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Reactions of ferrocene-derived bis(hydroxymethyl) phosphine sulfides $FcCH(R)P(S)(CH_2OH)_2$ (R = H, CH_3) with cyclic thionylphosphazenes: crystal structures of $FcCH_2P(S)(CH_2O)_2PN(NPCl_2)[NS(O)Ph]$ and $FcCH_2P(S)(CH_2O)_2PN_2P[N(Me)CH_2]_2[NS(O)Ph]$ (Fc = ferrocenyl)

T.V.V. Ramakrishna, Anil J. Elias *

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

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Abstract

The cyclic six-membered thionylphosphazenes, $(NPCl_2)_2[NS(O)X]$ X = Cl (**1**), Ph (**2**) and 4-Cl–C_6H_4 (**3**) as well as the monospirocyclic derivatives $(NPCl_2)NP[N(Me)CH_2]_2[NS(O)Ph]$ (**4**) and $(NPCl_2)NP[N(Me)CH_2]_2[NS(O)4\text{-}Cl\text{–}C_6H_4]$ (**5**) were synthesized. Reactions of these compounds were carried out with dilithiated ferrocene-derived hydroxymethyl phosphine sulfides, $FcCH_2P(S)(CH_2OH)_2$ (**6**) and $FcCH(CH_3)P(S)(CH_2OH)_2$ (**7**) under different conditions. Reactions of **1** with **6** and **7** did not yield any desired products. In contrast, 1:1 reactions of **2** with **6** and **7** readily yielded air stable monospirocyclic compounds $FcCH_2P(S)(CH_2O)_2PN(NPCl_2)[NS(O)Ph]$ (**8**) and $FcCH(CH_3)P(S)(CH_2O)_2PN(NPCl_2)[NS(O)Ph]$ (**9**), respectively. Controlled reactions of **4** and **5** with **6** were performed in which dispirocyclic compounds $FcCH_2P(S)(CH_2O)_2PN_2P[N(Me)CH_2]_2[NS(O)Ph]$ (**10**) and $FcCH_2P(S)(CH_2O)_2PN_2P[N(Me)CH_2]_2[NS(O)4\text{-}Cl\text{–}C_6H_4]$ (**11**) were isolated. The product obtained in the 1:1 reaction of $HOCH_2(CF_2)_2CH_2OH$ with $(NPCl_2)_2[NS(O)4\text{-}Cl\text{–}C_6H_4]$ (**3**) when reacted with **6** resulted in the dispirocyclic compound $FcCH_2P(S)[(CH_2O)_2PN_2P\ (OCH_2CF_2)_2][NS(O)4\text{-}Cl\text{–}C_6H_4]$ (**12**). Compound **12** was found to exist as isomers. To confirm the formation of isomers, $\{[CH_2N(Me)]_2PN_2P(OCH_2CF_2)_2\}[NS(O)Ph]$ (**13**) was synthesized by the reaction of **4** with $HOCH_2(CF_2)_2CH_2OH$ which was also found to exist as isomers. Attempts to synthesize intermolecular bridged compounds of **2** with **6** and **7** resulted in compounds **8** and **9** exclusively. The crystal structures of compounds **8** and **10** were determined.

Keywords: Ferrocene; Hydroxymethyl phosphine sulfide; Thionylphosphazene; Spirocycles

1. Introduction

The chemistry of ferrocene-derived amines and phosphines has attracted a lot of interest in recent years primarily from their proven usefulness as chiral auxiliaries in catalytic transformations [1]. Togni and others have extensively used a variety of such amines and phosphines in the preparation of useful catalysts [2]. Ferrocene-derived hydroxymethyl phosphines have also been reported by Henderson and co-workers which were found to be highly stable [3]. We also have recently reported the synthesis of a hydroxymethyl phosphine $FcCH(CH_3)P(CH_2OH)_2$ having an asymmetric carbon center [4]. Interestingly, unlike the phosphines, the hydroxymethyl groups of the corresponding phosphine sulfides were found to behave as normal diols in their reactions.

The structural constraints provided by ferrocene-derived phosphine sulfides were found to reflect in their chemistry. Reactions of $FcCH_2P(S)(CH_2OLi)_2$ with the perfluorinated cyclophosphazene, $N_3P_3F_6$ resulted in the exclusive formation of novel *exo* and *endo* transannular substituted cyclophosphazenes which are difficult to prepare otherwise [5]. In addition, introducing ferrocenyl moieties on cyclophosphazenes have been found

* Corresponding author. Fax: +91-512-597436.
E-mail address: elias@iitk.ac.in (A.J. Elias).

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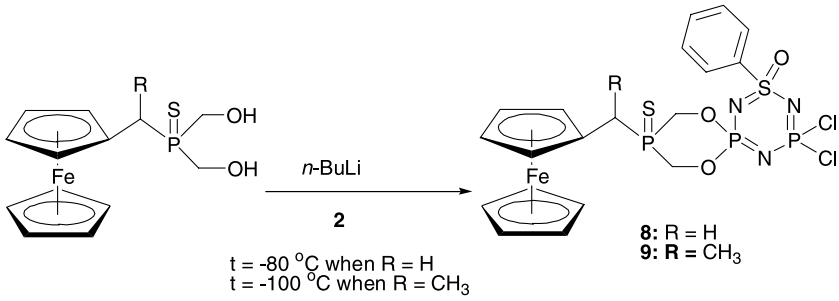


Scheme 1.

to induce electroactivity in the assembly and such heterocycles on ring opening polymerization have yielded novel ferrocene pendant polyphosphazenes that showed promise in catalytic systems, as electrode mediators and as electroactive solid state materials [6,7]. In tune with this interest, we have recently reported the first example of a ferrocene-derived cyclocarbaphosphazene, a hybrid inorganic–organic heterocycle [8]. In this paper we report the first reactions of ferrocene-derived hydroxymethyl phosphine sulfides with a series of chlorinated and partially aryl/amino substituted thionylphosphazene, a well known inorganic heterocycle [9]. Regiospecificity in nucleophilic substitution reactions as well as ring opening polymerization reactions of thionylphosphazenes has been well documented [10]. We also describe the crystal structures of two of the novel ferrocene-derived thionylphosphazenes prepared in this study.

2. Results and discussion

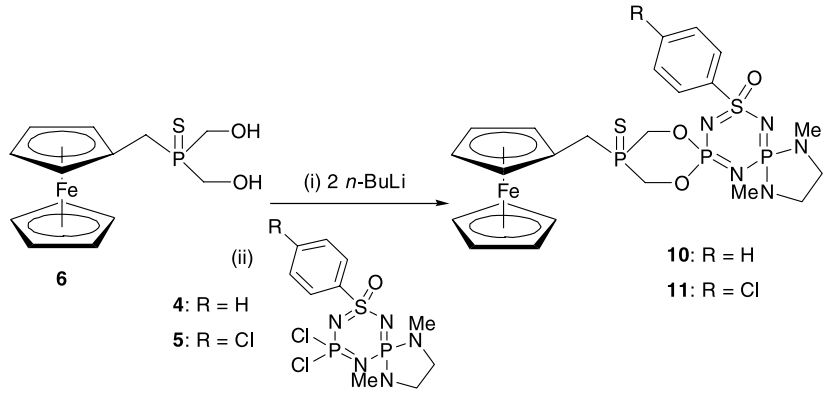
Initial reactions of $(NPCl_2)_2[NS(O)Cl]$ (**1**) with dilithiated salts of $FcCH(R)P(S)(CH_2OH)_2$ ($R = H$, CH_3) in 1:1 molar ratio at -80 °C resulted in mixtures of products which could not be isolated in pure form and characterized. A similar experience was reported by Van de Grampel and co-workers in the reaction between secondary diamines and $(NPCl_2)_2[NS(O)Cl]$ [10e]. Hence, to understand the reactivity of the heterocycle, 1:1 molar reaction of $FcCH_2P(S)(CH_2OLi)_2$ with S-phenyl substituted thionylphosphazene **2** was performed under similar conditions. This reaction was found to proceed smoothly yielding an air stable monospirocyclic compound **8** as an orange solid. It was interesting to see that a similar reaction between dilithiated $FcCH(CH_3)P(S)(CH_2OH)_2$ (**7**) and **2** did not result in any desirable products at -80 °C. However, this reaction was achieved by lithiating **7** at -100 °C, which resulted in compound **9** (Scheme 1). This behavior of the diol **7** can be due to the competing reaction between the proton adjacent to the ferrocene moiety and the protons of hydroxy groups during the lithiation at -80 °C. By carrying out the reaction at -100 °C side reactions were avoided.

The presence of free P–Cl bonds in both **8** and **9** increases the viability towards thermal ring opening polymerization of these ring systems similar to cyclotriphosphazenes. The exclusive formation of the monospirocycles over the other possible substituted products such as: (i) *ansa* (the two functional groups attached to different phosphorus atoms of the same molecule); (ii) intermolecular bridging (each functional group attached to two different rings); and (iii) dangling (only one end of the difunctional reagent attached to the ring) [11], indicates a geminal pathway followed by the reaction between **2** and diols. These results were similar to the observation made by Shaw and co-workers in a 1:1 molar reaction of 2,2,4,4-tetrachloro-6,6-diphenyl phosphazene, $N_3P_3Ph_2Cl_4$ with 1,3-propanediol, in which monospirocyclic product was predominantly formed [12].

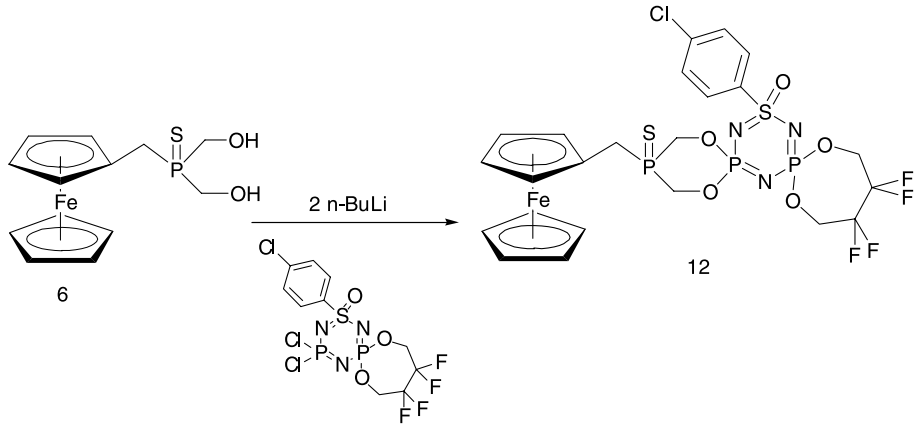
With an intention to achieve selective substitution on the ring phosphorus atoms of the thionylphosphazene, diamino substituted monospirocycles **4** and **5** were synthesized and further reacted with dilithiated salt of **6** to yield the dispirocycles **10** and **11** which have amino substituent on one phosphorus and a ferrocenyl diol substitution on other phosphorus atom (Scheme 2). A similar substitution was observed when $FcCH_2P(S)(CH_2OH)_2$ was dilithiated and reacted with the carbaphosphazene $(NCNMe_2)_2(NPCl_2)$ [8].

The product obtained in the 1:1 molar reaction between the dilithiated salt of $(CF_2CH_2OH)_2$ with **3** was reacted with equimolar quantities of $FcCH_2P(S)(CH_2OLi)_2$ to afford compound **12** in about 65% yield (Scheme 3).

It was interesting to note that with these dilithiated reagents, only spirocyclic products were obtained when reacted with **2** or **3** which is in contrast to the reactions of the dilithiated ferrocene-derived diols with $N_3P_3F_6$ [5]. The ^{31}P-NMR spectrum of **12** showed the presence of two possible isomers with slight difference in δ values (~ 1.50–3.00 ppm) in 1:1 ratio according to signal intensities. Attempts to separate these isomers by column chromatography were unsuccessful. To com-



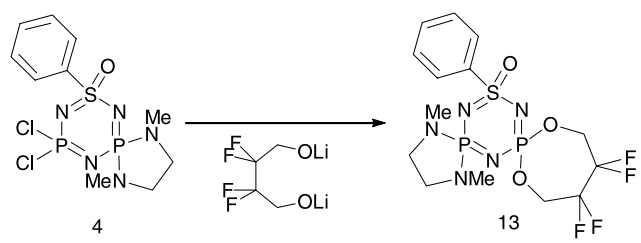
Scheme 2.



Scheme 3.

pare and verify the above result, an equimolar reaction of **4** with the dilithiated salt of $HOCH_2(CF_2)_2CH_2OH$ was performed to realize compound **13** (Scheme 4). The ^{31}P-NMR spectrum of the crude reaction mixture of **11** also showed formation of isomers in almost equal amounts. Unlike **12**, these isomers were separated by column chromatography and showed very little difference in their ^{1}H- and ^{13}C-NMR chemical shifts. The formation of isomers in the compounds **12** and **13** can be due to the conformational effects of the seven-membered spirocycle with respect to the ring. The determination of stereochemistry of substitution of these compounds was not possible using the ^{31}P-NMR spectral data alone.

With a view to synthesize intermolecular bridged compounds of **2** with $FcCH(R)P(S)(CH_2OH)_2$ (R = H, CH_3), 2:1 molar reactions of **2** with dilithiated **6** and **7** were carried out at -80 and -100 °C, respectively. Surprisingly, in both the cases, monospirocyclic compounds **8** and **9** were isolated exclusively in almost 81–85% yields. The FAB mass spectra of **8**–**12** and EI mass spectrum of **13** gave molecular ion peaks. For compounds **8**, **10**–**12** the base peak was 199 indicating the most stable fragment as $FcCH_2^+$. Compound **13** had base peak at m/e 398 ($M^+ - Ph$) and **9** had base peak at m/e 213 corresponding to $FcCH(CH_3)^+$ fragment. In the ^{1}H-NMR spectra of compounds **8**–**12**, it was noticed that the PCH_2 protons were deshielded to δ 4.40–4.52 ppm from δ 3.87–3.91 ppm observed for **6** and **7**. It was also noticed that the substitution on one of the ring phosphorus atoms did not affect the ^{1}H-NMR chemical shifts of the substituents on the other phosphorus atom. The N–CH_3 protons of **10**, **11** and **13** gave a doublet for each at δ 2.20–2.80 ppm indicating their magnetic inequivalence. The ^{13}C-NMR chemical shifts were within the range expected for these compounds.



Scheme 4.

Table 1
^{31}P-NMR spectral data of substituted thionylphosphazenes

Compound	^{31}P-NMR, δ (ppm)			$^{2}J_{P-P}$ (Hz)	$^{3}J_{P-P}$ (Hz)	Ref.
	P=S	P_1	P_2			
2		20.82 (PCl_2)				[17a]
4		26.72 (PCl_2)	18.30 [$P\{N(Me)CH_2\}_2$]	51.60		[10e]
6	44.00					[3]
7	61.84					[4]
8	21.15	5.07	23.13	67.91	17.79	This study
9	30.80	5.25	23.17	67.91	14.60	This study
10	23.09	14.90	21.30	61.45	16.17	This study
11	22.76	14.78	21.29	63.06	14.60	This study
12 (I)	21.99	10.76	11.09	84.08	14.60	This study
12 (II)	19.79	9.63	13.89	103.49	17.78	This study
13 (I)		17.39	22.57	71.15		This study
13 (II)		17.61	22.63	71.15		This study

For compounds **7**–**11** $P_1 = P(OCH_2)_2P(S)$ while for compounds **4** and **13** $P_2 = P[N(Me)CH_2]_2$.

The ^{31}P-NMR chemical shifts were found to be very sensitive towards the ring substitution and structure. Table 1 summarizes the ^{31}P-NMR chemical shifts and their relative coupling constants for some of the compounds used or synthesized in this study. (Ring phosphorus atoms are labeled as P_1 and P_2 while phosphorus atom of the ferrocene moiety is represented as P=S). The ^{31}P-NMR chemical shifts and coupling constants observed for compounds **8**–**13** were in good agreement with similar spirocyclic compounds of **1**, **2** and substituted cyclotriphosphazenes [10e,12–14].

The spirocyclic compounds **8**–**12** have shown three resonance signals corresponding to three phosphorus atoms P=S, P_1 and P_2, respectively. The P=S and P_2 signals were observed as doublets due to the $^{3}J_{P-P}$ and $^{2}J_{P-P}$ coupling with P_1, respectively, while P_1 was resonating as a doublet of doublet due to the $^{2}J_{P-P}$ coupling with P_2 and $^{3}J_{P-P}$ coupling with exocyclic P=S. Depending on the type of substituents and structure, the $^{3}J_{P-P}$ and $^{2}J_{P-P}$ values were observed in the range 14.60–17.78 and 61.45–103.49 Hz, respectively.

X-ray structures of compounds **8** and **10** are given in Figs. 1 and 2, respectively, and their crystallographic data is given in Table 2. Selected bond distances and angles for compounds **8** and **10** are listed in Tables 3 and 4, respectively. Compounds **8** and **10** are the first structural examples of thionylphosphazenes having ferrocene-derived substituents. Although one example of ferrocene-bound fluorinated thionylphosphazene was cited in a review article by Van de Grampel [9a] there exist no experimental and structural details for the same till date. In both the compounds **8** and **10** the six-membered spirocycle formed on the phosphorus of the heterocycle was found to adopt a chair conformation. The CH_2–P(1) bond distances of **8** and **10** were found to be 1.807(7) and 1.788(13) Å, respectively, which were shorter than the CH_2–P bond distance in $FcCH_2P(S)(CH_2OH)_2$ (**6**) reported by Henderson and co-workers (1.817(2) Å) [3]. The cyclopentadienyl rings in **10** were staggered by around 26°. In contrast, the

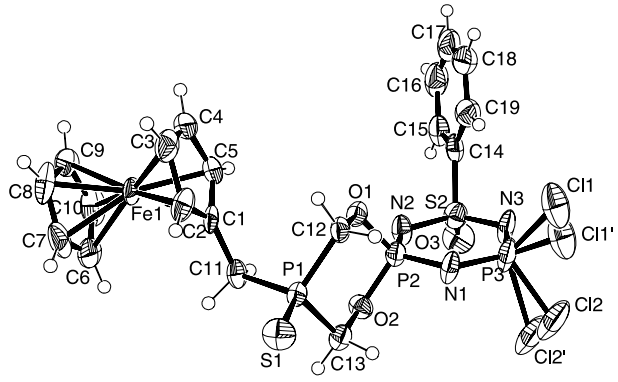


Fig. 1. Molecular structure of $FcCH_2P(S)(CH_2O)_2PN(NPCl_2)$-[NS(O)Ph] (**8**).

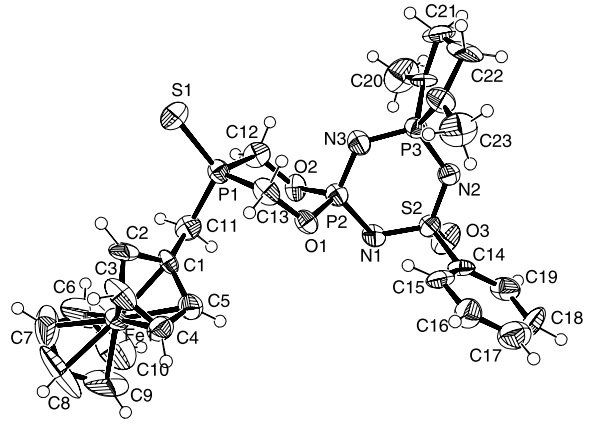


Fig. 2. Molecular structure of $FcCH_2P(S)(CH_2O)_2PN_2P[N(Me)$-$CH_2]_2][NS(O)Ph]$ (**10**).

Table 2
Crystallographic data and structure refinement parameters for compounds **8** and **10**

Compound	**8**	**10**
Empirical formula	$C_{19}H_{20}Cl_2FeN_3O_3P_3S_2$	$C_{23}H_{30}FeN_5O_3P_3S_2$
Formula weight	622.12	637.40
Temperature (K)	293(2)	293(2)
Crystal system	Triclinic	Orthorhombic
Space group	*P*-1	*Pnaa*
Unit cell dimensions		
a (Å)	6.135	11.886
b (Å)	11.146	17.877
c (Å)	18.257	26.787
α (°)	95.10	90
β (°)	97.50	90
γ (°)	95.90	90
V (Å^3)	1224.5	5692.1
Z	2	8
D_{calc} (g cm^{-3})	1.67	1.448
Absorbtion coefficent (mm^{-1})	1.229	0.880
F(000)	632	2640
2θ (max) (°)	22.48	22.47
Index ranges	$0 \le h \le 6$, $-11 \le k \le 11$, $-19 \le l \le 19$	$0 \le h \le 12$, $0 \le k \le 19$, $0 \le l \le 28$
Reflections collected	3526	3700
Unique data (R_{int})	0.0316	0.00
Parameters refined	305	336
Final *R* indices (2σ data)	$R_1 = 0.049$, $wR_2 = 0.1236$	$R_1 = 0.063$, $wR_2 = 0.1552$
R indices (all data) [a]	$R_1 = 0.099$, $wR_2 = 0.1565$	$R_1 = 0.227$, $wR_2 = 0.2392$
Goodness-of-fit on F^2	1.047	1.061
Largest difference peak and hole (e Å^{-3})	0.497 and −0.566	0.583 and −0.797

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

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

Bond lengths			
P(3)–Cl(2)	1.941(5)	P(2)–O(1)	1.569(5)
C(13)–O(2)	1.445(8)	S(2)–N(2)	1.574(6)
C(11)–P(1)	1.808(7)	P(2)–N(2)	1.562(7)
Bond angles			
O(1)–C(12)–P(1)	110.3(4)	N(3)–P(3)–N(1)	119.1(3)
N(1)–P(3)–Cl(2)	111.5(3)	N(1)–P(2)–O(2)	109.7(3)
O(2)–P(2)–O(1)	104.0(3)	O(3)–S(2)–N(2)	111.5(4)

cyclopentadienyl rings of **8** were in an almost eclipsed conformation with a negligible staggering of 1.6° similar to **6** [3]. The geometry around P(2) and the P–O bond distances were similar to that of the compound obtained in the reaction of $FcCH_2P(S)(CH_2OLi)_2$ with the carbaphosphazene $(NCNMe_2)_2(NPCl_2)$ [8].

The sum of the ring angles were 719.66° for **8** and 719.63° for **10**, which were both close to the expected value of 720° for a planar hexagon. Within the S–N–P moiety, the mean N–P bond length in **10** was 1.614(10) Å, which was similar to **1** (1.606(4) Å) [15]. The analogous N–P bond length in **8** was 1.564(6) Å, which was slightly less than that in **1** reflecting increased π character in the ring. Within the P–N–P moiety, the average P–N bond lengths in **10** (1.573(10) Å) and **1** (1.574(3) Å) were comparable while in **8** it was slightly less (1.565(6) Å). Interestingly, the mean S–N bond distance in **10** (1.546(10) Å) was slightly less than in **1** (1.557(3) Å) while, in **8** it was slightly greater than in **1** (1.568(6) Å). The ring parameters of **8** were in good agreement with alkoxy derivatives of thionylphosphazenes reported by Manners and co-workers [10f]. In contrast, bond parameters of **10** were close to that of $(NPCl_2)_2[NS(O)Cl]$ (**1**) [15]. Both the P–Cl bonds of **8** were found to be disordered and were modeled using the PART command in SHELXL-97 and occupancies were refined as a free variable [19]. The major component of this disorder was refined to 77.75% occupancy for both the Cl atoms.

Table 4
Selected bond lengths (Å) and bond angles (°) for **10**

Bond lengths			
P(2)–O(1)	1.594	C(11)–P(1)	1.788(13)
P(2)–N(3)	1.568(11)	S(2)–C(14)	1.760(13)
P(3)–N(5)	1.615(12)	P(3)–N(4)	1.625(10)
Bond angles			
C(12)–O(2)–P(2)	116.2(7)	O(3)–S(2)–N(2)	112.3(6)
N(2)–S(2)–C(14)	103.4(6)	O(2)–P(2)–O(1)	102.8(5)
P(2)–N(3)–P(3)	123.8(7)	N(5)–P(3)–N(2)	112.1(6)

In conclusion, the reactions of the dilithiated ferrocene-derived hydroxymethyl phosphine sulfides, $FcCH(CH_3)P(S)(CH_2OH)_2$ and $FcCH_2P(S)(CH_2OH)_2$ with *S*-aryl substituted thionylphosphazenes, $(NPCl_2)_2[NS(O)Ph]$ and $(NPCl_2)_2[NS(O)4\text{-}Cl\text{–}C_6H_4]$ follow a geminal pathway leading to the exclusive formation of spirocyclic compounds which is in contrast to similar reactions with the fluorinated phosphazene, $N_3P_3F_6$. These reactions provide a model study for substitution reactions of chlorinated thionylphosphazenes with difunctional oxygen based nucleophiles.

3. Experimental

3.1. Materials

Sulfamide, PCl_5, hexamethyldisilazane, ferrocene, CH_3I, tetrakis(hydroxymethyl)phosphonium chloride (80% w/w aqueous solution), *N*,*N*′-dimethylethylenediamine, $AlCl_3$ and *n*-BuLi (Fluka) were procured and used as such. $HOCH_2(CF_2)_2CH_2OH$ (Fluka) was vacuum sublimed before use. Benzene, chlorobenzene, THF, MeOH, EtOAc, Et_2O and light petroleum (66–

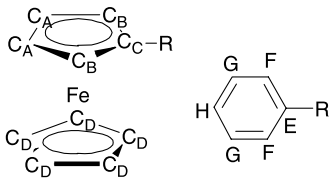


Fig. 3.

68 °C) were distilled and dried by standard procedures. The following compounds $(NPCl_2)_2[NS(O)Cl]$ (**1**) [16], $(NPCl_2)_2[NS(O)Ph]$ (**2**), $(NPCl_2)_2[NS(O)4\text{-}Cl\text{–}C_6H_4]$ (**3**) [17], $(NPCl_2)NP[N(Me)CH_2]_2[NS(O)Ph]$ (**4**), $(NPCl_2)NP[N(Me)CH_2]_2[NS(O)4\text{-}Cl\text{–}C_6H_4]$ (**5**) [10e], $FcCH_2P(S)(CH_2OH)_2$ (**6**) [3] and $FcCH(CH_3)P(S)(CH_2OH)_2$ (**7**) [4] were prepared by previously reported procedures.

3.2. General procedures

A conventional vacuum line equipped with dry nitrogen facility and Schlenk glassware was used for all reactions. Reactions were carried out under an atmosphere of dry nitrogen. Infrared spectra were recorded on a Perkin–Elmer 1320 spectrometer as Nujol mulls or as such. ^{1}H-, ^{13}C-, ^{31}P-NMR spectra were recorded using JEOL JNM-LA400 FT-NMR spectrometer with $CDCl_3$ as a solvent and Me_4Si and H_3PO_4 as references and the mass spectra on a JEOL SX 102/DA 6000 mass spectrometer in FAB mode or JEOL D-300 (EI/CI) spectrometer in the EI mode. Analyses were carried out on Carlo Erba CHNS-O 1108 elemental analyzer. Atom labeling used in ^{1}H- and ^{13}C-NMR of the cyclopentadienyl ring and phenyl ring are in accordance with Fig. 3 and the notation Fc represents ferrocenyl moiety.

3.3. X-ray diffraction studies

Data collection for **8** and **10** was carried out on an Enraf Nonius CAD4 diffractometer and structure solved by direct methods using WINGX program [18] and refined on F^2 using full-matrix least-squares (SHELXL-97) [19]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference electron-density maps and were included in the refinement process in an isotropic manner. Table 2 lists the crystal data and data collection parameters for compounds **8** and **10**.

3.4. Synthesis

3.4.1. $FcCH_2P(S)(CH_2O)_2PN(NPCl_2)[NS(O)Ph]$ (8)

n-Butyllithium (1.93 ml, 3.00 mmol), was added slowly to a stirring solution of $FcCH_2P(S)(CH_2OH)_2$ (**6**) (0.50 g, 1.54 mmol) in THF (15 ml) at −80 °C and brought to room temperature (r.t.) over a period of 4 h. The mixture was again cooled to −80 °C and $(NPCl_2)[NS(O)Ph]$ (**2**) (0.57 g, 1.54 mmol) in THF (10 ml) was added dropwise using a syringe. This reaction mixture was slowly brought to r.t. and stirred for 10 h. THF was evaporated off and the residue obtained was purified over silica gel using EtOAc and hexane (0.7:9.3) as eluent. The solid obtained was recrystallized from a mixture of CH_2Cl_2 and hexane (5:5) to yield orange crystals of $FcCH_2P(S)(CH_2O)_2PN(NPCl_2)[NS(O)Ph]$ (**8**) (0.84 g, 88%); m.p.: 180 °C. IR (cm^{-1}, Nujol): 1290m, 1255s, 1220s, 1200vs, 1120w, 1100w, 1040s, 900w, 870 w, 850w, 840w, 810w, 795m, 740w and 715m. ^{1}H-NMR ($CDCl_3$): δ 3.45 (m, Fc–CH_2, 2H), 4.15–4.89 (m, C_AH, C_BH, C_DH, and PCH_2O, 13H), 7.57 (m, C_GH, C_HH, 3H), 7.90 (d, C_FH, 2H). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 29.69 (Fc–CH_2), 66.79 (P–CH_2–O), 68.87 (C_A), 69.08 (C_D), 69.49 (C_B), 125.19 (C_G), 129.09 (C_F) 132.74 (C_H), 144.27 (C_E); ^{31}P{^{1}H}-NMR($CDCl_3$): δ 5.07 (dd, $^3J_{P-P} = 17.79$ Hz, $^2J_{P-P} = 67.91$ Hz, CH_2OP), 21.15 (d, $^3J_{P-P} = 17.79$ Hz, $FcCH_2P$) 23.13 (d, $^2J_{P-P} = 67.91$ Hz, PCl_2). FABMS; *m*/*e* (fragment, relative intensity): 621 ([M$^+$], 60), 390 ([M$^+$ − $FcCH_2$ − S, 40]), 199 ([$FcCH_2^+$], 40), 136 ([P_2N_3S], 60). Anal. Found: C, 36.63; H, 3.27; N, 6.67. Calc. for $C_{19}H_{20}Cl_2FeN_3O_3P_3S_2$: C, 36.68; H, 3.24; N, 6.75%.

3.4.2. $FcCH(CH_3)P(S)[(CH_2O)_2PN_2PCl_2][NS(O)Ph]$ (9)

n-Butyllithium (1.85 ml, 2.95 mmol), $FcCH(CH_3)P(S)(CH_2OH)_2$ (**7**) (0.50 g, 1.48 mmol) in THF (15 ml) and $(NPCl_2)[NS(O)Ph]$ (**2**) (0.55 g, 1.48 mmol) in THF (10 ml) were reacted at −100 °C and worked up as described for **8**. The residue obtained was purified over silica gel using EtOAc and hexane (1.5:8.5) to afford an orange–red solid which was identified as $FcCH(CH_3)P(S)[(CH_2O)_2PN_2PCl_2][NS(O)Ph]$ (**9**) (0.80 g, 85%); m.p.: 174 °C. IR (cm^{-1}, Nujol): 1365m, 1290m, 1250s, 1210vs, 1180s, 1100m, 1030vs, 885w, 850w, 830w, 780w, 740w, 715w, 710w. ^{1}H-NMR ($CDCl_3$): δ 1.63 (dd, $FcCHCH_3$, 3H), 3.54 (m, Fc–$CHCH_3$, 1H), 4.11–4.93 (m, C_AH, C_BH, C_DH, and PCH_2O, 13H), 7.50 (m, C_GH, C_HH, 3H), 7.84 (d, C_FH, 2H). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 13.55 (Fc–$CHCH_3$), 29.53 (Fc–$CHCH_3$), 66.56 (P–CH_2–O), 67.88, 68.04 (C_A), 68.56, 68.58 (C_B), 68.83 (C_D), 83.52 (C_C), 125.20 (C_G), 129.10 (C_F), 132.73 (C_H), 144.30(C_E). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 5.25 (dd, $^3J_{P-P} = 14.60$ Hz, $^2J_{P-P} =$ 67.91 Hz, CH_2OP), 23.17 (d, $^2J_{P-P} = 67.91$ Hz, PCl_2), 30.80 [d, $^3J_{P-P} = 14.60$ Hz, $FcCH(CH_3)P$]. FABMS; *m*/*e* (fragment, relative intensity): 635 ([M$^+$ − 1] 60), 213 ([$FcCH(CH_3)^+$], 100). Anal. Found: C, 37.68; H, 3.54; N, 6.62. Calc. for $C_{20}H_{22}Cl_2FeN_3O_3P_3S_2$: C, 37.76; H, 3.49; N, 6.60%.

3.4.3. $FcCH_2P(S)(CH_2O)_2PN_2P[N(Me)CH_2]_2[NS(O)Ph]$ (10)

n-Butyllithium (1.93 ml, 3.00 mmol), $FcCH_2P(S)(CH_2OH)_2$ (**6**) (0.50 g, 1.54 mmol) in THF (15 ml) and $(NPCl_2)NP[N(Me)CH_2]_2[NS(O)Ph]$ (**4**) (0.60 g, 1.55 mmol) in THF (5 ml) were reacted and worked up as described for **8**. The solid obtained was purified over a silica gel column using a mixture of hexane and EtOAc (7.7:2.3) as eluent. Recrystallization from CH_2Cl_2–hexane mixture (3:7) gave orange–red crystals, which were identified as $FcCH_2P(S)(CH_2O)_2PN_2P[N(Me)CH_2]_2[NS(O)Ph]$ (**10**) (0.66g, 70%); m.p.: 210 °C. IR (cm^{-1}, Nujol): 1295w, 1240s, 1220s, 1200vs, 1190s, 1160s, 1095w, 1040vs, 930w, 895w, 875s, 800s, 720m, 700w, 680w, 630w. ^{1}H-NMR ($CDCl_3$): δ 2.19 (d, N–CH_3, 3H), 2.51 (d, N–CH_3, 3H), 3.13 (m, N–CH_2, 4H), 3.40 (m, Fc–CH_2, 2H), 4.12–4.84 (m, C_AH, C_BH, C_DH, and PCH_2O, 13H), 7.37 (m, C_GH, C_HH, 3H), 7.87 (m, C_FH, 2H). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 29.35 (Fc–CH_2), 30.85 (N–CH_3), 47.16 (N–CH_2–CH_2–N), 65.96 (P–CH_2–O), 68.68 (C_A), 69.02 (C_D), 69.57 (C_B), 75.51 (C_C), 125.13 (C_G), 128.64 (C_F), 131.51 (C_H). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 14.90 (dd, $^2J_{p-p} = 61.45$ Hz, $^3J_{p-p} = 16.17$ Hz, CH_2–O–*P*), 21.38 [d, $^2J_{p-p} = 61.45$ Hz, *P*–N(CH_3)CH_2], 23.09 [d, $^3J_{p-p} = 16.17$ Hz, Fc–CH_2–*P*(S)]. FABMS; *m*/*e* (fragment, relative intensity): 637 ([M^+], 100), 199 ([$FcCH_2^+$], 90), 212 ([$P_2N_3S - Ph$], 2), 136 ([P_2N_3S], 20).

3.4.4. $FcCH_2P(S)(CH_2O)_2PN_2P(N(Me)CH_2)_2]$-$[NS(O)4\text{-}Cl\text{–}C_6H_4]$ (11)

n-Butyllithium (1.93 ml, 3.00 mmol), $FcCH_2P(S)(CH_2OH)_2$ (**6**) (0.50 g, 1.54 mmol) in THF (15 ml) and $(NPCl_2)NP[N(Me)CH_2]_2[NS(O)4\text{-}Cl\text{–}C_6H_4]$ (**5**) (0.65 g, 1.55 mmol) in THF (10 ml) were reacted and worked up as described for **8**. The solid obtained was purified over a silica gel column using a mixture of EtOAc and hexane (3:7) as eluent. The orange product obtained was characterized as $FcCH_2P(S)(CH_2O)_2PN_2P[N(Me)CH_2]_2[NS(O)4\text{-}Cl\text{–}C_6H_4]$ (**11**) (0.64g, 65%); m.p.: 190 °C. IR (cm^{-1}, Nujol): 1249s, 1230w, 1210vs, 1190w, 1169m, 1105m, 1037s, 950w, 890s, 820s, 730s, 707w, 638m. ^{1}H-NMR ($CDCl_3$): δ 2.21(d, N–CH_3, 3H), 2.53 (d, N–CH_3, 3H), 3.13 (m, N–CH_2, 4H), 3.4 (m, Fc–CH_2, 2H), 4.83–4.05 (m, C_AH, C_BH, C_DH, and PCH_2O, 13H), 7.35 (d, C_GH, 2H), 7.79 (d, C_FH, 2H). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 29.38 (Fc–CH_2), 30.84 (N–CH_3), 47.06 (N–CH_2–CH_2N), 66.00 (P–CH_2–O), 68.78 (C_A), 69.06 (C_D), 69.57 (C_B), 75.48 (C_C), 126.70 (C_G), 128.87 (C_F), 137.74 (C_H). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 14.78 (dd, $^2J_{p-p} = 63.06$ Hz, $^3J_{p-p} = 14.60$ Hz, CH_2–O–*P*), 21.29 [d, $^2J_{p-p} = 63.06$ Hz, *P*–N(CH_3)CH_2], 22.76 [d, $^3J_{p-p} = 14.60$ Hz, Fc–CH_2–*P*(S)]. FABMS; *m*/*e* (fragment, relative intensity): 671 ([M^+], 80), 199 ([$FcCH_2^+$], 100), 212 ([$P_2N_3S - Ph$], 2), 136 ([P_2N_3S], 60). Anal. Found: C, 41.08; H, 4.40; N, 10.38. Calc. for $C_{23}H_{29}ClFeN_5O_3P_3S_2$: C, 41.12; H, 4.35; N, 10.42%.

3.4.5. $FcCH_2P(S)[(CH_2O)_2PN_2P(OCH_2CF_2)_2]$-$[NS(O)4\text{-}Cl\text{–}C_6H_4]$ (12)

A solution of $(CF_2CH_2OH)_2$, (0.50 g, 3.08 mmol) in THF (15 ml), *n*-butyllithium (3.86 ml, 6.17 mmol) and $(NPCl_2)_2[NS(O)4\text{-}Cl\text{–}C_6H_4]$ (**3**) (1.30 g, 3.09 mmol) in THF (10 ml) were reacted as described for **8**. This reaction mixture was slowly added using a cannula to the solution of $FcCH_2P(S)(CH_2OH)_2$ (**6**) (1.00 g, 3.08 mmol) in THF (15 ml) and reacted with *n*-butyllithium (3.86 ml, 6.17 mmol) according to procedure described for **8** at −80 °C. The reaction mixture was slowly brought to r.t. and stirred for 10 h. The solvent was removed at reduced pressure and the crude sample obtained was purified over silica gel using EtOAc and hexane (1.6:8.5) as eluent to obtain an orange solid which was later identified as $FcCH_2P(S)[(CH_2O)_2PN_2P(OCH_2CF_2)_2][NS(O)4\text{-}Cl\text{–}C_6H_4]$ (**12**) (1.50 g, 65%); m.p.: 170 °C. IR (cm^{-1}, Nujol): 1290m, 1275m, 1250m, 1235s, 1195vs, 1165w, 1140s, 1080s, 1040vs, 1000w, 900m, 870w, 810m, 795w, 740s, 710w, 660w. ^{1}H-NMR ($CDCl_3$): δ 3.35 (m, Fc–CH_2, 2H), 4.93–4.08 (m, C_AH, C_BH, C_DH, OCH_2CF_2 and PCH_2O, 17H), 7.40 (d, C_GH, 2H), 7.72 (d, C_FH, 2H). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 29.52 (Fc–CH_2), 62.01 (OCH_2CF_2), 66.76 (P–CH_2–O), 68.89 (C_A), 69.09 (C_D), 69.51 (C_B), 75.10 (C_C), 112.32 (CF_2), 126.69 (C_GH), 129.26 (C_FH), 138.73(C_H). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 10.76 (dd, $^3J_{P-P} = 14.60$ Hz, $^2J_{P-P} = 84.08$ Hz, CH_2OP), 11.90 (d, $^2J_{P-P} = 84.08$ Hz, $POCH_2$), 21.99 (d, $^3J_{P-P} = 14.60$ Hz, $FcCH_2P$) (isomer **I**); 9.63 (dd, $^3J_{P-P} = 17.78$ Hz, $^2J_{P-P} = 103.49$ Hz, CH_2OP), 13.89 (d, $^2J_{P-P} = 103.49$ Hz, $POCH_2$), 19.79 (d, $^3J_{P-P} = 17.78$ Hz, $FcCH_2P$) (isomer **II**). FABMS; *m*/*e* (fragment, relative intensity): 745 ([M^+], 50), 744 ([$M^+ - 1$], 100), 199 ([$FcCH_2^+$], 100). Anal. Found: C, 37.11; H, 3.16; N, 5.59. Calc. for $C_{23}H_{23}ClF_4FeN_3O_5P_3S_2$: C, 37.04; H, 3.11; N, 5.63%.

3.4.6. $\{[CH_2N(Me)]_2PN_2P(OCH_2CF_2)_2\}[NS(O)Ph]$ (13)

n-Butyllithium (3.86 ml, 6.17 mmol), $(CF_2CH_2OH)_2$, (0.50 g, 3.08 mmol) in THF (15 ml) and $(NPCl_2)NP[N(Me)CH_2]_2[NS(O)Ph]$, (**4**) (1.19 g, 3.08 mmol) in THF (5 ml) were reacted and worked up as described for **8.** The residue obtained showed two close spots in TLC analysis and were separated over a silica gel column using a mixture of EtOAc and hexane (3:7) as eluent. The product obtained was a viscous liquid which was characterized as $\{[CH_2N(Me)]_2PN_2P(OCH_2CF_2)_2\}[NS(O)Ph]$ (**13**[1]) (1.02 g, 73% overall yield). IR (cm^{-1}, neat): 1233vs, 1139w, 1076vs, 925w, 809s, 752s, 670w, 625s. ^{1}H-NMR ($CDCl_3$): δ 2.23 (d, N–CH_3, 2H), 2.52 (d, N–CH_3, 2H), 3.13 (m, N–CH_2, 4H), 4.36 (m, O–CH_2, 4H), 7.34 (d, C_GH, 2H), 7.77 (d, C_FH, 2H). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 30.89 (N–CH_3),

[1] The ^{1}H- and ^{13}C-NMR shifts of these isomers showed very little difference.

47.15 (N–CH_2), 61.60 (O–CH_2), 112.59 (CF_2), 126.61 (C_G), 128.84 (C_F), 137.70 (C_H), 145.18 (C_E); $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 17.39 (d, $^2J_{P-P} = 71.15$ Hz, P–N–CH_3), 22.57 (d, $^2J_{P-P} = 71.15$ Hz, P–O–CH_2) (isomer **I**), 17.61 (d, $^2J_{P-P} = 71.15$ Hz, P–N–CH_3), 22.63 (d, $^2J_{P-P} = 71.15$ Hz, P–O–CH_2) (isomer **II**). EIMS; m/e (fragment, relative intensity): 475 ([M^+], 88), 398 ([$M^+ - C_6H_5$], 100), 391([$M^+ - 2F - 2CH_3 - O$], 56), 351 ([$M^+ - 4F - 2CH_3 - 2H - O$], 41), 136 ([$P_2N_3S$], 31), 86 ([$(CH_2N - Me)_2$], 70), 77 ([$C_6H_5$], 50). Anal. Found: C, 35.45; H, 3.96; N, 14.68. Calc. for $C_{14}H_{19}F_4FeN_5O_3P_2S$: C, 35.37; H, 4.03; N, 14.73%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 154245 and 154246 for compounds **8** and **10**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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