor in Sanford's [15] (tBu-bpy)PdF_2 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 ^{F}PNP complexes

The two equivalent fluorines of the ^{F}PNP ligand in (^{F}PNP)PdF resonated at −128.4 ppm. While the ^{19}F NMR resonances of the Pd complexes of the ^{F}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 (^{F}PNP)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 (^{F}PNP)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 ^{F}PNP ligand (amido–N) of other late transition metals (Table 2, entries 3–11) are generally within the −127 to −132 ppm range found in Pd complexes. In contrast, complexes of the N-methylated ^{F}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–^{F}PNP complexes.

Table 2
^{31}P and ^{19}F NMR chemical shifts arising from the ^{F}PNP ligand in a series of ^{F}PNP complexes [22,34,36,37], collected in C_6D_6 solutions.

#	Compound	δ, ^{31}P NMR	δ, ^{19}F NMR	Reference
1	[(^{F}PN(Me)P)PdCl]$^+$	43.6	−110.8	[22]
2	(^{F}PN(Me)P)RhCl	32.8	−116.3	[36]
3	(^{F}PNP)PtCl	40.7	−127.8	[34]
4	(^{F}PNP)NiCl	33.6	−128.1	[34]
5	(^{F}PNP)Rh(Me)(Cl)	36.5	−128.3	[36]
6	(^{F}PNP)Rh(CO)	61.5	−129.7	[37]
7	(^{F}PNP)RhH_2	63.8	−130.1	[37]
8	(^{F}PNP)PtH	58.8	−130.2	[34]
9	(^{F}PNP)PtMe	40.9	−130.3	[34]
10	(^{F}PNP)NiMe	35.4	−130.4	[34]
11	(^{F}PNP)NiH	56.0	−130.5	[34]

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 ^{F}PNP complexes, the increased donicity of the X ligand in (^{F}PNP)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 ^{F}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 (^{F}PNP)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. (^{F}PNP)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 ^{F}PNP ligand and demonstrated their relationship with the nature of ligand X in (^{F}PNP)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 NaK/Ph_2CO/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 (^{F}PNP)PdF in C_6D_6. Compounds (^{F}PNP)PdOTf [16], (^{F}PNP)PdH [34], (^{F}PNP)PdCl [34], (^{F}PNP)PdPh [16], (^{F}PNP)PdOMe [16], (^{F}PNP)PdOEt [16] have been previously synthesized via other methods. NMR spectra were recorded on a NMRS 500 (^{1}H 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 ^{1}H 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% CF_3CO_2H at −78.5 ppm. Elemental analysis was performed by CALI Labs, Parsippany, NJ, USA.

4.2. Synthesis of (^{F}PNP)PdF

(^{F}PNP)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 (^{F}PNP)PdF. ^{1}H NMR (C_6D_6): δ 7.23 (m, 2H, Ar–H), 6.67 (m, 2H, Ar–H), 6.60 (td, 2H), 1.96 (m, 4H, C*H*Me$_2$), 1.33 (app. quartet (dvt), 12 H, J = 9 Hz, PCHMe$_2$), 1.00 (app. quartet (dvt), 12H, J = 8 Hz, PCHMe$_2$); ^{13}C{^{1}H} NMR (C_6D_6): 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, *C*HMe$_2$), 19.0 (br s, CHMe$_2$), 18.4 (s, CHMe$_2$). ^{31}P{^{1}H} NMR (C6D6): δ 43.5. ^{19}F NMR (C_6D_6): δ −128.7 (m, C–F), −414.3 (br s, Pd–F). Anal. Calcd (Found) for $C_{24}H_{34}F_3NP_2Pd$, C, 51.30 (51.27); H, 6.10 (5.94).

4.3. Reaction of (^{F}PNP)PdF with Et_3SiH

In a J. Young tube, Et_3SiH (40 μL, 0.25 mmol) was added to a solution of (^{F}PNP)PdF (0.50 mL of 0.050 M solution in C_6D_6, 0.025 mmol). After 20 h the reaction yielded an equimolar amount of (^{F}PNP)PdH and Et_3SiF.

4.4. Reaction of (^{F}PNP)PdF with Me_3SiCl

In a J. Young tube, Me_3SiCl (32 μL, 0.25 mmol) was added to a solution of (^{F}PNP)PdF (0.50 mL of 0.050 M solution in C_6D_6, 0.025 mmol). After 1 h the reaction yielded an equimolar amount of (^{F}PNP)PdCl and Me_3SiF.

4.5. Reaction of (^{F}PNP)PdF and $(MeO)_3SiPh$

In a J. Young tube, $(MeO)_3SiPh$ (35 μL, 0.19 mmol) was added to a solution of (^{F}PNP)PdF (0.50 mL of 0.050 M solution in C_6D_6, 0.025 mmol). After 1 h the reaction yielded a mixture of (^{F}PNP)PdOMe (83%) and (^{F}PNP)Pd(C_6H_5) (17%).

4.6. Reaction of (^{F}PNP)PdF and $(EtO)_4Si$

In a J. Young tube, $(EtO)_4Si$ (35 μL, 0.16 mmol) was added to a solution of (^{F}PNP)PdF (0.50 mL of 0.050 M solution in C_6D_6, 0.025 mmol). The solution was allowed to react at RT for 1 h. The reaction yielded (^{F}PNP)PdOEt (80%) and two unknown products (20%).

4.7. Attempted reactions of (^{F}PNP)PdF with Me_3SiPh, $Me_3SiCH{=}CH_2$, Me_3SiOEt, and $Me_3SiC{\equiv}CMe$

In four J. Young tubes, 0.19 mmol of Me_3SiPh (25 μL), $Me_3SiCH{=}CH_2$ (28 μL), Me_3SiOEt (30 μL), $Me_3SiC{\equiv}CMe$ (35 μL) were each added to a separate solution of (^{F}PNP)PdF (0.50 mL of 0.050 M solution in C_6D_6, 0.025 mmol). After 20 h there was no observable change by NMR. The reactions with $Me_3SiCH{=}CH_2$ and Me_3SiOEt 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 (^{F}PNP)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.

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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.

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