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Chemistry of diphenyltetrafluorophosphazene: Reactions with dilithiated diols

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Abstract

Reaction of *gem*-diphenyltetrafluorophosphazene, $[1,1\text{-}(C_6H_5)_2]P_3N_3F_4$ (**1**) with $LiO(CH_2)_3OLi$ resulted in the formation of four products, spiro-$\{3,3\text{-}[O(CH_2)_3O]\}[1,1\text{-}(C_6H_5)_2]P_3N_3F_2$ (**2**), ansa-$\{3,5\text{-}[O(CH_2)_3O]\}[1,1\text{-}(C_6H_5)_2P_3N_3F_2]$ (**3**), bridged-$[1,1\text{-}(C_6H_5)_2N_3P_3F_3][O(CH_2)_3O][1,1\text{-}(C_6H_5)_2N_3P_3F_3]$ (**4**) and dangling-$[HO(CH_2)_3O][1,1\text{-}(C_6H_5)_2P_3N_3F_3]$ (**5**) derivatives of **1**, among which compound **5** was found to be the major product. Reaction of **1** with the dilithiated ferrocene derived diol, $FcCH_2P(S)(CH_2OLi)_2$ resulted in the formation of two isomers of ansa substituted fluorophosphazenes namely *endo*-$[1,1\text{-}(C_6H_5)_2]\{3,5\text{-}[FcCH_2P(S)(CH_2O)_2]\}P_3N_3F_2$ (**6**) and *exo*-$[1,1\text{-}(C_6H_5)_2]\{3,5\text{-}[FcCH_2P(S)(CH_2O)_2]\}P_3N_3F_2$ (**7**). These were formed along with the spiro isomer $[1,1\text{-}(C_6H_5)_2]\{3,3\text{-}[FcCH_2P(S)(CH_2O)_2]\}P_3N_3F_2$ (**8**) the dangling derivative $[1,1\text{-}(C_6H_5)_2P_3N_3F_3][OCH_2(FcCH_2)P(S)CH_2OH]$ (**9**) and the bridged compound $[1,1\text{-}(C_6H_5)_2P_3N_3F_3][OCH_2(FcCH_2)P(S)CH_2O][1,1\text{-}(C_6H_5)_2P_3N_3F_3]$ (**10**). All compounds were separated by column chromatography and characterized by ^1H, $^{31}P\{^1H\}$, ^{19}F NMR, mass spectra and elemental analysis. The spirocyclic compound **8** was also characterized by X-ray crystallography.

Keywords: *gem*-Diphenyltetrafluorophosphazene; Spiro; Ansa; Bridged; Dangling; Dilithiated diols

1. Introduction

Monoaryl and geminal diaryl substituted trimeric fluorophosphazenes are an interesting class of compounds, which unlike $N_3P_3F_6$, are easy to handle due to their lesser volatility [1]. A few of them have been reported as potential precursors for realizing high molecular weight phosphazene polymers [2]. A scan of the literature shows that unlike the reactions of the aryl and *gem*-diaryl chlorophosphazenes, the reactions of aryl substituted fluorophosphazenes have been little explored [3–5]. Quite interestingly, detailed studies on the reactions of *gem*-diphenyltetrachlorophosphazene, $[1,1\text{-}(C_6H_5)_2]P_3N_3Cl_4$ with a variety of short chain diols and amino alcohols yielded only spirocyclic products [6,7]. It is interesting to note that except for a report of a reaction of *gem*-diphenyltetrafluorophosphazene with dilithiated ferrocene, no other reactions of bifunctional reagents with aryl substituted fluorophosphazenes have been reported so far [8]. The replacement of geminal fluorines on the fluorophosphazene trimer by phenyl groups can be expected to have steric as well as electronic effects on the nature of products formed in the substitution reactions of this phosphazene with bifunctional reagents.

The reactions of dilithiated diol $FcCH_2P(S)(CH_2OLi)_2$ with $N_3P_3F_6$ and $N_3P_3Cl_6$ as well as the reactions of $LiO(CH_2)_3OLi$ with $N_4P_4F_8$ at −80 °C was found to yield the corresponding ansa substituted products [9–11]. We have also shown that lithiated diols react quite differently with fluorophosphazenes when compared to silylated diols with the former forming preferentially the kinetically controlled ansa substituted products [9]. Comparison of reactions of disodium and dilithium salts of a diol with $N_3P_3Cl_6$ also shows interesting differences in the nature and yield of cyclized products [12]. In this context, we were interested in exploring the reactions of *gem*-diphenyltetrafluorophosphazene, $[1,1\text{-}(C_6H_5)_2]P_3N_3F_4$ (**1**) with difunctional reagents, especially with dilithiated diols. In this paper we describe the first systematic study on the chemistry of *gem*-diphenyltetrafluorophosphazene with two different dilithiated diols $FcCH_2P(S)(CH_2OLi)_2$ and LiO

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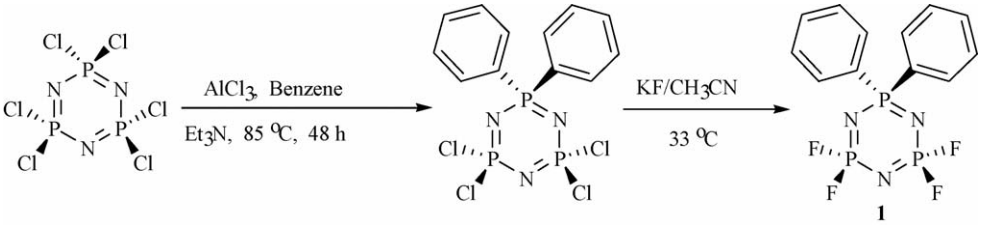


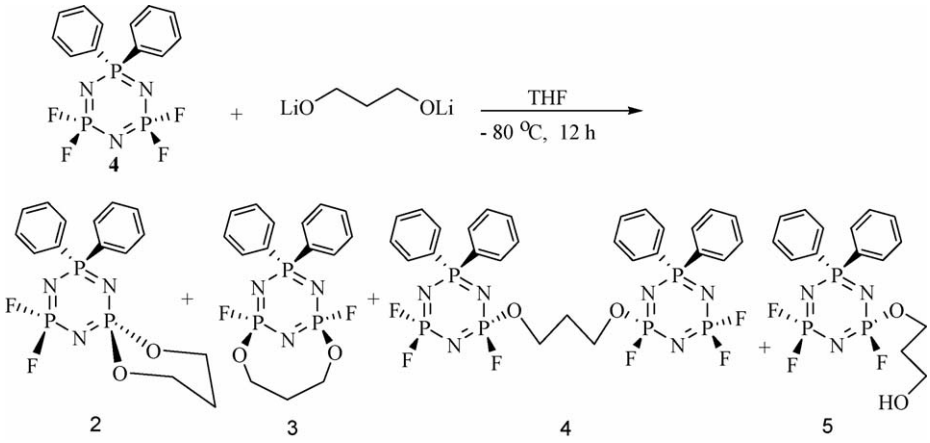
Scheme 1.

$(CH_2)_3OLi$. We also describe the preparation of the tetrafluorinated phosphazene (**1**) by an alternate and easier synthetic route, which does not involve the use of volatile $N_3P_3F_6$.

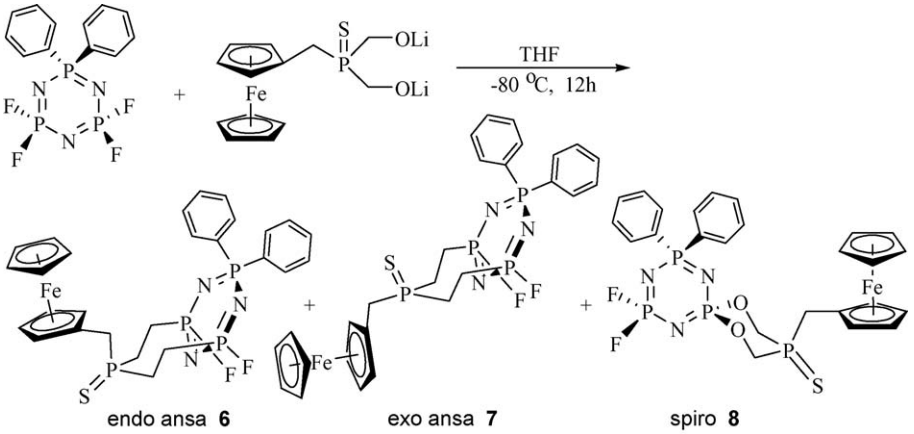
2. Results and discussion

The *gem*-diphenyltetrafluorophosphazene, $[1,1\text{-}(C_6H_5)_2]P_3N_3F_4$ (**1**) was prepared from $N_3P_3Cl_6$ as shown in Scheme 1 Compound **1** was prepared earlier by a three-step procedure starting from chlorophosphazene trimer, which involved fluorination of $N_3P_3Cl_6$ to $N_3P_3F_6$, reaction of $N_3P_3F_6$ with phenyllithium to yield $N_3P_3F_5(C_6H_5)$ followed by Friedel–Crafts arylation of $N_3P_3F_5(C_6H_5)$ [13]. This method involved loss of compounds in each step resulting in a moderate yield of **1**, based on $N_3P_3Cl_6$. The present method, which involves Friedel–Craft's arylation of $N_3P_3Cl_6$, followed by fluorination of the tetrachloro compound by KF/CH_3CN, reduces one step in comparison to the reported procedure, and does not involve handling of the volatile $N_3P_3F_6$, resulting in a good yield of **1**.

To explore the effect of the presence of two geminal phenyl groups on the fluorophosphazene on its reactions with bifunctional reagents, we have carried out reaction of dilithiated propanediol $LiO(CH_2)_3OLi$ with **1**. The reaction resulted in the formation of four products, viz. spiro-{3,3-$[O(CH_2)_3O]$}$[1,1\text{-}(C_6H_5)_2]P_3N_3F_2$ (**2**), ansa-{3,5-$[O(CH_2)_3O]$}$[1,1\text{-}(C_6H_5)_2]P_3N_3F_2$ (**3**), bridged-$[N_3P_3F_3(C_6H_5)_2][O(CH_2)_3O]$ $[N_3P_3F_3(C_6H_5)_2]$ (**4**) and dangling-$[HO(CH_2)_3O](C_6H_5)_2P_3N_3F_3$ (**5**) derivatives of *gem*-diphenyltetrafluorophospha-



Scheme 2.



Scheme 3.

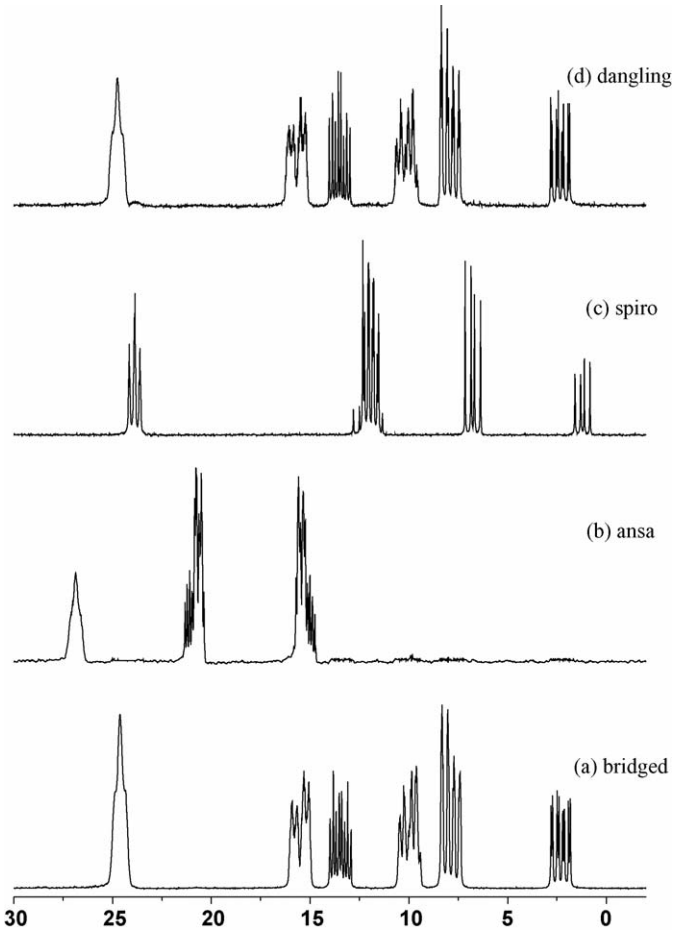


Fig. 1. $^{31}P\{^{1}H\}$ NMR spectra of (a) bridged **4**, (b) ansa **3**, (c) spiro **2** and (d) dangling **5** derivatives of 1,1-$(C_6H_5)_2P_3N_3F_4$ with 1,3-propanediol.

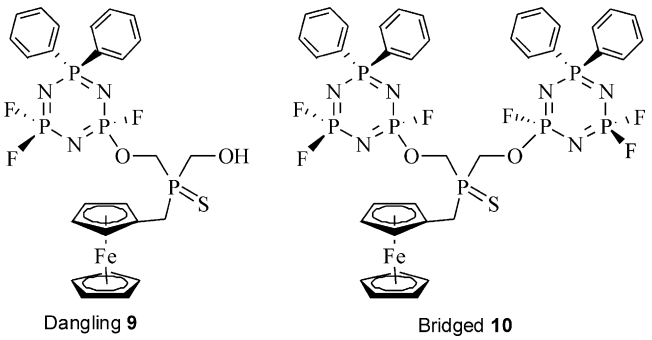
zene (Scheme 2). All these products were separated by column chromatography over silica gel and were characterized by $^{31}P\{^{1}H\}$, ^{19}F and ^{1}H NMR spectroscopic analysis.

Albeit this reaction yielded four possible products that are obtainable from a reaction of bifunctional reagents with cyclophosphazene trimer, the dangling derivative was obtained in higher yields when compared to the other products isolated from this reaction. Recent interest on the usefulness of exploring the chemistry of cyclic phosphazenes has been centered not only on their usefulness as precursors for phosphazene based polymers [14,15], but also in the use of the trimeric and tetrameric phosphazene as a stable core for the synthesis of dendrimers both by the convergent and divergent synthesis [16,17]. The dangling phosphazene derivatives are potential precursors for realizing phosphazene based dendrimers by convergent synthesis.

The conversion of the lithium alkoxy terminated dangling derivative to the hydroxy terminated dangling derivative possibly took place while working up the reaction by chromatography over silicagel. To cross check the propensity of this reaction for formation of higher yields of the dangling derivative, we have carried out reaction of **1** with monolithiated 1,3-propanediol. $LiO(CH_2)_3OH$, which was prepared in situ by controlled lithiation of 1,3-propanediol using *n*-BuLi. $LiO(CH_2)_3OH$ when reacted with compound **1** yielded the dangling derivative **5** in 70% yield. In this reaction, compound **1** was added to the monolithiated diol at −80 °C and the reaction was allowed to reach room temperature within 2 h. Then the mixture was stirred for 12 h at room temperature followed by reflux at 65 °C. This is one of the highest yields of dangling derivative of phosphazenes obtained in a reaction of cyclophosphazene with bifunctional reagents.

The reaction of the dilithiated diol, $FcCH_2P(S)(CH_2OLi)_2$ with the *gem*-diphenylfluorophosphazene (**1**) resulted in the formation of two ansa substituted fluorophosphazenes *endo*-[1,1-$(C_6H_5)_2$]{3,5-[$FcCH_2P(S)(CH_2O)_2$]}$P_3N_3F_2$ (**6**) and *exo*-[1,1-$(C_6H_5)_2$]{3,5-[$FcCH_2P(S)(CH_2O)_2$]}$P_3N_3F_2$ (**7**) along with their spiro isomer [1,1-$(C_6H_5)_2$]{3,3-[$FcCH_2P(S)(CH_2O)_2$]}$P_3N_3F_2$ (**8**) (Scheme 3).

This reaction also yielded the dangling $(C_6H_5)_2P_3N_3F_3$ [$OCH_2(FcCH_2)P(S)CH_2OH$] (**9**) and bridged [$(C_6H_5)_2P_3N_3F_3$] [$OCH_2(FcCH_2)P(S)CH_2O$][$(C_6H_5)_2P_3N_3F_3$] (**10**) derivatives of **1**. All the products were separated by column chromatography and were characterized by $^{31}P\{^{1}H\}$, ^{19}F NMR and mass spectra and elemental analysis. The spirocyclic compound **8** was also characterized by X-ray crystallography. Similar to the reaction of $LiO(CH_2)_3OLi$, the major product from the reactions of $FcCH_2P(S)(CH_2OLi)_2$ with **1** was the dangling derivative. These results differ significantly from the reactions of the same dilithiated diol with $N_3P_3F_6$ where under similar conditions ansa substituted compounds were found to be the major products [9].



2.1. Spectral studies on the gem-diphenylfluorophosphazene and its derivatives with diols

The $^{31}P\{^{1}H\}$ spectra of compounds **2**–**5** are shown in Fig. 1. The PF_2 groups are clearly identifiable by the triplet of multiplets with $^{1}J_{PF}$ around 900 Hz. In the case of the spirocyclic compound **2**, the phosphorus signal due to $P(OR)_2$ moiety has merged with the signal of the PF_2 triplet. Among the PF(OR) signals which appeared as doublet multiplets, the signal for the ansa compound **3** is found to be relatively more deshielded. The $^{31}P\{^{1}H\}$ NMR spectral data of compounds **2**–**10** along with **1** are given in Table 1. It is clear from the table that for all the compounds, the chemical shifts of phosphorus atoms bound to the diols are more deshielded as the electro negativity of the substituent group on the phosphorus has increased. It can be seen from Table 1 that as we move from PF_2

Table 1
$^{31}P\{^{1}H\}$ NMR spectral data of compound **1** and its derivatives with bifunctional reagents

Compound	$^{31}P\{^{1}H\}$ NMR (δ in ppm)			
	PF_2 ($^{1}J_{PF}$, Hz)	OPF ($^{1}J_{PF}$, Hz)	OPO ($^{2}J_{PNP}$, Hz)	$P(C_6H_5)_2$ ($^{2}J_{PNP}$, Hz)
1	mt, 7.6 (911)	–	–	t, 25.83 (49)
2	mt, 6.78 (906)	–	m, 11.78	t, 23.94 (43)
3	–	md, 18.06 (910)	–	tt, 26.88 (42)
4	md, 7.88 (902)	md, 12.77 (884)	–	t, 24.70 (44)
5	mt, 7.88 (902)	md, 12.74 (895)	–	t, 24.70 (43)
6	–	dd, 14.76 (955)	–	t, 25.41 (44)
7	–	dd, 12.28 (921)	–	t, 26.81 (40)
8	ddt, 4.95 (905)	–	ddt, 13.65 (56.1)	t, 24.54 (45)
9	mt, 7.58 (933)	md, 13.39 (921)	–	m, 25.01
10	mt, 7.45 (905)	md, 13.09 (916)	–	t, 25.25 (44)

to PPh_2, the corresponding chemical shifts are deshielded more for the groups PF_2, OPF, OPO and $P(C_6H_5)_2$, respectively. It can also be observed that the $P(C_6H_5)_2$ chemical shifts are not much altered in the $^{31}P\{^{1}H\}$ NMR spectra of the compounds **2–10** compared to that of the starting compound **1**.

A clear difference in the mobility while doing column chromatography over silica gel made it easy to separate the bridged and dangling derivatives, **4** and **5**. The $^{31}P\{^{1}H\}$ and ^{19}F NMR spectra of these two compounds are as expected, identical. But, they differ in ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra. In the ^{1}H NMR spectra of the bridged compound **4**, two sets of peaks for aliphatic groups are observed, while for the dangling derivative **5**, three sets of peaks are observed for the same. Apart from this, for the dangling derivative **5**, a broad peak corresponding to the OH group at 2.41 ppm is also observed. In the IR spectra of the compound **5**, a broad –OH stretching frequency at 3419 cm^{-1} is observed, which is not observed for the compound **4**. The identity of these compounds is also confirmed by mass spectroscopy and elemental analysis.

In the $^{31}P\{^{1}H\}$ NMR spectra of the compounds **6–10**, the P=S chemical shift of the ansa substituted compounds **6** and **7** were observed at 45.13 and 47.55 ppm, respectively, while for the spiro compound **8** it was observed at 19.19 ppm. Similar observations were noted for the eight and six membered ring compounds formed by $FcCH_2P(S)(CH_2OH)_2$ with other chloro and fluorophosphazenes [9,18]. As observed for the compounds **3** and **5**, the $^{31}P\{^{1}H\}$ and ^{19}F NMR spectra of dangling and bridged compounds, **9** and **10** were also identical. In the ^{31}P NMR spectra, the P=S peak appeared at 40.10 and 40.28 ppm, respectively for the compounds **9** and **10**. The presence of different signals for the CH_2OP and CH_2OH groups as well as the signal for OH group in the ^{1}H NMR confirmed the identity of the dangling compound **9**. Molecular ions peaks were obtained for all the new compounds in their mass spectra recorded in the FAB mode.

2.2. Crystal structure of spiro substituted compound 8

The X-ray crystal structure of the spiro substituted compound $[1,1\text{-}(C_6H_5)_2]\{3,3\text{-}[FcCH_2P(S)(CH_2O)_2]\}P_3N_3F_2$ (**8**) is given in Fig. 2. The details pertaining to data collection and structure solution for compound **8** are summarized in Table 2. The selected bond lengths and bond angles are given in Table 3.

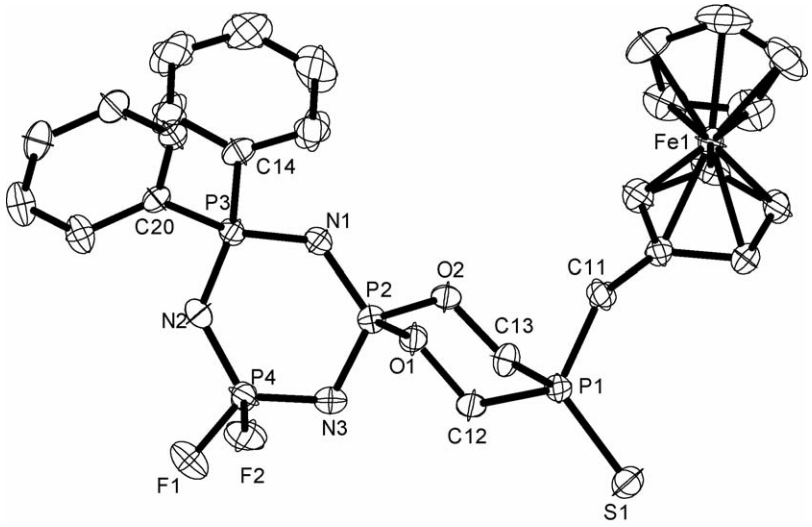


Fig. 2. Crystal structure of the spirocyclic compound **8**.

Table 2
X-ray crystallographic parameters for **8**

Formula	$C_{25}H_{25}F_2FeN_3O_2P_4S$
Fw	649.25
Cryst syst	Monoclinic
Space group	*C*2/*c*
a (Å)	28.932(3)
b (Å)	9.053(1)
c (Å)	23.677(2)
α (°)	90
β (°)	112.21(1)
γ (°)	90
V (Å^3)	5741.4(1)
Z	8
ρ_{calcd} (g cm^{-3})	1.502
μ (mm^{-1})	0.863
λ (Å)	0.71073
T (°C)	293 (2)
R_1, wR_2 [$I < 2\sigma(I)$][a]	0.0356, 0.0819
R_1, wR_2 (all data)[a]	0.0595, 0.0897
GoF	1.023

[a] $R = \sum|F_0| - |F_c|/\sum|F_c|$; $wR_2 = \sum[w(F_0^2 - F_c^2)]/\sum[w(F_0^2)^2]^{1/2}$.

Table 3
Selected bond lengths (Å) and bond angles (°) for the compound **8**

Bond lengths			
P3–N1	1.607(3)	P3–N2	1.609(3)
P3–C14	1.798(3)	P3–C2	1.790(3)
P2–N1	1.560(3)	P2–N3	1.588(3)
P2–O1	1.583(2)	P2–O2	1.594(2)
P4–N3	1.561(3)	P4–N2	1.550(3)
P4–F1	1.530(2)	P4–F2	1.533(2)
P1–C12	1.825(3)	P1–C13	1.817(3)
P1–C11	1.816(3)	P1–S1	1.9359(12)
Bond angles			
N2–P3–N1	115.40(14)	C20–P3–C14	105.27(14)
N2–P4–N3	119.78(14)	F1–P4–F2	96.72(12)
N3–P2–N1	119.15(14)	O1–P2–O2	103.73(11)
C12–P1–C13	101.01(15)	C12–P1–C11	102.47(16)
C13–P1–C11	105.88(15)	P4–N3–P2	119.51(17)
P2–N1–P3	121.06(16)	N1–P3–N2	115.40(14)

The crystal structure of the spirocyclic derivative of *gem*-diphenylfluorophosphazene (**8**) shows that the phosphazene ring is slightly puckered (Fig. 3b) from planarity in comparison to $N_3P_3F_6$ (Fig. 3a) [19,20]. It has been reported that one of the phosphorus atoms that is bearing the phenyl groups in the phosphazene ring of the *gem*-diphenyl tetrafluorophosphazene was deviated to a distance of 0.20 Å from the plane defined by the other five atoms of the phosphazene ring (Fig. 3d). But in the case of the spiro compound **8**, the same phosphorus atom is deviated only to a distance of 0.0037 Å from the mean plane defined by the other five atoms of the ring. But if the mean plane is defined by the all the six atoms of the phosphazene ring, five of the atoms are deviated significantly from the plane. This causes puckering of the N_3P_3 ring (Fig. 3c). This kind of puckering of the fluorophosphazenes ring, which was not observed for the monospiro compound of fluorophosphazene [9], indicates the possible electronic influence of geminal phenyl groups on the planarity of the phosphazene ring.

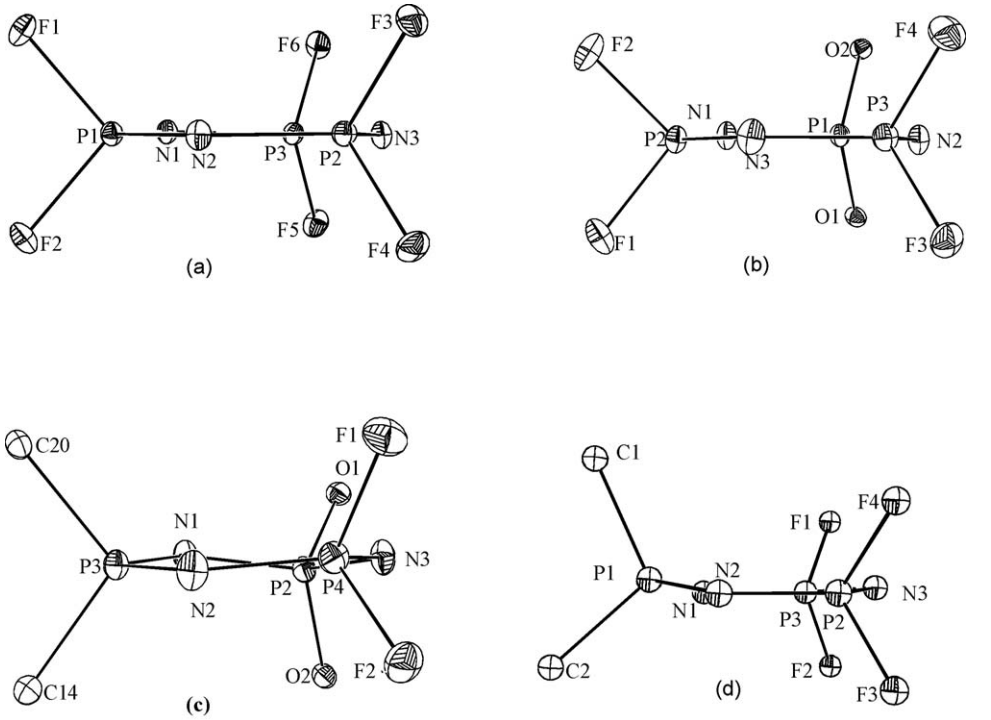


Fig. 3. The comparison of mean planes formed by phosphazene ring (a) of $N_3P_3F_6$ [19], (b) of monospiro {1,1-[$FcCH_2P(S)(CH_2O)_2$]}$N_3P_3F_4$ [9], (c) of monospiro [1,1-(C_6H_5)]{3,3-[$FcCH_2P(S)(CH_2O)_2$]}$N_3P_3F_2$ (**8**) and (d) of 1,1-(C_6H_5)$_2N_3P_3F_4$ [13].

3. Conclusions

The *gem*-diphenyltetrafluorophosphazene, $[1,1\text{-}(C_6H_5)_2]P_3N_3F_4$ was prepared by an alternate method in good yields by the fluorination of $[1,1\text{-}(C_6H_5)_2]P_3N_3Cl_4$ using KF/CH_3CN. A systematic study of its reactions with two dilithiated diols has been carried out. Unlike $[1,1\text{-}(C_6H_5)_2]P_3N_3Cl_4$, which yielded exclusively spiro substituted products with diols and aminoalcohols, the reactions of the *gem*-diphenyltetrafluorophosphazene yielded all the possible products of such a reaction namely the bridged, ansa, spiro and dangling derivatives. The study indicates the usefulness of dilithiation route for making ansa, bridged and dangling derivatives of the diphenyl fluorophosphazene. The experiments differ significantly when compared to similar reactions of $N_3P_3F_6$ and indicate that dangling derivative is the major product in these reactions thus providing a good synthetic route for the dangling derivatives of $[1,1\text{-}(C_6H_5)_2]P_3N_3F_4$. By doing the reaction with monolithiated diols, the yields of dangling derivatives has been increased further. Unlike the crystal structure of $[1,1\text{-}(C_6H_5)_2]N_3P_3F_4$, wherein the phenyl bearing P atom alone is found to be away from the mean plane of the ring, or the crystal structure of monospirocyclic compound $\{1,1\text{-}[FcCH_2P(S)(CH_2O)_2]\}N_3P_3F_4$ wherein the N_3P_3 ring is planar, the phosphazene ring in compound **8** is found to be puckered.

4. Experimental

4.1. General experimental procedures

A conventional vacuum line equipped with a dry nitrogen apparatus and Schlenk glassware was used for all reactions. Reactions and work up procedures were carried out under an atmosphere of dry nitrogen. $N_3P_3F_6$ was prepared from $N_3P_3Cl_6$ (Fluka) according to the literature method [21] and was purified by fractional distillation (caution: $N_3P_3F_6$ is a potentially toxic compound and has high vapor pressure at room temperature). The synthesis of the diol, $FcCH_2P(S)(CH_2OH)_2$, was carried out by literature method [22]. 1,3-propanediol was used as obtained from Lancaster. Hexane, ethylacetate, dichloromethane and tetrahydrofuran were distilled and dried by standard procedures.

4.2. Instrumentation

^1H, $^{31}P\{^1H\}$, ^{19}F and $^{13}C\{^1H\}$ NMR spectra were recorded using a JEOL JNM-LA 400 FT NMR and Bruker Spectrospin DPX-300 spectrometers with $CDCl_3$, as solvent. The chemical shifts are reported with respect to the internal standards, TMS (for ^1H), 85% H_3PO_4 [for $^{31}P\{^1H\}$], and $CFCl_3$ (for ^{19}F). Mass spectra were obtained on a JEOL D-300 spectrometer in the FAB mode. Elemental analyses were carried out Carlo-Erba CHNO 1108 elemental analyzer. IR spectra were recorded as KBr pellets on a Nicolet Protégé 460 FT-IR spectrometer operating at 400–4000 cm^{-1}.

4.3. Synthesis

4.3.1. Preparation of gem-diphenyltetrachlorophosphazene (1)

The compound $[1,1\text{-}(C_6H_5)_2]P_3N_3Cl_4$ [23] (3.26 g, 7.5 mmol) was dissolved in 50 mL of acetonitrile and potassium fluoride (2.19 g, 37.7 mmol) was added to it. The mixture was refluxed in acetonitrile for 10 h. Then the acetonitrile was evaporated off and the residue was dissolved in dichloromethane to filter off the KCl formed in the reaction. The mixture was purified by column chromatography over silica gel using a mixture of 2% dichloromethane in hexane as eluent to get the pure *gem*-diphenyl tetrafluorophosphazene, $[1,1\text{-}(C_6H_5)_2]P_3N_3F_4$ (**1**). Yield: 2.00 g, 72.4%; mp: 63 °C. NMR: $^{31}P\{^1H\}$, δ 25.83 [t ($^2J_{PF}$ = 49 Hz), $P(C_6H_5)_2$], 7.6 [mt ($^1J_{PF}$ = 911 Hz), PF_2]; ^{19}F, δ −67.57 [md ($^1J_{PF}$ = 937 Hz), PF_2].

4.3.2. Reaction of the $LiO(CH_2)_3OLi$ with compound 1

The diol, $HO(CH_2)_3OH$ (0.15 g, 2.0 mmol) was dilithiated by reacting with *n*-BuLi (2.50 mL, 4.0 mmol) at −80 °C in THF (20 mL). After 4 h of stirring, compound **1** (1.00 g, 2.7 mmol) dissolved in 20 mL of THF was added to the above solution dropwise at −80 °C with constant stirring. The mixture was allowed to reach room temperature over a period of 2 h, and then stirred further for 12 h. Afterwards, the THF was evaporated off and the mixture was dissolved in dichloromethane followed by filtration of LiF formed in the reaction. The mixture was analyzed by TLC and $^{31}P\{^1H\}$ NMR spectroscopy and the presence of four products were observed. The products were separated by column chromatography over silica gel using ethylacetate/hexane mixture as eluent. The first compound which came out of the column, obtained as viscous liquid was identified as the bridged-$[N_3P_3F_3(C_6H_5)_2]O(\text{-}CH_2)_3O[N_3P_3F_3(C_6H_5)_2]$ (**4**). Yield: 0.08 g, 10%. NMR: ^1H, δ 7.74–7.65 (m, 4H, C_6H_5), 7.40–7.32 (m, 6H, C_6H_5), 4.08–4.03 (m, 4H, CH_2O), 1.91 (quintet, 2H, $–CH_2–$); $^{31}P\{^1H\}$, δ 24.70 [t ($^2J_{PNP}$ = 44.4 Hz), $P(C_6H_5)_2$], 12.74 [md ($^1J_{PF}$ = 895.0 Hz), OPF], 7.88 [mt ($^1J_{PF}$ = 902.2 Hz), PF_2]; ^{19}F, δ −64.20 [md ($^1J_{PF}$ = 908.4 Hz), OPF], −66.83 [md ($^1J_{PF}$ = 907.1 Hz), PF_2], −67.44 [md ($^1J_{PF}$ = 912.9 Hz), PF_2]; $^{13}C\{^1H\}$, δ 30.46–30.14 (m, $–CH_2–$), 63.57 (d, CH_2O), 128.69–128.49 (m, *o*-C), 130.40–130.22 (m, *m*-C), 132.11–132.04 (m, *p*-C) 133.11 and 134.46 (s, *ipso* carbons). MS(FAB) [*m/e* (species)]: 766 (M^+), 662 $[N_3P_3(C_6H_5)_2]O(CH_2)_3O[(N_3P_3(C_6H_5)_2]$, 404 $[N_3P_3F_3(C_6H_5)_2]O(CH_2)_3O$, 362 $[N_3P_3F_3(C_6H_5)_2]O$. Anal. Calcd. for $C_{27}H_{26}O_2P_6N_6F_6$ (%): C, 42.32; H, 3.42; N, 10.97. Found: C, 42.20; H, 3.28; N, 10.81.

The second compound which was obtained as white solid was identified as ansa-$\{3,5\text{-}[O(CH_2)_3O]\}[1,1\text{-}(C_6H_5)_2]N_3P_3F_2$ (**3**). Yield: 0.04 g, 5%; mp: 98 °C. NMR: ^1H, δ 7.74–7.68 (m, 4H, C_6H_5), 7.41–7.31 (m, 6H, C_6H_5), 4.48–4.40 (m, 2H, CH_2O), 4.34–4.24 (m, 2H, CH_2O), 2.18–2.07 (m, 2H, CH_2P); $^{31}P\{^1H\}$, δ 26.88 [tt ($^2J_{PNP}$ = 42.0 Hz), $P(C_6H_5)_2$], 18.06 [md ($^1J_{PF}$ = 909.5 Hz), OPF]; ^{19}F, δ −71.92 [md ($^1J_{PF}$ = 910.4 Hz), OPF]; $^{13}C\{^1H\}$, δ 31.97 (m, $–CH_2–$), 66.82–66.78 (m, CH_2O), 128.61–128.36 (m, *o*-C), 130.60–130.32 (m, *m*-C), 131.84–131.66 (m, *p*-C), 132.08 and 132.81 (s, *ipso* carbons). MS(FAB)

[*m/e* (species)]: 401 (M^+), 324 $N_3P_3F_2(C_6H_5)[O(CH_2)_3O]$, 363 $N_3P_3(C_6H_5)_2[O(CH_2)_3O]$, 154 $N_3P_3F_1$, 135 N_3P_3. Anal. Calcd. for $C_{15}H_{16}O_2P_3N_3F_2$ (%): C, 44.90; H, 4.02; 10.47. Found: C, 44.81; H, 3.87; N, 10.40.

The third compound which obtained as a white solid was identified as spiro-{1,1-[$O(CH_2)_3O$]}[1,1-$(C_6H_5)_2$]$N_3P_3F_2$ (**2**). Yield: 0.07 g, 9%; mp: 144 °C. NMR: ^{1}H, δ 7.84–7.79 (m, 2H, C_6H_5), 7.73–7.67 (m, 2H, C_6H_5), 7.47–7.31 (m, 6H, C_6H_5), 4.34–7.24 (m, 2H, CH_2O), 4.04–3.95 (m, 2H, CH_2O), 2.03–1.90 (m, 2H, –CH_2–); ^{31}P{^{1}H}, δ 23.94 [t ($^2J_{PNP}$ = 42.8 Hz), $P(C_6H_5)_2$], 12.05–11.52 (m, OPO), 6.78 [mt ($^1J_{PF}$ = 906.3), PF_2]; ^{19}F, δ −66.72 [md ($^1J_{PF}$ = 909.3 Hz), PF_2]; ^{13}C{^{1}H}, δ 31.94 (s, –CH_2–), 66.80 (s, CH_2O), 128.60–128.35 (m, *o*-C), 130.57–130.46 (m, *m*-C), 131.80–131.66 (m, *p*-C), 134.02 and 135.31 (s, *ipso* carbons). MS(FAB) [*m/e* (species)]: 401 (M^+), 400 (M^+ − H), 382 $N_3P_3F(C_6H_5)_2[O(CH_2)_3O]$, 324 $N_3P_3F_2(C_6H_5)[O(CH_2)_3O]$, 247 $N_3P_3F_2[O(CH_2)_3O]$, 327 $N_3P_3F_2(C_6H_5)_2$, 135 N_3P_3, 77 C_6H_5.

The fourth compound which obtained as a viscous liquid was identified as dangling-$[HO(CH_2)_3O](C_6H_5)_2N_3P_3F_3$ (**5**). Yield: 0.31 g, 39%. IR (DCM) (cm^{-1}): 3419 (s, broad, OH). NMR: ^{1}H, δ 7.73–7.65 (m, 4H, C_6H_5), 7.42–7.31 (m, 6H, C_6H_5), 4.12–4.07 (m, 2H, CH_2O), 3.58 (t, 2H, –CH_2OH), 1.76 (quintet, 2H, –CH_2–), 2.41 (s, broad, 1H, –OH); ^{31}P{^{1}H}, δ 24.91 [t ($^2J_{PNP}$ = 44.4 Hz), $P(C_6H_5)_2$], 12.94 [md ($^1J_{PF}$ = 900.6 Hz), OPF], 8.03 [mt ($^1J_{PF}$ = 902.6 Hz), PF_2]; ^{19}F, δ −63.99 [md ($^1J_{PF}$ = 889.6 Hz), OPF], −66.66 [md ($^1J_{PF}$ = 917.4 Hz), PF_2], −67.49 [md ($^1J_{PF}$ = 902.4 Hz), PF_2]; ^{13}C{^{1}H}, δ 32.31 [d (J = 7 Hz), CH_2], 57.88 (s, CH_2OH), 64.77 [d (J = 6 Hz), CH_2O], 128.60–128.41 (m, *o*-C), 130.29–130.13 (m, *m*-C), 132.09–132.03 (m, *p*-C), 132.82 and 134.19 (s, *ipso* carbons). MS(FAB) [*m/e* (species)]: 421 (M^+), 404 $N_3P_3F_2(C_6H_5)_2[O(CH_2)_3]$, 344 $N_3P_3F_2(C_6H_5)[O(CH_2)_3O]$, 154 N_3P_3F, 135 N_3P_3. Anal. Calcd. for $C_{15}H_{16}O_2P_3N_3F_2$ (%): C, 42.77; H, 4.07; 9.98. Found: C, 42.59; H, 3.83; N, 10.18.

*4.3.3. Reaction of monolithiated 1,3-propanediol with compound **1***

The 1,3-propanediol (0.22 g, 2.9 mmol) was monolithiated in THF by the slow addition of *n*-BuLi (1.8 mL, 2.9 mmol) as THF (40 mL) solution at −80 °C and was stirred for 6 h at −80 °C. After 6 h, the *gem*-diphenylfluorophosphazene (**1**) (1.05 g, 2.9 mmol) dissolved in THF (20 mL) was added to the above solution at −80 °C and the mixture was allowed to reach room temperature over a period of 2 h. After the stirring of mixture at room temperature for 12 h, THF was evaporated off and the residue was dissolved in dichloromethane to filter off the LiF formed in the reaction. The mixture was analyzed by TLC and purified by column chromatography over silica gel using ethyl acetate/hexane mixture as eluent. The compound which came out of the column around 17–25% of ethyl acetate in hexane was characterized as the dangling derivative, $[HO(CH_2)_3O]N_3P_3F_3(C_6H_5)_2$ (**5**) (0.86 g, 71%). The spectral data of the compound obtained in this reaction was compared with that the compound obtained in the reaction of dilithiated propanediol with compound **1**. This reaction also yielded traces of other products ansa **3**, spiro **2** and bridged **4** derivatives.

*4.3.4. Reaction of the $FcCH_2P(S)(CH_2OLi)_2$ with compound **1***

The diol, $FcCH_2P(S)(CH_2OH)_2$ (0.88 g, 2.7 mmol) was lithiated by adding *n*-BuLi (3.42 mL, 5.5 mmol) at −80 °C in THF (20 mL). After 4 h of stirring, compound **1** (1.00 g, 2.7 mmol) dissolved in 20 mL of THF was added to the above solution dropwise with constant stirring at −80 °C. The mixture was allowed to reach room temperature over a period of 2 h, and then stirred further for 12 h. Afterwards, the THF was evaporated off, the mixture dissolved in dichloromethane and the LiF formed was filtered off. The mixture was analyzed by TLC and ^{31}P{^{1}H} NMR spectroscopy. The products were purified by column chromatography over silica gel using ethylacetate/hexane mixture as eluent. The analysis of the fractions collected first (0.25 g, 28%) showed the presence of ansa and spiro derivatives. Upon dissolving it in the ethylacetate/hexane and on cooling to 4 °C yielded crystals of spiro-[1,1-$(C_6H_5)_2$][3,3-$FcCH_2P(S)(CH_2O)_2$]$N_3P_3F_2$ (**8**). Yield: (0.11 g, 12%); mp: 199 °C. NMR: ^{1}H, δ 3.47 [d (J_{PH} = 11 Hz), 2H, $FcCH_2P$], 4.17 (s, 5H, C_5H_5), 4.18–4.17 (m, 2H,C_5H_4), 4.31–4.23 (m, 2H, PCH_2O), 4.35–4.30 (m, 2H, C_5H_4), 4.87–4.84 (m, 2H, PCH_2O), 7.42–7.38 (m, 4H, *o*-H of C_6H_5), 7.49–7.44 (m, 2H, *m*-H of C_6H_5), 7.74–7.69 (m, 4H, *p*-H of C_6H_5); ^{31}P{^{1}H}, δ 24.54 [t ($^2J_{PP}$ = 44 Hz), $P(C_6H_5)_2$], 19.19 [d ($^3J_{PP}$ = 15 Hz), P═S], 14.04–13.25 (m, OPO), 4.98 [ddt ($^1J_{PF}$ = 905 Hz, $^2J_{PP}$ = 72.7 and 45 Hz), PF_2]; ^{19}F, δ −66.91 [ddd ($^1J_{PF}$ = 906 Hz, $^3J_{PF}$ = 12 and 6 Hz), PF_2]; ^{13}C{^{1}H} δ 28.90 [d (J_{PC} = 46 Hz), $FcCH_2P$], 66.29 [d (J_{PC} = 50 Hz), PCH_2O], 68.71 (s, β-C of C_5H_4), 69.03 (s, C_5H_4), 69.68 (s, γ-C of C_5H_4), 75.65 (s, α-C of C_5H_4), 128.59 [d (J_{PC} = 14 Hz), *o*-C of C_6H_5], 130.58 [d (J_{PC} = 12 Hz), *m*-C of C_6H_5], 132.14 (s, *p*-C of C_6H_5), 132.92 and 134.35 (s, *ipso* carbons). MS(FAB) [*m/e* (species)]: 649 (M^+), 476 $N_3P_3F[FcCH_2P(S)(CH_2O)_2]$, 306 $FcCH_2P(S)(CH_2O)(CH_2^+)$, 199 $FcCH_2$, 154 N_3P_3F, 121 Fe(ηC$_5$H$_4$), 77 C_6H_5. Anal. Calcd. for $C_{25}H_{25}O_2P_4N_3F_2S_1Fe_1$ (%): C, 46.25; H, 3.88; N, 6.47. Found: C, 46.16; H, 3.65, N, 6.32.

Further keeping the mixture at 0 °C for 4 days yielded a precipitate which was characterized as *endo*-[1,1-$(C_6H_5)_2$][3,5-$FcCH_2P(S)(CH_2O)_2$]$N_3P_3F_2$ (**6**). Yield: (0.06 g, 7%); mp: 190 °C. NMR: ^{1}H, δ 2.86 [d (J = 11 Hz), $FcCH_2P$], 3.85 (s, 5H, C_5H_5), 4.05 to 4.04 (m, 4H,C_5H_4), 4.21–4.12 (m, 2H, CH_2O), 4.61–4.55 (m, 2H, CH_2O), 7.55–7.38 (m, 6H, C_6H_5), 7.74–7.69 (m, 2H, C_6H_5), 7.94–7.89 (m, 2H, C_6H_5); ^{31}P{^{1}H}, δ 45.13 (s, P═S), 25.41 [t ($^2J_{PP}$ = 44.4 Hz), $P(C_6H_5)_2$], 14.76 [dd ($^1J_{PF}$ = 954.8 Hz, $^2J_{PNP}$ = 44.4 Hz), OPF]; ^{19}F, δ −70.01 [md ($^1J_{PF}$ = 940.1 Hz), PF_2]; ^{13}C{^{1}H}, δ 27.03 (s, $FcCH_2$), 65.35 (s, CH_2O), 68.66 (s, β-C of C_5H_4), 69.01 (s, C_5H_5), 69.80 (s, γ-C of C_5H_4), 128.86–128.55 (m, *o*-C of C_6H_5), 130.52–130.41 (m, *m*-C of C_6H_5), 132.14 (s, *p*-C of C_6H_5) 132.45 and 132.11 (s, ipso carbons of C_6H_5). MS(FAB) [*m/e* (species)]: 649 (M^+), 476 $N_3P_3F[FcCH_2P(S)(CH_2O)_2]$, 307 $FcCH_2P(S)(CH_2O)(CH_2H)$, 199 $FcCH_2$, 154 N_3P_3F, 121 $Fe(C_5H_4)$. Anal. Calcd. for $C_{25}H_{25}O_2P_4N_3F_2S_1Fe_1$ (%): C, 46.25; H, 3.88; N, 6.47. Found: C, 46.35; H, 3.75, N, 6.40.

After the separation of the spiro and *endo* ansa compounds the remaining residue after removal of solvent was characterized as

exo-[1,1-$(C_6H_5)_2$][3,5-$FcCH_2P(S)(CH_2O)_2$]$N_3P_3F_2$ (**7**). Yield: (0.05 g, 6%); mp: 182 °C. NMR: ^1H, δ 3.12 [d (J = 11 Hz), $FcCH_2P$], 3.80 (s, 5H, C_5H_5), 4.16–4.14 (m, 4H, C_5H_4), 4.26–4.18 (m, 2H, CH_2O), 4.70–4.65 (m, 2H, CH_2O), 7.50–7.31 (m, 6H, C_6H_5), 7.78–7.63 (m, 2H, C_6H_5), 7.98–7.91 (m, 2H, C_6H_5); $^{31}P\{^1H\}$, δ 47.55 (s, P=S), 26.81 [t ($^2J_{PNP}$ = 39.6 Hz), $(C_6H_5)_2$], 14.28 [dd, OPF ($^1J_{PF}$ = 920.8 Hz, $^2J_{PNP}$ = 40.1 Hz)]; ^{19}F, δ −72.83 [md ($^1J_{PF}$ = 912.9 Hz), OPF]; $^{13}C\{^1H\}$, δ 29.68 (s, $FcCH_2$), 64.97 (s, CH_2O), 68.60 (s, β-C of C_5H_4), 69.11 (s, C_5H_5), 69.85 (s, γ-C of C_5H_4), 128.81–128.51 (m, *o*-C of C_6H_5), 130.57–130.46 (m, *m*-C of C_6H_5), 132.24 (s, *p*-C of C_6H_5) 132.48 and 132.17 (s, *ipso* carbons of C_6H_5). MS(FAB) [*m*/*e* (species)]: 649 (M^+), 476 $N_3P_3F[FcCH_2P(S)(CH_2O)_2]$, 307 $FcCH_2P(S)(CH_2O)(CH_2H)$, 199 $FcCH_2$, 154 N_3P_3F, 135 N_3P_3. Anal. Calcd. for $C_{25}H_{25}O_2P_4N_3F_2S_1Fe_1$ (%): C, 46.25; H, 3.88; N, 6.47. Found: C, 46.18; H, 3.75, N, 6.56.

The second fraction obtained from column chromatography was characterized as bridged derivative $[(C_6H_5)_2P_3N_3F_3][OCH_2(FcCH_2)P(S)CH_2O][(C_6H_5)_2P_3N_3F_3]$ (**10**) (0.14 g, 16%). Semi-solid charring around 102 °C. NMR: ^1H, δ 3.05–3.07 (m, 2H, $FcCH_2$), 4.05–4.00 (m, 9H, Fc), 4.24–4.16 (m, 4H, CH_2O), 7.43–7.38 (m, 12H, C_6H_5), 7.73–7.67 (m, 8H, C_6H_5); $^{31}P\{^1H\}$, δ 40.28 (t, P=S), 25.25 [t ($^2J_{PNP}$ = 44 Hz), $P(C_6H_5)_2$], 13.09 [md ($^2J_{PNP}$ = 917 Hz), OPF], 7.45 [mt ($^2J_{PNP}$ = 905 Hz), PF_2]; ^{19}F, δ −66.65 [md ($^1J_{PF}$ = 919 Hz), PF_2], −68.96 [md ($^1J_{PF}$ = 938 Hz), PF_2], −69.70 [md ($^1J_{PF}$ = 929 Hz), OPF]; $^{13}C\{^1H\}$ δ 29.53 (s, $FcCH_2$), 62.71 (s, CH_2O), 69.59 (s, β-C of C_5H_4), 69.95 (s,C_5H_5), 70.49 (s, γ-C of C_5H_4), 76.59 (s, α-C of C_5H_4), 128.69–128.55 (m, *o*-C of C_6H_5), 130.28 to 130.20 (m, *m*-C of C_6H_5), 132.22 (*p*-C of C_6H_5), 132.70 and 133.94 (s, *ipso* carbons). MS(FAB): 1014 (M^+), 706 $[P_3N_3F_3][OCH_2(FcCH_2)P(S)CH_2O][P_3N_3F_3]$, 306 $FcCH_2P(S)(CH_2O)(CH_2–)$, 199 $FcCH_2$. Anal. Calcd. for $C_{37}H_{35}O_2P_7N_6F_6SFe$ (%): C, 43.81; H, 3.48; N, 8.28. Found: C, 43.58; H, 3.56, N, 8.36.

The third fraction obtained from chromatography was characterized as dangling derivative $(C_6H_5)_2P_3N_3F_3[OCH_2(FcCH_2)P(S)CH_2OH]$ (**9**) (0.25 g, 29%). Semi-solid charring around 120 °C. IR (nujol) (cm^{-1}): 3423 s (broad, OH), NMR: ^1H, δ 1.35 (s, 1H, OH), 3.05–3.08 (m, 2H, $FcCH_2$), 3.88–3.81 (m, 2H, CH_2O), 4.25–4.03 (m, 9H, Fc), 4.91–4.81 (m, 2H, CH_2O), 7.71–7.18 (two set of multiplets, 10H, C_6H_5); $^{31}P\{^1H\}$, δ 40.46 (m, P=S), 25.01 (m, $P(C_6H_5)_2$), 13.39 [md ($^2J_{PNP}$ = 921 Hz), OPF], 7.58 [mt ($^2J_{PNP}$ = 934 Hz), PF_2]; ^{19}F, δ −66.54 [md ($^1J_{PF}$ = 902 Hz), PF_2), −68.72 [md ($^1J_{PF}$ = 928 Hz), PF_2], −69.50 [md ($^1J_{PF}$ = 934 Hz), OPF]; $^{13}C\{^1H\}$ δ 29.09 ($FcCH_2$), 59.97–59.12 (m, CH_2O), 62.98–61.74 (m, CH_2O), 68.87 (s, β-C of C_5H_4), 69.38 (s, C_5H_5), 69.85 (s, γ-C of C_5H_4) 128.55 (m, *o*-C of C_6H_5), 130.10 (m, *m*-C of C_5H_4), 132.14 (m, *p*-C of C_5H_4), 133.67 (s, *ipso* carbon). MS(FAB): 669 (M^+). Anal. Calcd. $C_{25}H_{26}O_2P_4N_3F_3SFe$ (%): C, 44.86; H, 3.92; N, 6.28. Found: C, 44.70; H, 3.84; N, 6.15.

4.4. X-ray diffraction studies

The X-ray diffraction data for compound **8** was collected on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by SHELXS-97 and refined by SHELXL-97 [24]. The structure was refined against F^2 with a full-matrix least-squares algorithm. All non-hydrogen atoms were refined anisotropically. The X-ray data pertaining to data collection, crystal system, and structure solution as well the selected bond distances and angles for the compound **8** are given in Tables 2 and 3. Complete crystallographic information has been deposited with the CCDC (deposition number CCDC 609231). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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