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Dealkylation reactions of dialkylaminomethylferrocenes with cyclic chlorocarbaphosphazene, $(ClCN)_2(Cl_2PN)$☆

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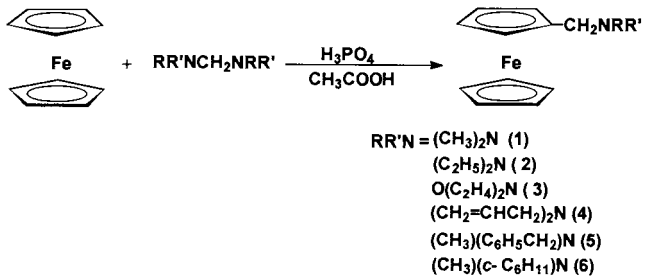
Abstract

Dialkylaminomethylferrocenes, $FcCH_2NRR'$ ($NRR' = NMe_2$ (**1**), NEt_2 (**2**), $N(CH_2CH=CH_2)_2$ (**3**), $N(CH_2CH_2)_2O$ (**4**), N(Me)(CH_2Ph) (**5**) and N(Me)(*c*-C_6H_{11}) (**6**) (Fc = Ferrocenyl) were synthesized by the reaction of ferrocene with the corresponding diamines, $RR'NCH_2NRR'$. The identity of **3** was further confirmed by X-ray structural analysis of its hydrochloride, $FcCH_2NH(CH_2CH=CH_2)_2^+Cl^-$ (**7**). Reactions of compounds **1**–**6** were carried out with tetrachlorodicarbaphosphatriazene, $(ClCN)_2(Cl_2PN)$ in diethylether medium at room temperature or in refluxing toluene. The amines **1**, **2**, **4**, **5** and **6** were found to undergo a facile C–N bond cleavage at the bridging methylene group irrespective of the nature of substituents on the nitrogen. The cleaved dialkylamino groups were found to substitute regiospecifically at the ring carbon atoms of the carbaphosphazene, yielding the dialkylamino substituted carbaphosphazenes $[(RR'N)CN]_2(Cl_2PN)$ **8**–**12**. The X-ray crystal structure of the substituted carbaphosphazene $(Me_2NCN)_2(Cl_2PN)$ **8** has also been determined.

Keywords: Phosphazene; Ferrocene; Tetrachlorodicarbaphosphatriazine; Dialkylaminomethylferrocenes; Cyclocarbaphosphazene; Dealkylation reaction; Regiospecificity

1. Introduction

Synthesis and reaction chemistry of aminomethyl ferrocenes [1] and phosphinomethyl ferrocenes [2] have been attracting considerable attention in recent years. The majority of these studies have been centred on *N*,*N*-dimethylaminomethylferrocene [3] as well as the optically active [1-(*N*,*N*-dimethylamino)ethyl] ferrocene [4] both of which undergo facile lithiation at the 2-position of the aminomethyl substituted cyclopentadienyl group. These have been found to react with a variety of main group and transition metal reagents yielding molecules where the dimethyl amino group effectively coordinates with metal centres [3]. Some of such systems have been found to absorb molecular nitrogen, whereas C–H activation of the bridging methylene groups has been observed in some examples. Chiral ferrocenyl phosphines [4] as well as selenides [5] prepared from [1-(*N*,*N*-dimethylamino)ethyl] ferrocene have been found to be highly efficient chiral ligands for homogeneous catalysts in assymetric transformations [6].



Scheme 1.

☆ Dedicated to Professor H.W. Roesky on the occasion of his 63rd birthday.

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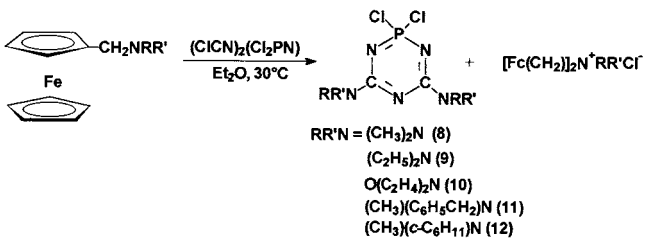

Scheme 2.

Halogenated cyclocarbaphosphazenes, which can be considered as hybrid heterocycles of inorganic cyclophosphazenes and organic *s*-triazines, have been reported to show regiospecificity in substitution reactions [7]. Quite recently, Shreeve and coworkers have reported on the unusual dealkylation of trialkylamines shown by these heterocycles [8]. The present study was aimed to prepare and characterize a variety of dialkylaminomethylferrocenes and study their reactivity and mode of cleavage with the dealkylating carbaphosphazene, $(ClCN)_2(Cl_2PN)$. By varying the substituents on the nitrogen we have tried to understand the preference of alkyl groups of the aminomethylferrocenes for cleavage and the effect of the stability of the leaving group in deciding the course of this reaction.

2. Results and discussion

Among the few methods that are known for the synthesis of aminomethyl-ferrocenes $FcCH_2NR_2$, using various ferrocene based precursors [9–11], we have tried to evaluate the usefulness of the simple reaction of ferrocene with the corresponding methylenebis amine [11], $R_2NCH_2NR_2$ (Scheme 1). The aminomethylferrocenes **1**–**6** were purified by vacuum distillation or recrystallization and characterized by spectral and analytical methods. The yields of the sterically bulky amines were poor and our attempts to make dicyclohexyl and dibenzyl aminomethylferrocenes by this method were not quite successful.

Reactions of compounds **1**–**6** were carried out with $(ClCN)_2(Cl_2PN)$ in diethyl ether at room temperature or in refluxing toluene. The amines were found to undergo a facile cleavage at the bridging methylene group and the cleaved dialkylamino groups were found to substitute on the carbaphosphazene heterocycle (Scheme 2). The substitution was found to be regiospecific with only the C–Cl bonds of $(ClCN)_2(Cl_2PN)$ taking part in the reaction and the P–Cl bonds remaining inactive. The analysis of the reaction residue indicated that the cleaved ferrocenyl group had reacted with one more molecule of the amine to give a tetraalkylammonium halide.

Unlike the dealkylation reactions of trialkyl amines with carbaphosphazene reported previously, these reactions were found to proceed even at room temperature in diethylether medium. The reaction shows similarities to the von Braun cyanogen bromide reaction reported for dimethylaminomethylferrocene, in the mode of cleavage at the bridging methylene group as well as the formation of the tetraalkylammonium halide as the side product [12]. It is noteworthy that as the side product, possible formation of tetraalkylammonium halide was predicted in S_N1Ar reactions of heteroaromatic halides with trialkylamines [13].

Kapnang and Charles have reported the dealkylation of unsymmetrical tertiary amines with carbonochloridate reagents [14]. From their studies it was observed that the stability of the formed carbocation plays a role in deciding the nature of the group which gets cleaved during a dealkylation reaction in case of an unsymmetrical trialkylamine. Our recent studies on dealkylation reactions of unsymmetrical tertiary amines with cyanuric chloride [15] and carbaphosphazenes [16] were in agreement with these observations. In the dealkylation reactions of $(c\text{-}C_6H_{11})_2MeN$, $(allyl)_2MeN$ and $(PhCH_2)_2MeN$ we have observed that the groups which get cleaved are cyclohexyl, allyl and benzyl, respectively. However, in the reactions of **5** and **6** with $(ClCN)_2(Cl_2PN)$, we observe that the cleavage is not occurring at the benzyl and cyclohexyl groups but at the bridging methylene group indicating the high stability of the ferrocenyl methyl carbocation in deciding the course of these reactions. Reaction of **4** with $(ClCN)_2(Cl_2PN)$ was surprisingly quite sluggish even under rigorous conditions and a large amount of unreacted amine was recovered from the reaction mixture. Spectral analysis of the reaction mixture did not show any evidence for the formation of dealkylated products.

Figs. 1 and 2 show the single crystal X-ray structures of diallylaminomethyl-ferrocene hydrochloride **7** and the substituted carbaphosphazene $(Me_2NCN)_2(Cl_2PN)$ **8**. Table 1 lists the crystal and structure refinement parameters for **7** and **8** while Table 2 lists the selected bond distances and angles for **7** and **8**. The structure of **8** shows similarities to that of $(Me_2NCN)_2[(CF_2CH_2O)_2PN]$ [8] and $(Me_2NCN)_2$ $[(Me_2N)_2PN]$ [17]. The exocyclic C–N bonds are located in a planar environment as suggested by the sum of the angles around N(3) as 360°. The exocyclic C–N bond distance is also 1.343 Å which is same as that of the endocyclic C–N distances indicating increased double bond character. It is noteworthy that the other two C–N bonds originating from N(3) are 1.454 and 1.464 Å.

As most of the dialkylaminomethyl and aminoethylferrocenes are found to be liquids, available X-ray structural data on such compounds have been restricted mainly to their ammonium salts or other derivatives

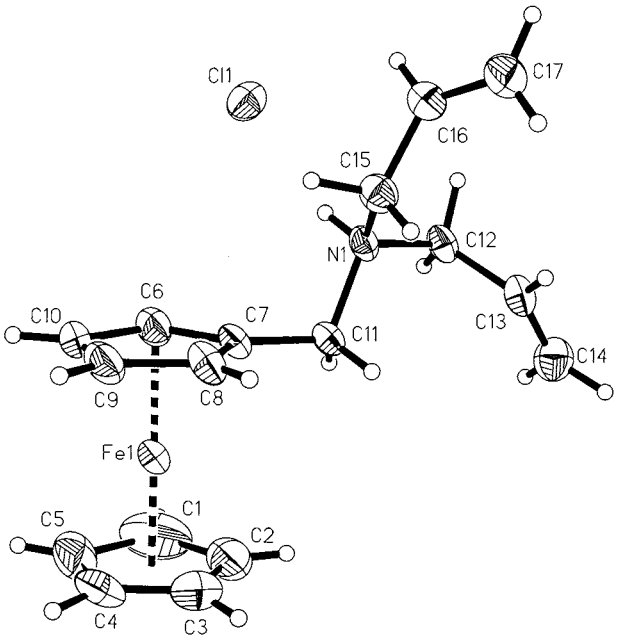

Fig. 1. Molecular structure of $FcCH_2NH(CH_2CH{=}CH_2)_2^+ Cl^-$.

with further substitution on the cyclopentadienyl group [3a,18]. The structure of **7** showed similarities to those of [1-(*N*,*N*-dimethylammonium)ethyl]ferrocene tartarate dihydrate [19], *N*-formylaminomethyl ferrocene [20] and [1-(2-diphenylphosphinoferrocenyl)ethyl]-dimethylamine [18]. The two cyclopentadienyl rings are found to be in an eclipsed configuration. The average of the ferrocenyl Fe–C distances are 2.033 Å. The C–N–C bond angles around the nitrogen range from 110.8 to 114.3°. If there is only lone-pair electron density on the nitrogen, one would expect these angles to be less than 109°. The three C–N bond lengths are also of the order

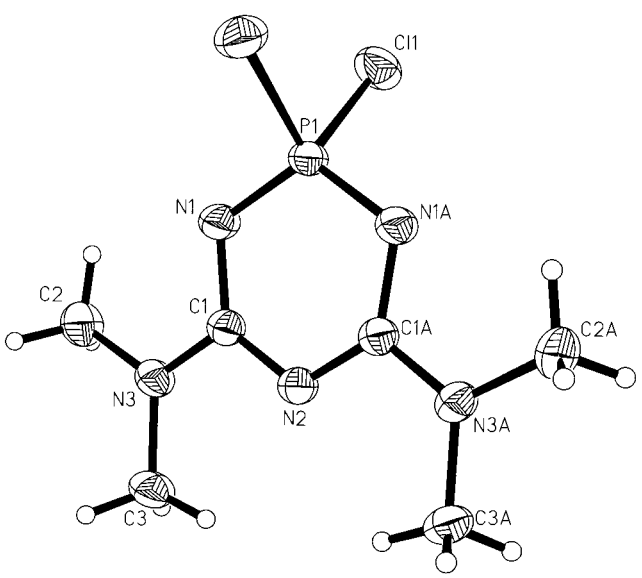

Fig. 2. Molecular structure of $[(Me_2N)CN]_2(Cl_2PN)$.

of 1.506–1.519 Å, which is longer than the average C–N single bond distance. The fact that the methylene carbon C(11), lies in the same plane as the C(1)–C(5) cyclopentadienyl ring is assenting the extra stability of the ferrocenyl methyl carbocation.

3. Conclusions

A variety of dialkylaminomethyl ferrocenes were synthesized and their reactivity with chlorinated dicarbaphosphatriazene, $(ClCN)_2(Cl_2PN)$ evaluated. The amines were found to undergo cleavage preferentially at the bridging methylene group, despite having good leaving groups such as benzyl and cyclohexyl on the amino nitrogen. This is indicative of the extra high stability of the ferrocenyl methyl cation over other carbocations which could have formed otherwise. Unlike the case of trialkylamines, cleavage of the ferrocenylmethylamines were found to occur at room temperature by using diethylether as solvent. The reactions show similarities to the von Braun cyanogen bromide reaction of tertiary amines. Currently we are synthesizing new ferrocenylamines and phosphines with increased chain length and varied substituents to compare their reactivity with these aminomethylferrocenes.

4. Experimental

4.1. Materials

Diethylamine, morpholine, diallylamine, cyclohexylmethylamine and benzylmethylamine (Fluka) were dried and distilled prior to use. *N*,*N*-dimethylaminomethyl ferrocene (Lancaster) was used directly. $(ClCN)_2(Cl_2PN)$ was prepared and purified by a literature method [21]. Solvents were dried and distilled by standard procedures prior to use.

4.2. General procedures

A conventional vacuum line equipped with dry nitrogen facility and schlenk glassware was used for all reactions. Reactions were carried out and worked up under an atmosphere of dry nitrogen. Infrared spectra were recorded on a Perkin–Elmer 1320 spectrometer as Nujol mulls. The ^{1}H- and ^{31}P-NMR spectra were recorded using a Bruker WM-400 or a Jeol JNM-PMX60SI spectrometers using $CDCl_3$ as a solvent. Mass spectra were obtained on a JEOL D-300 (EI/CI) spectrometer in the EI mode. Elemental analysis were carried out on a Carlo Erba CHNS-O 1108 elemental analyser.

Table 1
Crystallographic data of compounds **7** and **8**

Compound	**7**	**8**
Empirical formula	$C_{17}H_{22}ClFeN$	$C_6H_{12}Cl_2N_5P$
Formula weight	331.66	256.08
Colour	Reddish brown	Colourless
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, *Cmcm*
Unit cell dimensions		
a (Å)	13.0025(4)	13.134
b (Å)	10.4735(2)	11.7123(3)
c (Å)	13.6074(4)	7.1763(2)
α (°)	90	90
β (°)	114.3070(10)	90
γ (°)	90	90
V (Å^3)	1688.81(8)	1103.96(4)
Z	4	4
D_{calc} (g cm^{-3})	1.304	1.541
$F(000)$	696	528
Absorption coefficient (mm^{-1})	1.041	0.703
Temp (K)	298(2)	213(2)
θ (max) (°)	28.26	28.33
Index ranges	$-16 \le h \le 15,\ -13 \le k \le 7,\ -17 \le l \le 18$	$-17 \le h \le 11,\ -15 \le k \le 15,\ -9 \le l \le 9$
Reflections collected	10138	3503
Unique data (R_{int})	3970, (0.0368)	768, (0.0358)
Parameters refined	266	46
Final indices (2σ data), $R_1(wR_2)$	0.0412(0.0834)	0.0383(0.1104)
All data, $R_1(wR_2)$[a]	0.0979(0.1142)	0.0434(0.1143)
Goodness-of-fit, S (F^2)	1.106	1.181
Largest difference peak (e Å^{-3})	0.304	0.389
Largest difference hole (e Å^{-3})	−0.159	−0.517

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

4.3. X-ray diffraction studies

The X-ray diffraction data on compounds **7** and **8** were collected on a Siemens SMART diffractometer. Data collection parameters are listed in Table 1. The frame data were acquired with the SMART [22] software using a Siemens 3-circle platform using Mo–K_α radiation ($\alpha = 0.71073$ Å) from a fine focus tube. The χ-axis on this platform was fixed at 54.74° and the diffractometer was equipped with a CCD detector maintained near − 54°C. Cell constants are determined from 60 10 s frames. The structures were solved by direct methods using SHELXS-90 program [23] and refined by least squares method on F^2, SHELX-93 [24] incorporated in SHELXTL-PC v. 5.03. 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 X-ray crystallographic parameters and Table 2 lists the selected bond distances and angles for compounds **7** and **8** [25].

4.4. Preparation of dialkylaminomethylferrocenes

The reported procedure for the synthesis of dimethylaminomethylferrocene [11] was adopted for the synthesis of compounds **2**–**6**. The methylenebisamines were first synthesized by the reaction of the corresponding secondary amine with formaldehyde and purified by distillation. These were further reacted with ferrocene in acetic acid in the presence of phosphoric acid to prepare compounds **2**–**6**. The reactions were performed at 100°C for 10–24 h. The compounds were purified by high vacuum distillation using a Kugelrohr unit and were obtained as dark red to reddish–brown liquids except for **3** which was recrystallized from hot hexane as orange-brown needles.

4.4.1. *N,N*-Diethylaminomethylferrocene (**2**)

Yield: 67%, b.p. 150°C (0.9 mmHg), ^{1}H-NMR: ($CDCl_3$) δ, 0.92 (t, CH_3, 6H), 2.34 (q, CH_2, 4H), 3.36 (s, CH_2, 2H), 4.00 (s, Cp, 9H); MS (EI) m/e (fragment) intensity: 271 (M^+) 52, 199 (M^+-NEt_2) 100, 186

(Cp_2Fe) 61, 121 (CpFe) 71. Anal. Calc. for $C_{15}H_{21}NFe$; C, 66.44; H, 7.81; N, 5.16: Found: C, 66.65: H, 7.82, N, 5.05.

4.4.2. Morpholinomethylferrocene (3)

Yield: 79%, m.p. 68 °C, ^{1}H-NMR: ($CDCl_3$) δ, 2.28 (t, NCH_2, 4H), 3.25 (s, NCH_2, 2H), 3.52 (t, OCH_2, 4H), 4.02(s, Cp, 9H); MS (EI) m/e (fragment) intensity: 285 (M^+) 66, 199 (M^+-NC_4H_8O) 100, 121 (CpFe) 55. Anal. Calc. for $C_{15}H_{19}NOFe$; C, 63.18; H, 6.72; N, 4.91. Found: C, 63.10; H, 6.78; N, 5.00.

4.4.3. N,N-Diallylaminomethylferrocene (4)

Yield: 40%, b.p. 180°C (0.2 mmHg); ^{1}H-NMR: ($CDCl_3$) δ, 2.90 (d, NCH_2 $CHCH_2$, 4H), 3.33 (s, $CpCH_2N$, 2H), 3.95 (s, Cp, 9H), 5.00 (m, NCH_2CHCH_2, 4H), 5.65 (m, NCH_2CHCH_2, 2H); MS (EI) m/e (fragment) intensity: 295 (M^+) 96, 199 [M^+ − N(allyl)$_2$] 100.

Table 2
Selected bond distances (Å) and angles (°) for compounds **7** and **8**[a]

Compound **7**			
Bond distances			
Fe(1)–C(1)	2.015 (4)	Fe(1)–C(2)	2.019(4)
Fe(1)–C(6)	2.030(3)	Fe(1)–C(10)	2.034(3)
Fe(1)–C(7)	2.034(2)	C(7)–C(11)	1.497(4)
N(1)–C(11)	1.519(3)	N(1)–C(12)	1.507(3)
N(1)–C(15)	1.506(4)	C(12)–C(13)	1.486(4)
C(13)–C(14)	1.297(5)	C(15)–C(16)	1.491(4)
C(16)–C(17)	1.304(5)	C(7)–C(8)	1.421(4)
Bond angles			
C(1)–Fe(1)–C(6)	107.5(2)	C(7)–C(11)–N(1)	112.1(2)
C(11)–N(1)–C(12)	110.8(2)	C(12)–N(1)–C(15)	114.3(2)
C(11)–N(1)–C(15)	111.3(2)	N(1)–C(12)–C(13)	113.7(2)
C(12)–C(13)–C(14)	124.2(4)	N(1)–C(15)–C(16)	114.0(2)
C(15)–C(16)–C(17)	122.4(4)	C(6)–C(7)–C(8)	107.0(3)
C(6)–C(7)–C(11)	126.2(3)	C(8)–C(7)–C(11)	126.8(3)
Compound **8**			
Bond distances			
Cl(1)–P(1)	2.0219(10)	P(1)–N(1)	1.576 (3)
P(1)–N(1A)[b]	1.576(3)	P(1)–Cl(1A)[c]	2.0219(10)
N(1)–C(1)	1.373(4)	N(2)–C(1)	1.343(3)
N(2)–C(1A)[b]	1.343(3)	N(3)–C(1)	1.343(4)
N(3)–C(2)	1.454(4)	N(3)–C(3)	1.464(3)
Bond angles			
N(1)–P(1)–N(1A)[b]	117.3(2)	N(1)–P(1)–Cl(1)	109.85(5)
Cl(1)–P(1)–Cl(1A)[c]	98.49(7)	Cl(1)–N(1)–P(1)	113.6(2)
C(1)–N(2)–C(1A)[b]	119.6(3)	C(1)–N(3)–C(2)	120.8(2)
C(1)–N(3)–C(3)	121.1(3)	C(2)–N(3)–C(3)	118.1(2)
N(2)–C(1)–N(3)	117.3(3)	N(2)–C(1)–N(1)	127.9(3)
N(3)–C(1)–N(1)	114.8(2)		

[a] Symmetry transformations used to generate equivalent atoms.
[b] In **8**, $-x+1$, y, $-z+1/2$.
[c] In **8**, x, y, $-z+1/2$.

4.4.4. N-Methyl, N-benzylaminomethylferrocene (5)

Yield: 30%, b.p. 160°C (0.2 mmHg); ^{1}H-NMR: ($CDCl_3$) δ, 1.80 (s, NCH_3, 3H), 3.17 s, $PhCH_2$, 2H), 3.20 (s, $CpCH_2N$, 2H), 3.86 (m, Cp, 9H), 7.10 (d, Ph, 5H); MS (EI) m/e (fragment) intensity: 319 (M^+) 42, 243 ($M^+ - C_6H_4$) 85, 199 [M^+ − N(Me)(CH_2Ph)]100, 121 ($PhCH_2$(Me)NH) 81, 106 ($PhCH_2NH$) 29, 91 ($PhCH_2$) 67. Anal. Calc. for $C_{19}H_{21}NFe$: C, 71.49; H, 6.63; N, 4.39. Found: C, 71.58; H, 6.50; N, 4.35.

4.4.5. N-Methyl, N-cyclohexylaminomethyl ferrocene (6)

Yield 20%, b.p. 160°C (0.06 mmHg); ^{1}H-NMR: ($CDCl_3$) δ, 1.25–1.80 (m, C_6H_{11}, 11H), 2.15 (s, CH_3, 3H), 3.50 (s, CH_2, 2H), 4.15 (s, Cp, 9H); MS (EI) m/e (fragment) intensity: 311 (M^+) 27, 199 [M^+ − NMe(c-C_6H_{11})]100, 121 (CpFe) 67. Anal. Calc. for $C_{18}H_{25}NFe$: C, 69.45; H, 8.10; N, 4.50. Found: C, 69.60; H, 8.20; N, 4.36.

4.4.6. N,N-Diallylaminomethylferrocene hydrochloride (7)

The amine hydrochloride **7** was prepared by disslving about 0.40 g of the amine in 1 ml of CCl_4 and keeping the solution at 30°C for 24 h followed by cooling at 0°C overnight. Orange-red crystals of $FcCH_2NH(CH_2CH{=}CH_2)_2^+Cl^-$ **7** were found to form which were separated by filtration. M.p. 117–118°C, ^{1}H-NMR: ($CDCl_3$) δ, 3.45 (d, NCH_2 $CHCH_2$, 4H), 4.10–4.33 (m, Cp, 9H), 4.39 (s, $CpCH_2$, 2H), 5.57 (m, NCH_2CHCH_2, 4H), 6.27 (m, NCH_2CHCH_2, 2H). MS (EI) m/e (fragment) intensity: 295 (M^+ − HCl) 56, 234 ($FcCH_2Cl$) 26, 199 ($FcCH_2$) 100.

4.5. Reaction of 1 with $(ClCN)_2(Cl_2PN)$ in 4:1 molar ratio

$(ClCN)_2(Cl_2PN)$ (0.42 g, 1.76 mmol) was taken in a dry 50 ml round-bottomed flask under nitrogen and diethylether (20 ml) was added. The mixture was stirred well and **1** (1.71 g, 7.03 mmol) was added dropwise using a syringe. The flask was kept under nitrogen and stirred well for 5 h at room temperature (28°C). The mixture was filtered using a frit under nitrogen. The filtrate was evaporated to dryness and toluene (7 ml) was added. The toluene soluble portion was separated and kept at 0°C overnight to yield colorless crystals which were characterized as $[(Me_2N)CN]_2(Cl_2PN)$ **8** (3.83 g, 85%), m.p. 145°C, ^{1}H-NMR: ($CDCl_3$) δ, 3.10 (s, NCH_3, 6H); MS (EI) m/e (fragment) intensity; 255 (M^+) 24. Anal. Calc. for $C_6H_{12}N_5PCl_2$: C, 28.13; H, 4.72; N, 27.34. Found: C, 28.26; H, 4.55; N, 27.23.

The toluene insoluble part and the residue collected in the frit were found to be the same and was identified as $[CpFe(C_5H_4CH_2)]_2(CH_3)_2N^+Cl^-$ (1.20 g 76%); ^{1}H-NMR: ($CDCl_3$) δ, 2.98 (s, NCH_3, 6H), 4.35–4.55 (m,

Cp, C_5H_4, 18H), 4.78 (s, NCH_2, 4H); Anal. Calc. for $C_{24}H_{28}Fe_2NCl$; C, 60.35; H, 5.91; N, 2.93. Found C, 59.95; H, 5.89; N, 3.10.

4.6. Reaction of **2** with $(ClCN)_2(Cl_2PN)$ in 4:1 molar ratio

$(ClCN)_2(Cl_2PN)$ (0.62 g, 2.60 mmol) was reacted with **2** (2.82 g, 10.40 mmol) in toluene (15 ml) as described for **8**. The reaction mixture was filtered after 24 h and the filtrate was evaporated to dryness. Hexane (5 ml) was added and the clear solution was decanted, the solvent was reduced under vacuum and kept at 0°C to obtain colorless crystals of $(Et_2NCN)_2(Cl_2PN)$ **9** (0.66 g, 82%) m.p. 67°C: ^{1}H-NMR ($CDCl_3$) δ, 1.15 (t, CH_3, 12H), 3.51 (m, NCH_2, 8H); MS (EI) m/e (fragment) intensity; 311 (M^+) 60, 296 ($M^+ - CH_3$) 23, 282 ($M^+ - C_2H_5$) 100, 276 ($M^+ - Cl$) 30, 268 [$NPCl_2NCN(C_2H_5)_2NCNCH_3$] 27. The physical and spectral characteristics of this compound were found to agree with the reported data [8,26].

4.7. Reaction of **3** with $(ClCN)_2(Cl_2PN)$ in 4:1 molar ratio

To a stirred solution of $(ClCN)_2(Cl_2PN)$ (0.51 g, 2.14 mmol) in toluene was added a solution of **3** (2.44 g, 8.56 mmol) in 5 ml of toluene. The reddish brown mixture was refluxed for 24 h and filtered. The volume of the filtrate was reduced to 4 ml and kept at 0°C to get colorless crystals of $[(OC_4H_8N)CN]_2(Cl_2PN)$ **10** (0.62 g, 85%); m.p. 222°C, ^{1}H-NMR ($CDCl_3$) δ, 3.65 (m, NCH_2 and OCH_2): ^{31}P-NMR δ, 57.8 (s, PCl_2). MS (EI) m/e (fragment) intensity; 339 (M^+)100, 309 ($M^+ - CH_2O$) 65, 253 [$M^+ - N(CH_2CH_2)_2O$]24, 274 [$M^+ - (CH_2O + Cl)$] 43, 86 [$N(CH_2CH_2)_2O$] 80. The spectral data agreed with the reported values for the same in a mixture [8].

4.8. Reaction of **4** with $(ClCN)_2(Cl_2PN)$ in 4:1 molar ratio

$(ClCN)_2(Cl_2PN)$ (0.19 g, 0.80 mmol) in diethylether (20 ml) was reacted with **4** (0.94 g, 3.19 mmol) as described for the synthesis of **8** and to the ether soluble portion, hexane (5 ml) was added. The clear solution was decanted and hexane was evaporated. The residue was found to be unreacted **4** (0.50 g). Analysis of the reaction mixture by ^{1}H- and ^{31}P-NMR did not give any evidence for the dialkyalmino substituted carbaphosphazene product.

4.9. Reaction of **5** with $(ClCN)_2(Cl_2PN)$ in 4:1 molar ratio

N-Methyl, *N*-benzyl aminomethyl ferrocene (0.61 g, 1.82 mmol) was reacted with $(ClCN)_2(Cl_2PN)$ (0.11 g, 0.46 mmol) at room temperature for 5 h in diethylether (10 ml). The resultant mixture was worked up as described for compound **6**. The toluene soluble part was evaporated to dryness, redissolved in 2 ml of CCl_4 and kept at 0°C overnight to get a white solid. This was characterized as $[(Me)(PhCH_2)NCN]_2(Cl_2PN)$ **11** (0.17 g, 90%) m.p. 155°C; ^{1}H-NMR: ($CDCl_3$) δ, 3.10 (s, NCH_3, 6H), 4.67 (s, NCH_2, 4H), 7.17 (m, C_6H_5, 10H), MS(EI): m/e (fragment) intensity; 407 (M^+) 93, 392 ($M^+ - CH_3$) 51, 372 ($M^+ - Cl$) 11, 316 ($M^+ - CH_2Ph$) 18, 120 [$(CH_3)(CH_2Ph)N$] 33, 91 ($PhCH_2$) 100. Anal. Calc. for $C_{18}H_{20}N_5PCl_2$: C, 52.95; H, 4.94; N, 17.16. Found: C, 52.75; H, 5.01; N, 17.08.

4.10. Reaction of **6** with $(ClCN)_2(Cl_2PN)$ in 4:1 molar ratio

N-Methyl, *N*-cyclohexylaminomethyl ferrocene (1.89 g, 6.07 mmol) was reacted with $(ClCN)_2(Cl_2PN)$ (0.36 g, 1.51 mmol) in diethylether at room temperature for 24 h. The reaction mixture was filtered and the volatiles removed and the residue was purifed on a silicagel column using a mixture of chloroform and hexane (10:90) as eluant. The major fraction was found to be $[(c\text{-}C_6H_{11})MeNCN]_2(Cl_2PN)$ **12** (0.35 g, 60%) m.p. 52–54°C, ^{1}H-NMR: ($CDCl_3$) δ, 1.20–1.95 (m, CH_2, 20H), 3.00, 3.10 (NCH_3, 6H), 4.60 (m, br, NCH, 2H); MS (EI): m/e (fragment) intensity; 391 (M^+) 29, 376 ($M^+ - CH_3$)21, 307 ($M^+ - C_6H_{12}$) 57, 225 [$M^+ - 2(C_6H_{11})$]22, 196 [$(CN)_2NMe(NPCl_2]$ 100. Anal. Calc. for $C_{16}H_{28}N_5PCl_2$: C, 48.99; H, 7.19; N, 17.86. Found: C, 49.01; H, 7.10; N, 17.75.

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