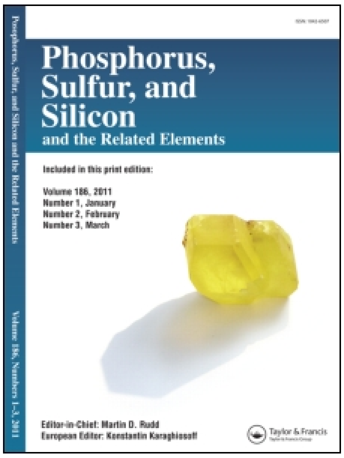

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Synthesis and Characterization of Ferrocene Derived Cyclic Carbaphosphazenes

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SYNTHESIS AND CHARACTERIZATION OF FERROCENE DERIVED CYCLIC CARBAPHOSPHAZENES

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Dialkylamino substituted cyclic carbaphosphazenes, $(R_2NCN)_2(NPCl_2)$ *were prepared and reacted with the ferrocene derived hydroxymethyl phosphine sulfide* $FcCH(CH_3)P(S)(CH_2OH)_2$ *after dilithiation to yield a series of new spirocyclic derivatives of cyclic carbaphosphazenes having ferrocenyl pendant groups. To confirm the formation of six membered spirocycles and to compare their spectral features, transesterification reactions of* $FcCH(CH_3)P(S)(CH_2OH)_2$ *also were carried out with* $P(NR_2)_3$*, yielding the six membered heterocycles* $FcCH_2P(S)(CH_2O)_2PNR_2$ *(R = Me, Et). The compounds were characterized by* ^1H, ^{31}P, ^{13}C *NMR, mass spectra, and elemental analysis.*

Keywords: Carbaphosphazene; ferrocene; hydroxymethyl; phosphine sulfide; spirocycle; transesterification

INTRODUCTION

Synthesis of inorganic heterocycles having redox active units as substituents continue to be a matter of interest in recent years. The electrochemical behavior of ferrocene units bound to cyclophosphazene rings and polymers directly or through a spacer group has been the focus of substantive studies.[1,16,17] The well characterized one electron oxidation of ferrocene which is electrochemically and chemically reversible makes it an excellent choice as a redox center on these molecules. Phosphazene polymers having ferrocenyl substituents also showed

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promise in catalytic systems, as electrode mediators and as electroactive materials.[2,3] In contrast to cyclophosphazenes, only very few examples of other inorganic heterocycles having ferrocene as a substituent have been reported.[4]

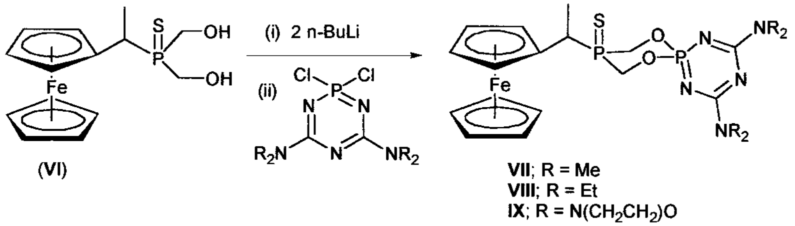
Cyclic carbaphosphazenes are heterocycles containing both P—N and C—N moieties in the ring framework and these molecules show properties similar to both cyclophosphazenes and *s*-triazines.[5] Similar to perhalogenated cyclophosphazenes, they undergo ring opening polymerization to yield carbaphosphazene polymers.[6] The P—Cl and C—Cl bonds of the perchlorinated examples of these heterocycles also show interesting selectivity in their substitution reactions which recently has been the subject of detailed investigations.[7–11,20] The organometallic chemistry of cyclic carbaphosphazenes is still in its infancy and only recently, the first example of a ferrocenyl derivative of a carbaphosphazene was reported.[12]

We recently have reported the synthesis of a new stable ferrocene derived diol, $FcCH(CH_3)P(S)(CH_2OH)_2$ (**VI**) (Fc = ferrocenyl) having an asymmetric carbon center attached to the cyclopentadienyl ring.[13] In this article we report the synthesis and characterization of a series of ferrocene derived spirocyclic carbaphosphazenes obtained from the reaction of this diol with the C-diakylamino substituted carbaphosphazenes. To compare their spectral features, transesterification reactions of $FcCH(CH_3)P(S)(CH_2OH)_2$ were also carried out with $P(NR_2)_3$ (R = Me, Et) yielding the six membered heterocycles, $FcCH_2P(S)(CH_2O)_2PNR_2$.

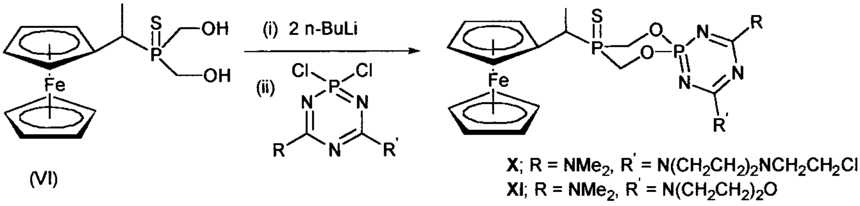
RESULTS AND DISCUSSION

Reactions of symmetrically substituted cyclocarbaphosphazenes $(NCNMe_2)_2(NPCl_2)$ (**I**), $(NCNEt_2)_2(NPCl_2)$ (**II**) and $[NC(NC_4H_8O)]_2(NPCl_2)$ (**III**) with $FcCH(CH_3)P(S)(CH_2OLi)_2$ at −80°C in THF as solvent were found to proceed smoothly leading to the formation of spirocyclic compounds $FcCH(CH_3)P(S)(CH_2O)_2(PN)(NCNMe_2)_2$ (**VII**), $FcCH(CH_3)P(S)(CH_2O)_2(PN)(NCNEt_2)_2$ (**VIII**) and $FcCH(CH_3)P(S)(CH_2O)_2(PN)[NC(NC_4H_8O)]_2$ (**IX**) (Scheme 1).

To compare the reactions with symmetrically substituted carbaphosphazenes and to observe the effect of variation in C-substitution, carbaphosphazenes having two different substituents on the ring carbon atoms $[(NCNMe_2)[NCN(CH_2CH_2)_2N\ CH_2CH_2Cl](NPCl_2)$ (**IV**) and $(NCNMe_2)[NC(NC_4H_8O)](NPCl_2)$ (**V**) were synthesized and reacted with the dilithiated salt of (**VI**) to yield spirocyclic compounds (**X**, **XI**). (Scheme 2). The yields of the compounds (**VII–XI**)



SCHEME 1



SCHEME 2

were in the range 65% to 82% after purification over a silicagel column.

The ^{1}H-NMR spectra of the compounds (**VII–XI**) were in good agreement for the expected products. It was noticed that the Fc-C*H* proton was deshielded to δ 3.68–3.79 ppm from δ 3.22 ppm in (**VI**) after forming the spirocyclic carbaphosphazene, while the chemical shifts of the Fc—CH(C*H*$_3$) protons were found to be unaffected. It was also observed that the substitution on the phosphorus atom of the carbaphosphazene ring has no effect on the ^{1}H-NMR chemical shifts of dialkylamino substituents on the carbon atoms. In the ^{13}C-NMR spectra of the compounds (**VII–XI**), ferrocenyl carbon atoms were observed in the range of δ 66.45–69.02 ppm, and the carbon atoms of the carbaphosphazene ring were observed as a doublet around δ 163.74–165.33 ppm. It was observed that the P—CH$_2$ carbon atom was deshielded to δ 65.03–65.42 ppm from δ 56.75–58.67 ppm in (**VI**).

Compounds (**VII–XI**) gave two doublets with a $^3J_{\text{p-p}}$ coupling of 14.55 Hz in their ^{31}P NMR spectra. The doublet around δ 36.84–37.14 ppm corresponds to the phosphorus atom of the carbaphosphazene ring, which was found to get shifted upfield from δ 56.19–57.80 ppm in the C-dialkyamino substituted carbaphosphazenes, $(R_2NCN)_2(NPCl_2)$. Table I compares the ^{31}P NMR chemical shifts before and after substitution of PCl_2 bonds with $FcCH(R)P(S)(CH_2OH)_2$ ($R = H$, CH_3). It is clearly observed that the upfield shift experienced by the phosphorus

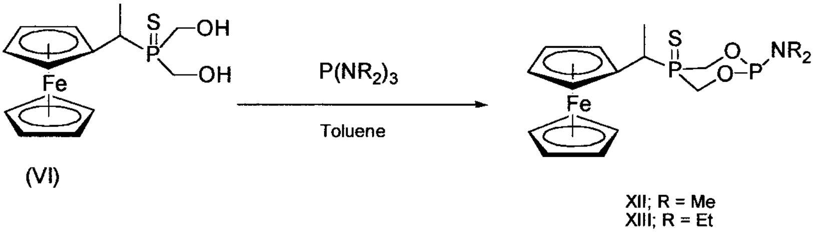
TABLE I Comparative ^{31}P Chemical Shifts of Carbaphosphazene Derivatives

S. No.	$(R_2NCN)(R'_2NCN)$ (Cl_2PN)	$^{31}P/\delta$ NPN	$(R_2NCN)(R'_2NCN)[(RO)_2PN]$	$^{31}P/\delta$ NPN
1.	$(NCNMe_2)_2(NPCl_2)^{\#}$	56.55	$FcCH_2P(S)(CH_2O)_2PN$ $(NCNMe_2)_2$^{a}	36.79
2.	$(NCNR'R)_2(NPCl_2)^{\#}$ (R = Me, R′ = benzyl)	56.62	$FcCH_2P(S)(CH_2O)_2PN(NCNR'\ R)_2$^{a} (R = Me, R′ = benzyl)	36.84
3.	$(NCNMe_2)_2(NPCl_2)$	56.55	$FcCH(CH_3)P(S)(CH_2O)_2PN$ $(NCNMe_2)_2$	37.00
4.	$(NCNEt_2)_2(NPCl_2)$	56.19	$FcCH(CH_3)P(S)(CH_2O)_2PN$ $(NCNEt_2)_2$	37.03
5.	$[NC(NC_4H_8O)]_2(NPCl_2)$	57.80	$FcCH(CH_3)P(S)(CH_2O)_2PN$ $[NC(NC_4H_8O)]_2$	37.09
6.	$(NCNMe_2)[NCN$ $(CH_2CH_2)_2NCH_2CH_2Cl]$ $(NPCl_2)$	57.51	$FcCH(CH_3)P(S)(CH_2O)_2PN$ $[NCN(CH_2CH_2)_2NCH_2CH_2Cl]$ $(NCNMe_2)$	37.14
7.	$(NCNMe_2)$ $[NC(NC_4H_8O)]_2(NPCl_2)$	56.99	$FcCH(CH_3)P(S)(CH_2O)_2PN$ $[NC(NC_4H_8O)]_2$ $(NCNMe_2)$	36.84

[a] Ref. 12.

atom upon substitution is almost independent of the nature of substituents present on the carbon atoms. The P=S group in (**VII–XI**) was resonating as a doublet at δ 32.50–33.20 ppm which showed an upfield shift from δ 61.84 ppm of (**VI**).

To confirm the formation of six membered spirocyclic rings in these compounds, we have carried out transesterification reactions of the diol (**VI**) with $P(NMe_2)_3$ and $P(NEt_2)_3$. These reactions were found to result in the formation of the compounds $FcCH_2P(S)(CH_2O)_2PNR_2$ (R=Me, Et) in 86–88% yields (Scheme 3).



SCHEME 3

It was of interest to note from the ^{31}P NMR spectra that the P=S group is quite sensitive to the size of the ring formed by the hydroxymethyl groups. For the six membered heterocycles, $FcCH(CH_3)$-$P(S)(CH_2O)_2PNMe_2$ (**XII**), and $FcCH(CH_3)P(S)(CH_2O)_2PNEt_2$ (**XIII**) the P=S groups are observed at δ 33.35 and 33.04 ppm, respectively, which are similar to the ^{31}P NMR chemical shifts of the P=S group of compounds (**VII–IX**). However, for the eight membered heterocycle $FcCH(CH_3)P(S)(CH_2OSiMe_2)_2O$ it was observed at δ 53.39 ppm.[13] A similar differnce for the ^{31}P NMR chemical shifts were observed for six and eight membered rings formed of $FcCH_2P(S)(CH_2OH)_2$ with cyclic fluorophosphazenes.[15] All the compounds in this study gave M^+ peak in their FAB mass spectra. In the compounds (**VII–XIII**), base peak was at m/e 213 corresponding to $FcCH(CH_3)^+$ as the most stable fragment. Similar achiral derivatives derived from $FcCH_2P(S)(CH_2OH)_2$ have given a base peak at m/e 199 representing $FcCH_2^+$ fragment.[12]

EXPERIMENTAL

All reactions are carried out under a dry oxygen free nitrogen atmosphere using Schlenk glassware. The compounds $(NCNMe_2)_2(NPCl_2)$ (**I**), $(NCNEt_2)_2(NPCl_2)$ (**II**) and $[NC(NC_4H_8O)]_2(NPCl_2)$ (**III**) were synthesized according to the literature methods.[10] Similar carbaphosphazene derivatives $(NCNMe_2)[NCN(CH_2CH_2)_2N\ CH_2CH_2Cl](NPCl_2)$ (**IV**) and $(NCNMe_2)[NC(NC_4H_8O)](NPCl_2)$ (**V**) having two different substituents on the carbon atoms were synthesized by controlled stochiometric reactions of the respective tertiary amines with tetrachlorodicarbaphosphazene.[14] Preparation of the diol $FcCH(CH_3)P(S)(CH_2OH)_2$ (**VI**) has been described elsewhere.[13]

The notation Fc in this study represents ferrocenyl and the labelling of the ring carbon atoms of the ferrocenyl group is according to Figure 1.

Preparation of $FcCH(CH_3)P(S)(CH_2O)_2(PN)(NCNMe_2)_2$ (VII)

$FcCH(CH_3)P(S)(CH_2OH)_2$ (0.50 g, 1.48 mmol) in THF (10 mL) was taken in a dry 50 ml round bottomed flask under nitrogen atmosphere and *n*-Butyllithium (1.85 mL 2.95 mmol), was added dropwise

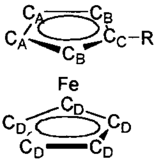


FIGURE 1

using a syringe at −100°C. The mixture was brought to room temperature over a period of 4 h. The mixture was cooled again to −80°C and $(NCNMe_2)_2(NPCl_2)$, (1.38 g, 1.48 mmol) in THF (10 mL) was added slowly using a syringe. The reaction was brought to room temperature and stirred for 12 h. THF was evaporated under reduced pressure and the solid obtained was purified over a silica gel column using a mixture of hexane and ethyl acetate (9:1 v/v) as eluent which gave an orange solid which was characterized as $FcCH(CH_3)P(S)(CH_2O)_2(PN)(NCNMe_2)_2$ (**VII**) (0.63 g, 82%) m.p.: 230°C (Decomp). NMR: ^1H, δ 1.70 (dd, FcCH*CH₃*, 3H), 3.07 (s, NMe_2, 12H), 3.79 (m, Fc-*CH*CH_3, 1H), 4.16–4.93 (m, C_AH, C_BH, C_DH, and P*CH₂*O, 13H); ^{13}C, δ 13.57 (FcCH*CH₃*), 29.53 (Fc—CH*CH₃*), 36.16 (N—Me_2), 65.07 (P—*CH₂*—O), 67.47, 67.78 (C_A), 68.56, 68.61 (C_B), 68.68 (C_D), 84.25 (C_C), 165.33 (d,$^2J_{C\text{-}P}$ =108.13 Hz, NCN); ^{13}P, δ 32.91 (d,$^3J_{P\text{-}P}$ =14.55 Hz, P=S), 37.00 (d,$^3J_{P\text{-}P}$ =14.55 Hz, NPN). MS (FAB) [m/e (species) intensity]: 521 (M^+) 100, 213 [$FcCH(CH_3)^+$] 90. Anal. Calcd. for $C_{20}H_{29}FeN_5O_2P_2S$: C, 46.08; H, 5.61; N, 13.43. Found: C, 46.00; H, 5.68; N, 13.46%.

Preparation of $FcCH(CH_3)P(S)(CH_2O)_2(PN)(NCNEt_2)_2$ (VIII)

$FcCH(CH_3)P(S)(CH_2OH)_2$, (0.50 g, 1.48 mmol) in THF (10 mL), *n*-Butyllithium (1.85 mL 2.95 mmol) and $(NCNEt_2)_2(NPCl_2)$, (0.85 g, 1.47 mmol) were reacted and worked up according to procedure described for (**VII**). The solid obtained upon purification over a silicagel column using hexane and ethyl acetate (9.5: 0.5) as eluent gave an orange solid which was identified as $FcCH(CH_3)P(S)(CH_2O)_2(PN)(NCNEt_2)_2$ (**VIII**) (0.66 g, 78%) m.p.: 120°C. NMR: ^1H, δ 1.06 (t, N—CH_2-*CH₃*, 12H) 1.63 (dd, FcCH*CH₃*, 3H), 3.43 (q, N—*CH₂*—CH_3, 8H), 3.75 (m, Fc—*CH*CH_3, 1H), 4.08–4.94 (m, C_AH, C_BH, C_DH, and P*CH₂*O, 13H); ^{13}C, δ 13.36 (N—CH_2—*CH₃*), 13.63 (FcCH*CH₃*), 29.33 (Fc—*CH*CH_3), 41.32 (N—CH_2), 65.16 (P—*CH₂*—O), 67.41, 67.74 (C_A), 68.55, 68.69 (C_B), 68.77 (C_D), 84.40, (C_C) 163.74 (d,$^2J_{C\text{-}P}$ =108.13 Hz, NCN); ^{31}P, δ 33.21 (d, $^3J_{P\text{-}P}$ =14.55 Hz, P=S), 37.03 (d,$^3J_{P\text{-}P}$ = 14.55 Hz, NPN). MS (FAB) [m/e (species) intensity]: 577 (M^+) 50, 213 [$FcCH(CH_3)^+$] 100. Anal. Calcd. for $C_{24}H_{37}FeN_5O_2P_2S$: C, 49.92; H, 6.46; N, 12.13. Found: C, 49.90; H, 6.51; N, 12.20%.

Preparation of $FcCH(CH_3)P(S)(CH_2O)_2(PN)[NC(NC_4H_8O)]_2$ (IX)

$FcCH(CH_3)P(S)(CH_2OH)_2$, (0.50 g, 1.48 mmol) in THF (10 mL), *n*-Butyllithium (1.85 mL 2.95 mmol) and $[NC(NC_4H_8O)]_2(NPCl_2)$, (0.90 g, 1.48 mmol) were reacted and worked up according to procedure described for (**VII**). The solid obtained was purified over a silicagel column using hexane and ethyl acetate (8.7:1.3) as eluent to obtain a orange solid which was characterized as $FcCH(CH_3)P(S)(CH_2O)_2(PN)[NC(NC_4H_8O)]_2$ (**IX**) (0.67 g, 75%) m.p.: 190°C. NMR: ^1H, δ 1.69 (dd, $FcCH\mathit{CH_3}$, 3H), 3.71 (m, Fc—$\mathit{CH}CH_3$, N—CH_2, O—CH_2 17H), 4.15–4.97 (m, C_AH, C_BH, C_DH, and $P\mathit{CH_2}O$, 13H); ^{13}C, δ 13.62 ($FcCH\mathit{CH_3}$), 29.47 (Fc—$\mathit{CH}CH_3$), 43.99 (N—CH_2), 53.41 (CH_2—O), 65.32 (P—$\mathit{CH_2}$—O), 66.70, 67.44 (C_A), 67.84, 68.51 (C_B), 68.71 (C_D), 84.09 (C_C), 165.02 (d,$^2J_{C\text{-}P} = 178.19$ Hz, NCN); ^{31}P, δ 32.64 (d,$^3J_{P\text{-}P} = 14.55$ Hz, P=S), 37.09 (d,$^3J_{P\text{-}P} = 14.55$ Hz, NPN). MS (FAB) [m/e (species) intensity]: 605 (M^+) 90, 213 [$FcCH(CH_3)^+$] 100. Anal. Calcd. for $C_{24}H_{33}FeN_5O_4P_2S$: C, 47.61; H, 5.49; N, 11.57. Found:C, 47.66; H, 5.46; N, 11.65%.

Preparation of $(NCNMe_2)[NCN(CH_2CH_2)_2NCH_2CH_2Cl]$ (X)

$FcCH(CH_3)P(S)(CH_2OH)_2$, (0.50 g, 1.48 mmol) in THF (10 mL), *n*-Butyllithium (1.85 mL, 2.95 mmol) and $(NCNMe_2)[NCN(CH_2CH_2)_2N CH_2CH_2Cl](NPCl_2)$, (0.92 g, 1.47 mmol) were reacted and worked up according to procedure described for (**VII**). The solid obtained upon purification over a silicagel column using hexane and ethyl acetate (8.4:1.6) as eluent gave an orange solid which was identified as $FcCH(CH_3)P(S)(CH_2O)_2(NP)$ $(NCNMe_2)[NCN(CH_2CH_2)_2NCH_2CH_2Cl]$ (**X**) (0.63 g, 68%) m.p.: 147°C. NMR: ^1H, δ 1.63 (dd, $FcCH\mathit{CH_3}$, 3H), 2.45 [t, $N(CH_2\mathit{CH_2})_2N(CH_2)_2Cl$, 4H], 2.69 [t, $N(\mathit{CH_2}CH_2)_2N(CH_2)_2Cl$, 4H], 3.01 (s, N—$CH_3$ 6H), 3.54 [t, $N(CH_2CH_2)_2NCH_2\mathit{CH_2}Cl$, 2H] 3.71 (m, Fc—$\mathit{CH}CH_3$, $N(CH_2CH_2)_2N\mathit{CH_2}CH_2Cl$, 3H), 4.09–4.94 (m, C_AH, C_BH, C_DH, and $P\mathit{CH_2}O$, 13H); ^{13}C, δ 13.60 ($FcCH\mathit{CH_3}$), 29.63 (Fc—$\mathit{CH}CH_3$), 36.27 (N—CH_3), 40.61 ($N(CH_2\mathit{CH_2})_2N(CH_2)_2Cl$), 43.10 ($N(\mathit{CH_2}CH_2)_2N(CH_2)_2Cl$), 52.97, 59.71 ($N\mathit{CH_2}CH_2Cl$), 65.03 (P—$\mathit{CH_2}$—O), 66.45, 67.80 ($C_A$), 68.54 ($C_B$), 68.64 ($C_D$), 84.15 ($C_C$), 165.19 (d, $^2J_{C\text{-}P} = 152.96$ Hz, NCN); ^{31}P, δ 32.66 (d, $^3J_{P\text{-}P} = 14.55$ Hz, P=S), 37.14 (d,$^3J_{P\text{-}P} = 14.55$ Hz, NPN). MS (FAB) [m/e (species) intensity]: 624 (M^+) 30,213 [$FcCH(CH_3)^+$] 100. Anal. Calcd. for $C_{24}H_{35}ClFeN_6O_2P_2S$: C, 46.13; H, 5.65; N, 13.45. Found: C, 46.18; H, 5.60; N, 13.49%.

Preparation of $FcCH(CH_3)P(S)(CH_2O)_2(NP)(NCNMe_2)[NC(NC_4H_8O)]$ (XI)

$FcCH(CH_3)P(S)(CH_2OH)_2$, (0.50 g, 1.48 mmol) in THF (10 mL), *n*-Butyllithium (1.85 mL 2.95 mmol) and above obtained $(NCNMe_2)$-$[NC(NC_4H_8O)](NPCl_2)$, (**V**) (0.44 g, 1.47 mmol) were reacted and worked up according to procedure described for (**VII**). The orange solid obtained was purified over a silicagel column using hexane and ethyl acetate (8.2:1.8) as eluent which afforded an orange solid which was characterized as $FcCH(CH_3)P(S)(CH_2O)_2(NP)(NCNMe_2)$ $[NC(NC_4H_8O)]$ (**XI**) (0.54 g, 65%) m.p.: 135°C. NMR: ^1H, δ 1.63 (dd, $FcCH\mathit{CH_3}$, 3H), 3.04(N—CH_3), 3.68(m, Fc-$\mathit{CH}CH_3$, N—CH_2, O—CH_2 9H), 4.12–4.95 (m, C_AH, C_BH, C_DH, and $P\mathit{CH_2}O$, 13H); ^{13}C, δ 13.61 ($FcCH\mathit{CH_3}$), 29.47 (Fc-$\mathit{CH}CH_3$), 36.41 (N—CH_3), 43.94 (N—CH_2), 53.41 (CH_2—O), 65.26 (P—$\mathit{CH_2}$—O), 66.74, 67.45 (C_A), 67.81, 68.60 (C_B), 68.70 (C_D), 84.16 (C_C), 165.13 (d, $^2J_{C\text{-}P} = 205.35$ Hz, NCN); ^{31}P, δ 32.54 (d,$^3J_{P\text{-}P} = 14.55$ Hz, P=S), 37.10 (d,$^3J_{P\text{-}P} = 14.55$ Hz, NPN). MS (FAB) [m/e (species) intensity]: 563 (M^+) 60,213 $[FcCH(CH_3)^+]$ 100.

Preparation of $FcCH(CH_3)P(S)(CH_2O)_2PNMe_2$ (XII)

$FcCH(CH_3)P(S)(CH_2OH)_2$ (0.50 g, 1.48 mmol) and hexamethylphosphorus triamide (0.25 g, 1.53 mmol) were reacted in toluene (10 mL) under an atmosphere of nitrogen. The reaction mixture was refluxed at 110°C for 10 h. Afterwards, the solvent was evaporated under reduced pressure and fresh toluene (5 mL) was added and cooled at −4°C for 12 h. This resulted in an orange crystalline product which was identified as $FcCH(CH_3)P(S)(CH_2O)_2PNMe_2$ (**XII**) (0.52 g, 85.52%) m.p.: 116°C. NMR: ^1H, δ 1.54 ($FcCH\mathit{CH_3}$, dd, 3H), 2.22 ($N\mathit{CH_3}$, d, 6H), 3.73 ($Fc\mathit{CH}CH_3$, m, 1H), 3.91–4.44 ($C_A\mathit{H}$, C_B H, $C_D\mathit{H}$, $P\mathit{CH_2}$, m, 13H); ^{13}C, δ 13.55 ($FcCH\mathit{CH_3}$), 28.42 ($N\mathit{CH_3}$), 34.92 ($Fc\mathit{CH}CH_3$, d), 65.70 ($P\mathit{CH_2}$, t), 67.81, 68.31 (C_A), 68.60, 68.66 (C_B), 68.89 (C_D); ^{31}P, δ 33.35, (P=S, d) 150.71 [$\mathit{P}N(CH_3)_2$, d]. MS (EI) [m/e (Species) Intensity]: 411 (M^+) 42.6, 366 (M^+ - NMe_2) 16.8, 213 $[FcCH(CH_3)]$ 88.8, 121 (C_5H_5Fe) 50. Anal. Calcd for $C_{16}H_{23}FeNO_2P_2S$ C, 46.73; H, 5.64; N, 3.41. Found. C, 46.58; H, 5.71; N, 3.45%.

Preparation of $FcCH(CH_3)P(S)(CH_2O)_2PNEt_2$ (XIII)

$FcCH(CH_3)P(S)(CH_2OH)_2$ (0.50 g, 1.48 mmol) and hexaethylphosphorus triamide (0.37 g, 1.49 mmol) were reacted in toluene (10 mL) and worked up according to the reaction procedure given for (**XII**) to yield bright orange-red crystals which were identified as $FcCH(CH_3)P(S)(CH_2O)_2PNEt_2$ (**XIII**). (0.57 g, 87.69%) m.p.: 137°C. NMR: ^1H, δ 1.17 ($NCH_2\mathit{CH_3}$, t, 6H), 1.67 ($FcCH\mathit{CH_3}$, dd, 3H), 3.21 ($N\mathit{CH_2}CH_3$, m, 4H), 3.74 ($Fc\mathit{CH}CH_3$, m, 1H), 4.13–4.56 ($C_A\mathit{H}$, $C_B\mathit{H}$, $C_D\mathit{H}$, $P\mathit{CH_2}$, m, 13 H); ^{13}C, δ 13.05 ($FcCH\mathit{CH_3}$), 15.29 ($NCH_2\mathit{CH_3}$), 27.93 ($N\mathit{CH_2}CH_3$, d), 38.81 ($Fc\mathit{CH}CH_3$, d), 65.24 ($P\mathit{CH_2}$, t), 67.68, 67.81 (C_A), 68.13, 68.46 (C_B), 68.58 (C_D), 84.47 (C_C); ^{31}P, δ 33.04 (P=S, d), 153.09 (*P*NEt_2, d). MS (EI)[m/e (Species) Intensity]: 439 (M^+) 69.3, 366 (M^+ - NEt_2) 92, 213 [$FcCH(CH_3)$] 100, (C_5H_5Fe) 50. Anal. Calcd for $C_{18}H_{23}FeNO_2P_2S$ C, 49.22; H, 6.20; N, 3.19. Found. C, 49.22; H, 6.18; N, 3.22%.

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