ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 602 (2000) 125–132

Journal of Organometallic Chemistry

Synthesis and reactions of the ferrocene derived hydroxymethyl phosphine $FcCH(CH_3)P(CH_2OH)_2$ and its sulfide: crystal structures of $[FcCH(CH_3)P(S)R_2]$ $R = CH_2OH$, CH_2CH_2CN and $FcCH(CH_3)P(S)(CH_2O)_2PPh$ (Fc = ferrocenyl)

T.V.V. Ramakrishna [a], Anil J. Elias [a,*], Ashwani Vij [b]

[a] *Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India*
[b] *Single Crystal X-ray Diffraction Laboratory, University of Idaho, Moscow, ID 83843, USA*

Received 7 January 2000; received in revised form 18 February 2000

Dedicated to Professor S.S. Krishnamurthy on the occasion of his 60th birthday

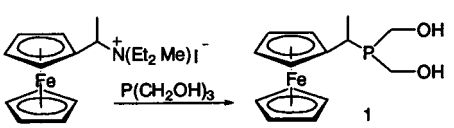
Abstract

The racemic ferrocene derived hydroxymethyl phosphine $FcCH(CH_3)P(CH_2OH)_2$ (**1**) (Fc = ferrocenyl) was prepared by the reaction of $P(CH_2OH)_3$ with $[FcCH(CH_3)\ NEt_2Me]^+I^-$. The latter was prepared by the reduction of acetyl ferrocene to the corresponding alcohol, which was converted into its acetate and reacted further with diethylamine, followed by methyl iodide. Reaction of **1** with acrylonitrile yielded the phosphine $FcCH(CH_3)P(CH_2CH_2CN)_2$ (**2**), while reaction of **1** with morpholine yielded $FcCH(CH_3)P[CH_2(NC_4H_8O)]_2$ (**3**). Reactions of compounds **1**–**3** with elemental sulfur yielded the corresponding phosphine sulfides **4**–**6**. The hydroxymethyl groups of the phosphine sulfide $FcCHCH_3P(S)(CH_2OH)_2$ (**4**) reacted readily with $PhPCl_2$ and $O(SiMe_2Cl)_2$ forming six- and eight-membered heterocycles $FcCH(CH_3)P(S)(CH_2O)_2PPh$ (**7**) and $FcCH(CH_3)P(S)(CH_2OSiMe_2)_2O$ (**8**), respectively. The crystal structures of compounds **4**, **5** and **7** were determined.

Keywords: Aminoethyl ferrocene; Hydroxymethyl phosphines; Phosphine sulfide; Racemic phosphine

1. Introduction

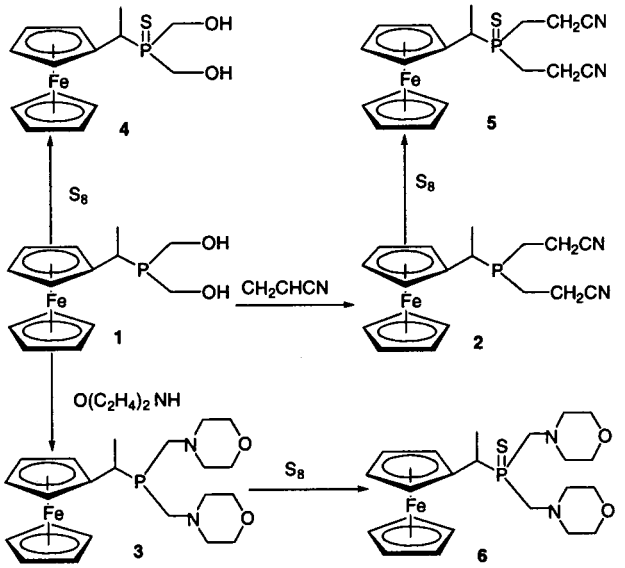
The synthesis and coordination chemistry of stable hydroxymethyl phosphines and diphosphines have attracted a lot of attention in recent years [1]. Katti and co-workers have shown that water soluble, chelating hydroxymethyl diphosphines coordinated to metals such as technetium, palladium, platinum and rhenium are potential candidates for biphasic catalysis and in the development of site specific radiopharmaceuticals [2]. Henderson and co-workers have prepared a ferrocene derived hydroxymethyl phosphine, $FcCH_2P(CH_2OH)_2$ [3] (Fc = ferrocenyl), which has been found to be an excellent precursor for a variety of other ferrocene derived phosphines including the highly stable primary phosphine $FcCH_2PH_2$ [3c]. The relevance of ferrocene based phosphines stems from the fact that a large number of chiral aminoethyl and phosphinoethyl ferrocenes have been found to be highly efficient chiral ligands for homogeneous catalysts in assymmetric transformations [4]. Many of these have been derived primarily from [1-(*N*,*N*-dimethylamino)ethyl] ferrocene with the further substitution of the substituted cyclopentadienyl group by a phosphine moiety [5]. Such compounds possess a planar chirality in addition to the central element of chirality resulting



Scheme 1.

* Corresponding author. Fax: +91-512-590007.
E-mail address: elias@iitk.ac.in (A.J. Elias)

0022-328X/00/$ - see front matter
PII: S0022-328X(00)00137-6



Scheme 2.

from a chiral carbon [6]. Further, ferrocenyl diphosphines as well as substituted phosphaferrocene ligands belonging to this category have been synthesized and their metal complexes prepared [7].

It is of interest to note that ferrocene derived hydroxymethyl phosphines having an assymmetric carbon atom linking the cyclopentadienyl group and the phosphorus atom have not been reported so far. Such compounds are potential precursors for a wide variety of novel chiral phosphines, diphosphines and metal complexes that can be used in assymmetric transformations. In this paper we report the synthesis of the ferrocene derived racemic hydroxymethyl phosphine $FcCH(CH_3)P(CH_2OH)_2$ (**1**) and its sulfide $FcCH(CH_3)P(S)(CH_2OH)_2$ (**4**). Reactions of **1** and **4** with other reagents have been carried out with a view to compare the reactivity of the hydroxymethyl groups. The crystal structures of the phosphine sulfides **4**, **5** and the cyclic phosphite $FcCH(CH_3)P(S)(CH_2O)_2PPh$ (**7**) have also been determined.

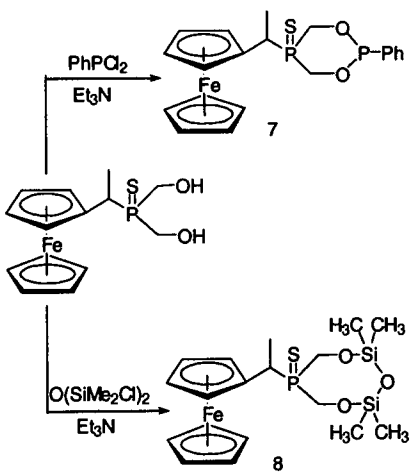
2. Results and discussion

Sodium borohydride reduction of acetyl ferrocene, followed by acetylation of the alcohol and reaction with diethyl amine gave the aminoethyl ferrocene $FcCH(CH_3)NEt_2$ in 92% yield [8]. Reaction of the amine with methyl iodide [9], followed by reaction with $P(CH_2OH)_4Cl$ and KOH along with excess of NEt_3 gave the hydroxymethyl phosphine $FcCH(CH_3)P(CH_2OH)_2$ (**1**) (Scheme 1). Reaction of **1** with acrylonitrile and morpholine was found to proceed in a similar manner to reactions carried out by Henderson and co-workers to yield the phosphines **2** and **3** (Scheme 2) [3]. Unlike the previously reported achiral phosphine $FcCH_2P(CH_2OH)_2$, phosphines **1**–**3** were viscous liquids and posed considerable difficulty in their purification. Attempts to purify these phosphines by high vacuum distillation using a kugelrohr apparatus were unsuccessful. The hydroxymethyl phosphine **1** could not be purified to obtain a reasonable level of purity for elemental analysis by various attempts of column chromatography. However, its identity was conclusively proved by NMR, mass spectral studies and by conversion to the crystalline phosphine sulfide **4**. Phosphines **2** and **3** were purified by column chromatography under a nitrogen atmosphere over silica gel by using a mixture of hexane–ethyl acetate and dichloromethane–methanol as the eluants, respectively.

The phosphine sulfides **4**–**6**, obtained by the reaction of compounds **1**–**3** with elemental sulfur, were crystalline solids and were purified by chromatography (Scheme 2). The EIMS spectra of **1**–**4** gave the molecular ion peak and the base peak was 213, indicating the ferrocenylethyl cation $FcCH(Me)^+$. The electrospray mass spectra of compounds **5** and **6** gave MH^+. The chemical shifts of the proton NMR spectra of all the phosphines showed agreement with similar chiral compounds reported by Togni et al. [5b]. The ^{31}P-NMR chemical shifts of compounds **1**–**3** were observed in the range -38 to -4 ppm and the sulfides **4**–**6** in the range 53–62 ppm.

As addition of formaldehyde to PH_3 is a reversible process [10], one can expect considerable differences in the reactivity of a hydroxymethyl group bonded to trivalent phosphorus in comparison with one bonded to a pentavalent phosphorus atom. The $P^{III}(CH_2OH)_2$ group of **1** was found to behave as a masked $P^{III}H_2$ group, as indicated by the addition reaction to acrylonitrile. However, our attempts to react the hydroxymethyl group of the phosphine **1** with organophosphorus and organosilicon halides were found to result in mixtures of products that could not be easily separated and identified. In contrast, the hydroxymethyl groups of the phosphine sulfide **4** were found to react readily with $PhPCl_2$ in the presence of triethylamine as an HCl scavenger to yield the six-membered heterocyclic phosphite **7** (Scheme 3). Reaction of **4** with $O(SiMe_2Cl)_2$ in the presence of triethylamine also proceeded smoothly yielding the eight-membered heterocycle **8**. A similar substitution was observed when $FcCH_2P(S)(CH_2OH)_2$ was dilithiated and reacted with the carbaphosphazene $(Me_2NCN)_2(Cl_2PN)$ [11]. These results indicate that the $P(CH_2OH)_2$ group in the phosphine sulfide **4** behaves like a simple diol and undergoes deprotonation readily. In contrast, the high nucleophilicity of the trivalent phosphorus site of **1** makes it an easy target for metallation and phosphonium salt formation. The EIMS of compounds **7** and **8** gave the molecular ion peak. For compound **7**, a pair of dou-

blets was observed in the ^{31}P-NMR spectrum at δ 35.82 and 149.00 ppm, the latter being due to the trivalent phosphorus atom. For compound **8**, the peak in the



Scheme 3.

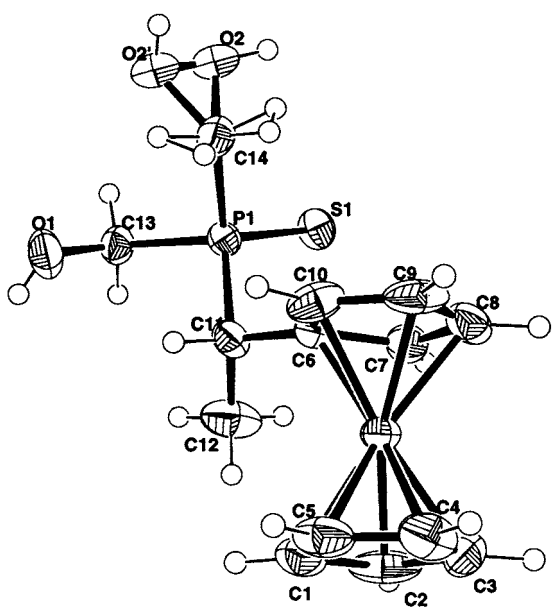


Fig. 1. Molecular structure of $FcCH(CH_3)P(S)(CH_2OH)_2$ (**4**).

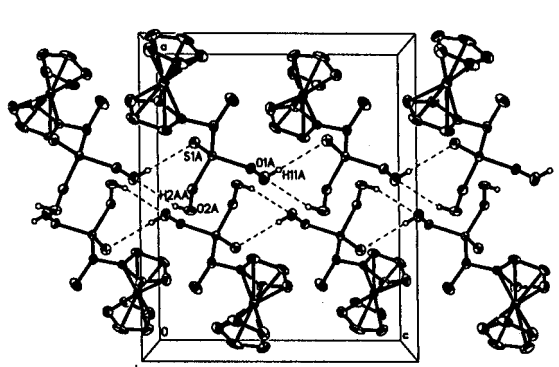


Fig. 2. Packing diagram of **4** showing hydrogen bonds.

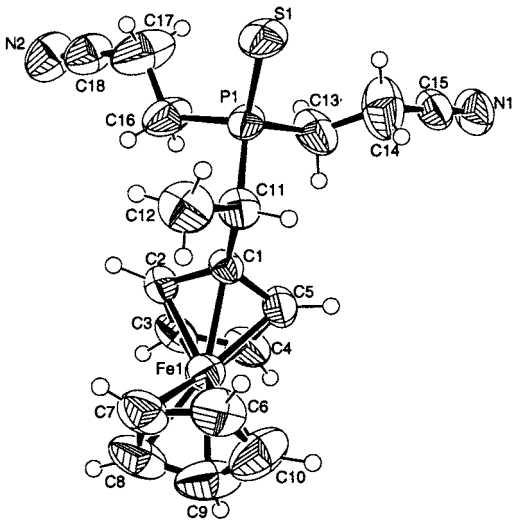


Fig. 3. Molecular structure of $FcCH(CH_3)P(S)(CH_2CH_2CN)_2$ (**5**).

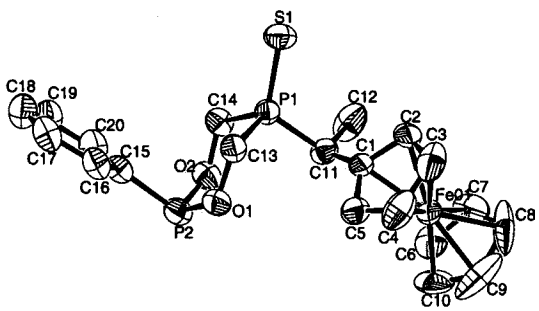


Fig. 4. Molecular structure of $FcCH(CH_3)P(S)(CH_2O)_2PPh$ (**7**).

^{31}P-NMR spectrum was observed at 53.39 ppm for the phosphine sulfide group.

The X ray structures of compounds **4**, **5** and **7** are given in Figs. 1–4. Tables 2–4 gives the selected bond distances and angles for compounds **4**, **5** and **7**, respectively. In the case of **4**, the OH group attached to C14 was found to be disordered. It was modelled using the PART command in SHELXTL 5.03 and the occupancies were refined as a free variable [15]. The major component of this disorder was refined to 90% occupancy. The hydrogen atoms were added at the calculated positions on O2 and O2′. In all the phosphine sulfide structures determined in this study, the P–CHR (R = H or Me) distances were observed shorter in comparison with those reported for the similar phosphines $FcCH_2P(CH_2OH)_2$ (average 1.857 Å) [3] and $FcCH_2PH_2$ (1.850 Å) [3c]. The shortest P–CHR distance has been observed for the cyanoethyl phosphine sulfide **5** (average 1.805 Å). The bond distances and angles of **4** show similarities to that of the phosphine sulfide $FcCH_2P(S)(CH_2OH)_2$ [3]. The sulfur atom of **4** shows bifurcated hydrogen bonding of 2.760 Å to H2′A and 2.480 Å to H11 (Fig. 2). This is supported by the S1–O1 and S1–O2′ distances of 3.215 and 3.040 Å. The

Table 1
Crystallographic data for compounds **4**, **5** and **7**

Compound	**4**	**5**	**7**
Empirical formula	$C_{14}H_{19}FeO_2PS$	$C_{18}H_{21}FeN_2PS$	$C_{20}H_{22}FeO_2P_2S$
Formula weight	338.17	384.25	444.23
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
Unit cell dimensions			
a (Å)	14.200(3)	9.700(4)	13.604
b (Å)	8.5594(13)	20.094(10)	7.299
c (Å)	11.9206(17)	10.527(3)	20.626
α (°)	90	90	90
β (°)	90.83(2)	116.75(2)	90.91
γ (°)	90	90	90
V (Å^3)	1448.7(4)	1832.2(13)	2047.7
Z	4	4	4
D_{calc} (g cm^{-3})	1.550	1.393	1.441
$F(000)$	704	800	920
Absorption coefficient (mm^{-1})	1.289	1.024	1.006
Temperature (K)	213(2)	213(2)	293(2)
2θ (max) (°)	23.25	23.26	24.97
Index ranges	$-15 \le h \le 5$, $-9 \le k \le 8$, $-13 \le l \le 13$	$-9 \le h \le 10$, $-22 \le k \le 22$, $-11 \le l \le 8$	$0 \le h \le 16$, $0 \le k \le 8$, $-24 \le l \le 24$
Reflections collected	2816	7822	3766
Unique data (R_{int})	0.0451	0.0738	0.0320
Parameters refined	180	209	236
Final indices (2σ data), R_1 (wR_2)	0.0492 (0.1019)	0.0683 (0.1486)	0.0373 (0.1073)
All data, R_1 (wR_2) [a]	0.0625 (0.118)	0.0931 (0.1618)	0.0820 (0.1349)
Goodness-of-fit	1.161	1.079	0.879
Largest difference peak (e Å^{-3})	0.381	0.617	0.360
Largest difference hole (e Å^{-3})	−0.341	−0.317	−0.332

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

X-ray structure of **7** shows the cyclic six-membered phosphite group in a chair conformation. The sum of the angles around the trivalent phosphorus P(2) is 305.3°, indicating a pyramidal phosphorus. In comparison to the P–O bonds in a similar six-membered heterocycle formed from the reaction of $FcCH_2P(S)(CH_2OLi)_2$ with the carbaphosphazene $(Me_2NCN)_2(Cl_2PN)$ [11], the P–O bonds in **7** are found to be elongated to an extent of 0.04 Å. For all the phosphine sulfides, the torsion angles between the P=S group and the methyl group attached to the chiral carbon were found to range from -57.8 to $+53.2$°.

3. Conclusions

We have synthesized the first example of ferrocene derived hydroxymethyl phosphine and phosphine sulfide having an assymmetric carbon atom linking the cyclopentadienyl group and the phosphorus atom. The hydroxymethyl groups of the phosphine reacts with acrylonitrile forming cyanoethyl groups and with morpholine forming morpholinomethyl groups. The phosphines were converted into the sulfides, which were crystalline solids and structurally characterized. The hydroxy groups of the phosphine sulfide were found to behave like a simple diol undergoing dehydrohalogenation with phosphorus and silicon dichlorides, leading to the ferrocene derived heterocycles **7** and **8**. We are currently exploring the reaction potential of these phosphines and phosphine sulfides.

Table 2
Selected bond distances (Å) and bond angles (°) for compound **4**

Bond lengths			
Fe–C [a]$_{av}$	2.0375(5)	C–C [a]$_{av}$	1.4015(8)
C(6)–C(11)	1.4990(7)	P(1)–C(11)	1.842(5)
P(1)–C(13)	1.8319(5)	O(2)–C(14)	1.430(7)
Bond angles			
C–C–C [b]$_{av}$	108.3(5)	C–C–C [c]$_{av}$	107.95(5)
C(14)–P(1)–C(13)	103.6(2)	C(6)–C(11)–P(1)	109.3(3)
O(2)–C(14)–P(1)	109.8(4)	C(11)–P(1)–C(13)	105.8(2)
C(7)–C(6)–C(11)	126.1(5)	C(6)–C(11)–C(12)	115.2(5)

[a] In cyclopentadienyl ring.
[b] In substituted cyclopentadienyl ring.
[c] In unsubstituted cyclopentadienyl ring.

Table 3
Selected bond distances (Å) and bond angles (°) for compound **5**

Bond lengths			
Fe–C $^{a}_{av}$	2.030(6)	C–C $^{a}_{av}$	1.411(11)
C(1)–C(11)	1.503(8)	P(1)–C(13)	1.801(7)
P(1)–C(16)	1.809(7)	N(1)–C(15)	1.098(8)
C(16)–C(17)	1.397(10)	C(14)–C(15)	1.476(10)
Bond angles			
C(1)–C(11)–P(1)	111.7(4)	C(14)–C(13)–P(1)	116.7(5)
C(2)–C(1)–C(11)	127.5(5)	C(13)–P(1)–C(16)	104.7(4)
C–C–C $^{b}_{av}$	108.0(5)	C–C–C $^{c}_{av}$	108.3(8)

[a] In cyclopentadienyl ring.
[b] In substituted cyclopentadienyl ring.
[c] In unsubstituted cyclopentadienyl ring.

Table 4
Selected bond distances (Å) and bond angles (°) for compound **7**

Bond lengths			
Fe–C $^{a}_{av}$	2.0255(4)	C–C $^{a}_{av}$	1.381(8)
C(1)–C(11)	1.501(5)	P(1)–C(13)	1.824(4)
O(1)–C(13)	1.436(4)	P(2)–C(15)	1.836(4)
P(2)–O(2)	1.635(3)		
Bond angles			
C(14)–P(1)–C(13)	100.18(18)	C(1)–C(11)–P(1)	110.5.(3)
O(1)–C(13)–P(1)	112.8(3)	C(11)–P(1)–C(13)	107.34(18)
O(1)–P(2)–O(2)	102.45(14)	O(2)–P(2)–C(15)	100.74(17)

[a] In cyclopentadienyl ring.

4. Experimental

4.1. Materials

Acrylonitrile, morpholine, acetic anhydride, diethylamine, and triethylamine (E. Merck) were dried and distilled prior to use. Tetrakis(hydroxymethyl)-phosphonium chloride (80% w/w aqueous solution), methyl iodide, ferrocene, dichlorophenyl phosphine (Fluka) and 1,3 dichloro-1,1,3,3-tetramethyl disiloxane (Lancaster) were used as such. Acetyl ferrocene was prepared by reported procedures and purified by recrystallization [12]. $FcCH(CH_3)NEt_2$ was prepared by the procedure of Kang and co-workers [8] in about 92% yield. Methanol, ethyl acetate, diethyl ether and light petroleum (66–68°C) were distilled and dried using standard procedures.

4.2. General procedures

A conventional vacuum line equipped with dry nitrogen facility and Schlenk glassware were used for all reactions. Reactions were carried out under an atmosphere of dry nitrogen wherever required. IR 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 a Jeol JNM-LA400 FT-NMR spectrometer with $CDCl_3$ as a solvent and TMS and H_3PO_4 as references and the mass spectra on a 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 is in accordance with the standard format used by previous authors [3d].

4.3. X-ray diffraction studies

A Siemens SMART diffractometer with a CCD detector at −54°C was employed for data collection of compounds **4** and **5**. The frame data for these were acquired using Siemens SMART software and processed on SGI-Indy/Indigo 2 workstation by using SAINT software [13]. The structures of compounds **4** and **5** were solved by direct methods using the SHELX 90 [14] program and refined by the full-matrix least-squares method on F^2 using SHELXL 93, incorporated in SHELXTL-PC V 5.03 [15]. Data collection of **7** was carried out on an Enraf–Nonius CAD4 diffractometer and structure solved by direct methods using the WINGX program [16] and refined on F^2 using full-matrix least-squares (SHELXL-97) [17]. 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 1 lists the crystal data and data collection parameters for compounds **4**, **5** and **7**.

4.4. Synthesis

4.4.1. $FcCH(CH_3)P(CH_2OH)_2$ (**1**)

A solution of $[P(CH_2OH)_4]Cl$ (1.00 g, 4.20 mmol) in methanol (5 ml) was deoxygenated and under nitrogen atmosphere KOH (0.24 g, 4.30 mmol) was added. The mixture was stirred for 1 h and was added dropwise to the solution of $[FcCH(CH_3)NEt_2Me]^+I^-$ (0.60 g, 1.40 mmol) in methanol (10 ml) under nitrogen with stirring. The reaction mixture was refluxed for 24 h and the solvent was removed under vacuum. To the precipitate obtained, water (3 ml), Et_2O (10 ml) and Et_3N (3 ml) were added and stirred for 1 h. The aqueous layer was extracted with Et_2O (15 ml) and both the extracts were washed with water (3 × 5 ml), dried over anhydrous sodium sulfate and filtered. Removal of Et_2O under reduced pressure yielded a viscous orange liquid, which was characterized as $FcCH(CH_3)P(CH_2OH)_2$ (**1**) (0.25 g, 60%). IR (cm^{-1}): 3340vs (Br), 3060s, 2960s, 2920s, 1440s, 1360s, 1100s, 1050s, 1000vs, 890w, 865w and 810s (neat); ^{1}H-NMR ($CDCl_3$): δ 1.49 (dd, $C_5H_4CHCH_3$, 3H), 3.29 (m, $C_5H_4CHCH_3$, 1H) and 3.86–4.33 (m, $C_A H$, $C_B H$, $C_D H$, PCH_2, 13H); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 17.13 (d, $C_5H_4CHCH_3$), 21.87 (d, $C_5H_4CHCH_3$), 60.66 (t, PCH_2), 65.55, 67.00 (C_A), 67.45, 67.85 (C_B), 68.41 (C_D) and 91.72 (C_C); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ −4.76; (MS) EI: m/e (frag-ment) intensity: 306 [M^+] 10, 276 [$M^+ - CH_2O$] 50, 246 [$M^+ - 2CH_2O$] 70 and 213 [$FcCH(CH_3)$] 100.

*4.4.2. $FcCH(CH_3)P(CH_2CH_2CN)_2$ (**2**)*

Compound **1** (0.50 g, 1.63 mmol) was dissolved in methanol (25 ml) and acrylonitrile (0.43 g, 8.10 mmol) was added. The solution was stirred for 5 h at room temperature (r.t.) and the solvent was removed in vacuum. The semi-solid obtained was purified by column chromatography over silica gel using 2:3 hexane–ethyl acetate as eluant under nitrogen, yielding a viscous orange liquid, which was characterized as $FcCH(CH_3)P(CH_2CH_2CN)_2$ (**2**) (0.37 g, 65%). IR (cm^{-1}): 2985s, 2960s, 2920s, 2225s, 1450s, 1420vs, 1360w, 1315w, 1210w, 1150w, 1100vs, 1050s, 1020s, 1000s, 895s, 810vs and 720w (neat); ^{1}H-NMR ($CDCl_3$): δ 1.38–1.80 (m, $C_5H_4CHCH_3$, CH_2CN, 7H), 2.04–2.64 (m, C_5H_4CH, PCH_2, 5H) and 3.94–4.22 (m, C_A *H*, C_B *H*, C_D *H*, 9H); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 14.73 (dd, PCH_2), 17.32 (d, $C_5H_4CHCH_3$), 20.09 (dd, CH_2CN), 30.95 (d, C_5H_4CH), 65.44, 67.51 (C_A), 67.62, 67.77 (C_B), 68.58 (C_D), 89.90 (C_C) and 119.24 (CN); $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −7.31; (MS) EI: *m*/*e* (fragment) intensity: 352 [M^+] 30, 213 [$FcCH(CH_3)$] 100, 186 ($CpFeC_5H_5$) 30 and 121 (CpFe) 68; Anal. Calc. for $C_{18}H_{21}N_2PFe$: C, 61.38; H, 6.01; N, 7.9. Found: C, 61.45; H, 5.91; N, 8.00%.

*4.4.3. $FcCH(CH_3)P[CH_2(NC_4H_8O)]_2$ (**3**)*

Compound **1** (0.30 g, 0.98 mmol) was dissolved in methanol (20 ml) and morpholine (0.42 g, 4.82 mmol) was added and stirred for 5 h. After removing the solvent under vacuum, the residue obtained was purified under nitrogen by column chromatography over silica gel using 24:1 dichloromethane–methanol as eluant, yielding an orange liquid, which was characterized as $FcCH(CH_3)P[CH_2(NC_4H_8O)]_2$ (**3**) (0.30 g, 70%). IR (cm^{-1}): 3080w, 2850s, 2800s, 1440s, 1360w, 1280s, 1250w, 1200w, 1115vs, 1065w, 1005s, 895w, 855s, 810w and 725w (neat); ^{1}H-NMR ($CDCl_3$): δ 1.57 (dd, $C_5H_4CHCH_3$, 3H), 2.05–2.65 (m, $CHCH_3$, PCH_2NCH_2, 13H), 3.61–3.68 (m, CH_2O, 8H) and 3.93–4.19 (m, C_A *H*, C_B *H*, C_D *H*, 9H); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 18.04 (d, $C_5H_4CHCH_3$), 29.29 (d, $C_5H_4CHCH_3$), 54.84 (dd, NCH_2CH_2O), 56.70 (dd, CH_2P), 65.90, 66.63 (C_A), 66.84 (NCH_2CH_2O), 67.62, 68.37 (C_D) and 90.76 (C_C); $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −37.77, (d); (MS) EI: *m*/*e* (fragment) intensity: 444 [M^+] 40, 345 [$M^+ - C_4H_8ONCH$] 20, 231 [$P(CH_2C_4H_8ON)_2$] 50, 213 [$FcCH(CH_3)$] 100 and 186 ($CpFeC_5H_5$) 22; Anal. Calc. for $C_{22}H_{33}N_2O_2FeP$: C, 59.47; H, 7.49; N, 7.28. Found: C, 59.40; H, 7.35; N, 7.55%.

*4.4.4. $FcCH(CH_3)P(S)(CH_2OH)_2$ (**4**)*

Compound **1** (0.50 g, 1.63 mmol) and elemental sulfur (0.21 g, 6.55 mmol) were dissolved in toluene (25 ml) with methanol (5 ml). The solution was refluxed for 5 h. The solvent was removed under vacuum and the orange solid obtained was purified over silica gel using 3:2 hexane–ethyl acetate as eluant yielding orange crystals, which were identified as $FcCH(CH_3)P(S)(CH_2OH)_2$ (**4**) (0.33 g, 60%), m.p. 90°C. IR (cm^{-1}): 3485s, 1270w, 1215w, 1150s, 1100s, 1020vs, 875s, 825s, 800s, 765vs, 705vs and 625vs (Nujol); ^{1}H-NMR ($CDCl_3$): δ 1.73 (dd, $C_5H_4CHCH_3$, 3H), 2.57 (d, OH, br, 2H), 3.22 (m, $C_5H_4CHCH_3$, 1H), 3.81 (m, PCH_2, 4H) and 4.13–4.25 (m, C_A *H*, C_B *H*, C_D *H*, 9H); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 14.17 (d, $C_5H_4CHCH_3$), 32.21 (d, $C_5H_4CHCH_3$), 56.75–58.67 (dd, PCH_2), 66.38, 68.10 (C_A), 68.38, 68.60 (C_B), 68.85 (C_D) and 85.05 (C_C); $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ +61.84, (t); (MS) EI: *m*/*e* (fragment) intensity: 338 [M^+] 74, 308 [$M^+ - CH_2O$] 32, 278 [$M^+ - 2CH_2O$] 20, and 213 [$FcCH(CH_3)$] 100; Anal. Calc. for $C_{14}H_{19}O_2FePS$: C, 49.72; H, 5.66. Found: C, 49.64; H, 5.69%.

*4.4.5. $FcCH(CH_3)P(S)(CH_2CH_2CN)_2$ (**5**)*

Compound **2** (0.21 g, 0.60 mmol) and elemental sulfur (0.04 g, 1.25 mmol) were reacted as given for the preparation of **4** to give $FcCH(CH_3)P(S)(CH_2CH_2CN)_2$ (**5**) (0.14 g, 64%), m.p. 143°C. IR (cm^{-1}): 2220s, 1225w, 1270w, 1220s, 1160s, 1100s, 1150s, 1020vs, 1000s, 1080w, 950s, 900s, 850w, 815vs, 780s, 735s, 685w, and 620w (Nujol); ^{1}H-NMR ($CDCl_3$): δ 1.80–2.23 (m, $C_5H_4CHCH_3$, CH_2CN, 7H), 2.45–2.71 (m, PCH_2, 4H), 3.05 (m, $C_5H_4CHCH_3$, 1H),4.15–4.31 (m, C_A *H*, C_B *H*, C_D *H*, 9H); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 11.27 (d, PCH_2), 14.69 ($C_5H_4CHCH_3$), 23.64 (d, CH_2CN), 37.73 (d, C_5H_4CH), 66.13, 68.56 (C_A), 68.84, 68.93 (C_B), 69.06 (C_D), 84.82 (C_C) and 118.64 (d, CN); $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ +60.14; ESMS, cone voltage 20 V: *m*/*z* 383.9 [$M+H$]$^+$; Anal. Calc. for $C_{18}H_{21}N_2FePS$: C, 56.26; H, 5.51; N, 7.29. Found: C, 56.22; H, 5.59; N, 7.35%.

*4.4.6. $FcCH(CH_3)P(S)(CH_2NC_4H_8O)_2$ (**6**)*

Compound **3** (0.33 g, 0.74 mmol) and elemental sulfur (0.05 g, 1.56 mmol) were reacted as given for compound **4** to yield $FcCH(CH_3)P(S)(CH_2NC_4H_8O)_2$ (**6**) (0.21 g, 58%), m.p. 105°C. IR (Nujol) (cm^{-1}): 1290s, 1220vs, 1115w, 1095w, 1080w, 1005s, 895vw, 855vs, 830s, 805s, 780s, 735w, 715w, 700w and 640s; ^{1}H-NMR ($CDCl_3$): δ 1.74 (dd, $C_5H_4CHCH_3$, 3H), 2.48–2.98 (PCH_2NCH_2, m, 12H), 3.07 (m, $C_5H_4CHCH_3$, 1H), 3.66 (m, OCH_2, 8H), 4.15–4.24 (m, C_A *H*, C_B *H*, C_D *H*, 9H); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 15.16 ($C_5H_4CHCH_3$), 34.31 (d, $C_5H_4CHCH_3$), 56.00 (dd, NCH_2), 56.93 (dd, PCH_2), 66.91 (CH_2O), 67.35 (C_B), 68.16 (C_A), 68.75 (C_D) and 86.47 (C_C); $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ +53.78; ESMS, cone voltage 20 V: *m*/*z* 477 [$M+H$]$^+$; Anal. Calc. for $C_{22}H_{33}N_2O_2FePS$: C, 55.47; H, 7.98; N, 5.88. Found: C, 55.50; H, 8.10; N, 5.91%.

*4.4.7. FcCH(CH$_3$) P(S)(CH$_2$O)$_2$PPh (**7**)*

Compound **4** (0.20 g, 0.59 mmol) and $PhPCl_2$ (0.11 g, 0.61 mmol) were reacted in the presence of NEt_3 (0.12 g, 1.12 mmol) in toluene (15 ml) for 15 h at r.t. The reaction mixture was then filtered to remove amine hydrochloride and the solvent was evaporated under vacuum. The residue obtained was dissolved in toluene (5 cm^3) and cooled for 5 days at 4°C to yield orange crystals of $FcCH(CH_3)P(S)(CH_2O)_2PPh$ (**7**) (0.21 g, 80%), m.p. 133°C. IR (Nujol) (cm^{-1}): 750m, 700vs, 675s, 800m, 875w, 915s, 950w, 980w, 1010vs, 1050w, 1100m, 1210w (Nujol); ^{1}H-NMR ($CDCl_3$): δ 1.64 (dd, $C_5H_4CHCH_3$, 3H), 3.77(m, $C_5H_4CHCH_3$, 1H), 3.95–4.37 (m, C_A H, C_B H, C_D H, PCH_2, 13H), 7.33–7.45 (m, PC_6H_5, 5H); ^{13}C{^{1}H}-NMR: 13.22 ($C_5H_4CHCH_3$), 28.01 (d, $C_5H_4CHCH_3$), 62.60 (dd, PCH_2), 67.56, 67.75 (C_A), 68.51, 68.55 (C_B), 68.78 (C_D), 84.33 (C_C), 129.19 (C16, C20), 129.27 (C17, C19), 129.76 (C18), 130.59 (C15); ^{31}P{^{1}H}-NMR: +35.82 (d, P=S), +149.00 (d, *P*Ph); (MS) EI: *m*/*e* (fragment) intensity: 444 [M$^+$] 11, 367 [M$^+$ − Ph] 27, 336 [M$^+$ − PPh] 17 and 213 [FcCH(CH$_3$)] 100; Anal. Calc. for $C_{20}H_{22}O_2FeP_2S$: C, 54.07; H, 4.99. Found: C, 54.11; H, 4.90%.

*4.4.8. FcCH(CH$_3$) P(S)(CH$_2$OSiMe$_2$)$_2$O (**8**)*

Compound **4** (0.20 g, 0.59 mmol) and $O(SiMe_2Cl)_2$ (0.12 g, 0.59 mmol) were reacted in the presence of NEt_3 (0.12 g, 1.12 mmol) in toluene (20 ml) for 15 h at r.t. The mixture was filtered to remove amine hydrochloride and the solvent was removed under vacuum. The orange semi-solid obtained was dissolved in 2:3 dichloromethane–hexane and cooled at −4°C for 24 h to yield an orange crystalline product, which was identified as $FcCH(CH_3)P(S)(CH_2OSiMe_2)_2O$ (**8**) (0.24 g, 85%), m.p. 145°C. IR (cm^{-1}): 730w, 795s, 840s, 1050w, 1085vs, 1345s; ^{1}H-NMR: −0.5 (m, $SiCH_3$, 12H), 1.45 (dd, $C_5H_4CHCH_3$, 3H), 3.22 (m, $C_5H_4CHCH_3$, 1H), 3.69–4.07 (m, C_A *H*, C_B *H*, C_D *H*, PCH_2, 13H); ^{13}C{^{1}H}-NMR: −2.26 ($SiCH_3$), 13.40 ($C_5H_4CHCH_3$), 28.53 (d, $C_5H_4CHCH_3$), 61.1 (t, PCH_2), 67.35 (C_A), 67.67 (C_B), 68.78 (C_D), 85.24 (C_C); ^{31}P{^{1}H}-NMR: +53.39s; (MS) EI: *m*/*e* (fragment) intensity: 468 [M$^+$] 42, 213 [FcCH(CH$_3$)] 100 and 121 (C_5H_5Fe) 50; Anal. Calc. for $C_{18}H_{29}O_3FePSSi_2$: C, 46.15; H, 6.24. Found: C, 46.22; H, 6.18%.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 138864, 138865 and 138866 for compounds **4**, **5** and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

A.J.E. thanks the Department of Science and Technology (DST), India and the Council of Scientific and Industrial Research (CSIR), India for financial assistance in the form of research grants. T.V.V.R. thanks CSIR, India for a senior research fellowship.

References

[1] (a) D.E. Bering, K.V. Katti, C.L. Barnes, W.A. Volkert, J. Am. Chem. Soc. 121 (1999) 1658. (b) V.S. Reddy, D.E. Berning, K.V. Katti, C.L. Barnes, W.A. Volkert, A.R. Ketring, Inorg. Chem. 35 (1996) 1753. (c) V.S. Reddy, K.V. Katti, W.A. Volkert, J. Chem. Soc. Dalton Trans. (1996) 4459. (d) V.S. Reddy, K.V. Katti, C.L. Barnes, J. Chem. Soc. Dalton Trans. (1996) 1301. (e) C.J. Smith, V.S. Reddy, S.R. Karra, K.V. Katti, L.J. Barbour, Inorg. Chem. 36 (1997) 1786. (f) W. Kemmitt, D.J. Law, D.R. Russel, J. Chem. Soc. Dalton Trans. (1993) 25.

[2] K.V. Katti, H. Gali, C.J. Smith, D.E. Bering, Acc. Chem. Res. 32 (1999) 9. (b) K.V. Katti, Curr. Sci. 70 (1996) 219.

[3] (a) N.J. Goodwin, W. Henderson, B.K. Nicholson, J.K. Sarfo, J. Fawcett, D.R. Russel, J. Chem. Soc. Dalton Trans. (1997) 4377. (b) N.J. Goodwin, W. Henderson, J.K. Sarfo, J. Chem. Soc. Chem. Commun. (1996) 1551. (c) N.J. Goodwin, W. Henderson, B.K. Nicholson, J. Chem. Soc. Chem. Commun. (1997) 31. (d) N.J. Goodwin, W. Henderson, B.K. Nicholson, J. Fawcett, D.R. Russel, J. Chem. Soc. Dalton Trans. (1999) 1785.

[4] (a) K.S. Gan, T.S.A. Hor, in: A. Togni, T. Hayashi (Eds.), Ferrocenes, VCH, Weinheim, 1995, p. 1. (b) M. Sawamura, Y. Ito, Chem. Rev. 92 (1992) 857. (c) M. Watanabe, N. Hashimoto, S. Araki, Y. Butsugen, J. Org. Chem. 57 (1992) 742.

[5] (a) A. Togni, Angew. Chem. Int. Ed. Engl. 35 (1996) 1475. (b) A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, J. Am. Chem. Soc. 116 (1994) 4062. (c) P. Barbaro, A. Togni, Organometallics (1995) 4549.

[6] See: G. Wagner, R. Herrmann, in: A. Togni, T. Hayashi (Eds.), Ferrocenes, VCH, Weinheim, 1995, p. 173.

[7] (a) L. Brassat, B. Ganter, C. Ganter, Chem. Eur. J. 4 (1998) 2148. (b) C. Ganter, L. Brassat, C. Glinsböckel, B. Ganter, Organometallics 16 (1997) 2862. (c) C. Ganter, L. Brassat, B. Ganter, Chem. Ber. 130 (1997) 1771.

[8] J. Kang, J.H. Lee, S. Ahn, J. Choi, Tetrahedron Lett. 39 (1998) 5523.

[9] D. Lednicer, C.R. Hauser, Org. Synth. 3 Coll. Vol. V 434 (1973).

[10] J.W. Ellis, K.N. Harrison, P.A.T. Hoye, A.G. Orpen, P.G. Pringle, M.B. Smith, Inorg. Chem. 31 (1992) 3026.

[11] N.D. Reddy, A.J. Elias, A. Vij, Inorg. Chem. Commun. 3 (2000) 29.

[12] P.J. Graham, R.V. Lindsey, G.W. Parshal, M.L. Peterson, G.M. Whitman, J. Am. Chem. Soc. 79 (1957) 3416.

[13] SMART V 4.043 and SAINT V 4.035 softwares for CCD detector system, Siemens Analytical Instruments Division, Madison, WI, 1995.

[14] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[15] (a) G.M. Sheldrick, SHELXL-93, Program for the refinement of crystal structure, University of Göttingen, Göttingen, Germany, 1993. (b) SHELXTL 5.03 (PC Version), Program library for structure solution and molecular graphics, Siemens Analytical Instruments Division, Madison, WI, 1995.
[16] L.J. Farrugia, WINGX — A windows program for crystal structure analysis, University of Glasgow, Glasgow, 1998.
[17] G.M. Sheldrick, SHELXL-97, Program for crystal structure analysis (release 97-2), University of Göttingen, Göttingen, Germany 1998.