



Dealkylation reactions of dialkylaminomethylferrocenes with cyclic chlorocarbaphosphazene, $(\text{ClCN})_2(\text{Cl}_2\text{PN})^\star$

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Received 2 September 1998

Abstract

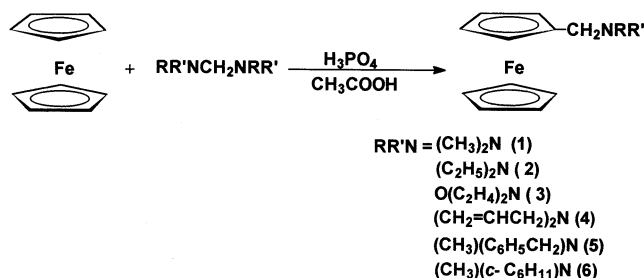
Dialkylaminomethylferrocenes, $\text{FcCH}_2\text{NRR}'$ ($\text{NRR}' = \text{NMe}_2$ (**1**), NEt_2 (**2**), $\text{N}(\text{CH}_2\text{CH}=\text{CH}_2)_2$ (**3**), $\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$ (**4**), $\text{N}(\text{Me})(\text{CH}_2\text{Ph})$ (**5**) and $\text{N}(\text{Me})(c\text{-C}_6\text{H}_{11})$ (**6**) (Fc = Ferrocenyl) were synthesized by the reaction of ferrocene with the corresponding diamines, $\text{RR}'\text{NCH}_2\text{NRR}'$. The identity of **3** was further confirmed by X-ray structural analysis of its hydrochloride, $\text{FcCH}_2\text{NH}(\text{CH}_2\text{CH}=\text{CH}_2)_2^+\text{Cl}^-$ (**7**). Reactions of compounds **1–6** were carried out with tetrachlorodiboraphosphazene, $(\text{ClCN})_2(\text{Cl}_2\text{PN})$ 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 $[(\text{RR}'\text{N})\text{CN}]_2(\text{Cl}_2\text{PN})$ **8–12**. The X-ray crystal structure of the substituted carbaphosphazene $(\text{Me}_2\text{NCN})_2(\text{Cl}_2\text{PN})$ **8** has also been determined. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Phosphazene; Ferrocene; Tetrachlorodiboraphosphazene; 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 sys-

tems 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 asymmetric transformations [6].



Scheme 1.

^{*} Dedicated to Professor H.W. Roesky on the occasion of his 63rd birthday.

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$$\begin{array}{c}
 \text{Cp} \\
 \text{Fe} \\
 \text{Cp}
 \end{array}
 \text{CH}_2\text{NRR}'
 \xrightarrow[\text{Et}_2\text{O}, 30^\circ\text{C}]{(\text{ClCN})_2(\text{C}_2\text{PN})}
 \begin{array}{c}
 \text{Cl} \quad \text{Cl} \\
 \diagup \quad \diagdown \\
 \text{N} \quad \text{P} \\
 \diagdown \quad \diagup \\
 \text{C} \quad \text{N} \\
 \diagup \quad \diagdown \\
 \text{RR}'\text{N} \quad \text{C} \quad \text{NRR}' \\
 \diagdown \quad \diagup \\
 \text{N} \quad \text{P} \\
 \diagup \quad \diagdown \\
 \text{Cl} \quad \text{Cl}
 \end{array}
 + [\text{Fc}(\text{CH}_2)_2\text{N}^+\text{RR}'\text{Cl}]^-$$

$\text{RR}'\text{N} = (\text{CH}_3)_2\text{N} \quad (8)$
 $(\text{C}_2\text{H}_5)_2\text{N} \quad (9)$
 $\text{O}(\text{C}_2\text{H}_4)_2\text{N} \quad (10)$
 $(\text{CH}_3)(\text{C}_6\text{H}_5\text{CH}_2)\text{N} \quad (11)$
 $(\text{CH}_3)(\text{C}-\text{C}_6\text{H}_{11})\text{N} \quad (12)$

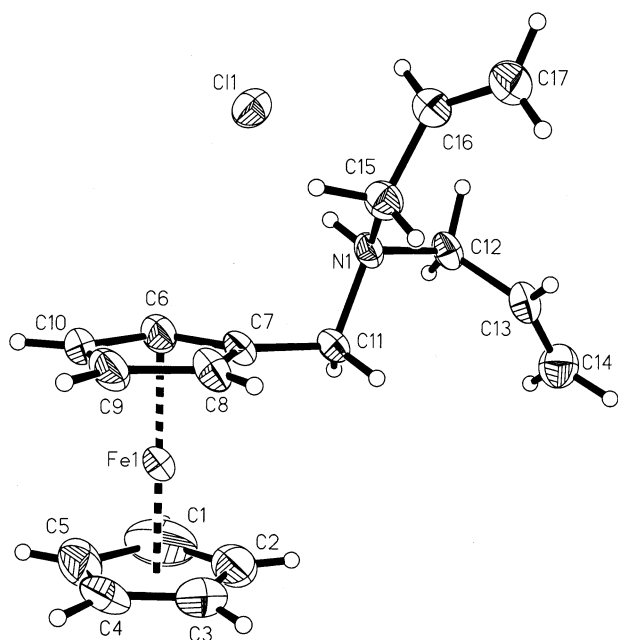


Fig. 1. Molecular structure of $\text{FcCH}_2\text{NH}(\text{CH}_2\text{CH}=\text{CH}_2)_2^+ \text{Cl}^-$.

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

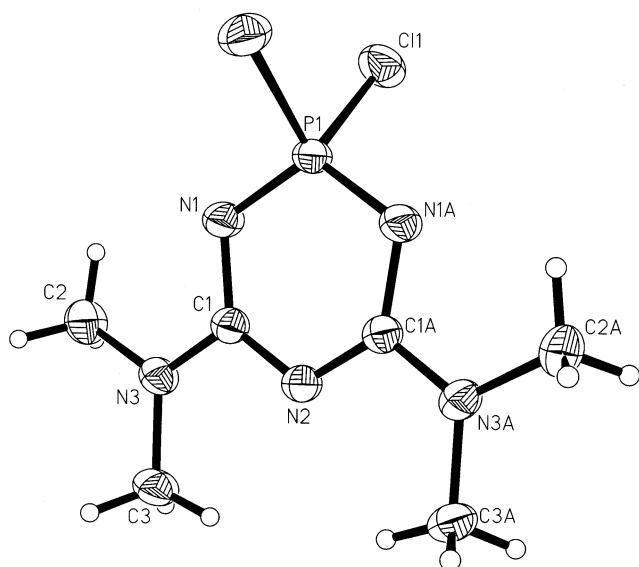


Fig. 2. Molecular structure of $[(\text{Me}_2\text{N})\text{CN}]_2(\text{Cl}_2\text{PN})$.

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 dicarbaphosphotriazene, $(\text{ClCN})_2(\text{Cl}_2\text{PN})$ 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. $(\text{ClCN})_2(\text{Cl}_2\text{PN})$ 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 ^1H - 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 ₆ H ₁₂ Cl ₂ N ₃ P
Formula weight	331.66	256.08
Colour	Reddish brown	Colourless
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Orthorhombic, <i>Cmcm</i>
Unit cell dimensions		
<i>a</i> (Å)	13.0025(4)	13.134
<i>b</i> (Å)	10.4735(2)	11.7123(3)
<i>c</i> (Å)	13.6074(4)	7.1763(2)
α (°)	90	90
β (°)	114.3070(10)	90
γ (°)	90	90
<i>V</i> (Å ³)	1688.81(8)	1103.96(4)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ^{−3})	1.304	1.541
<i>F</i> (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 ≤ <i>h</i> ≤ 15, −13 ≤ <i>k</i> ≤ 7, −17 ≤ <i>l</i> ≤ 18	−17 ≤ <i>h</i> ≤ 11, −15 ≤ <i>k</i> ≤ 15, −9 ≤ <i>l</i> ≤ 9
Reflections collected	10138	3503
Unique data (<i>R</i> _{int})	3970, (0.0368)	768, (0.0358)
Parameters refined	266	46
Final indices (2σ data), <i>R</i> ₁ (<i>wR</i> ₂)	0.0412(0.0834)	0.0383(0.1104)
All data, <i>R</i> ₁ (<i>wR</i> ₂) ^a	0.0979(0.1142)	0.0434(0.1143)
Goodness-of-fit, <i>S</i> (<i>F</i> 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), ¹H-NMR: (CDCl₃) δ , 0.92 (t, CH₃, 6H), 2.34 (q, CH₂, 4H), 3.36 (s, CH₂, 2H), 4.00 (s, Cp, 9H); MS (EI) *m/e* (fragment) intensity: 271 (M⁺) 52, 199 (M⁺-NEt₂) 100, 186

(Cp₂Fe) 61, 121 (CpFe) 71. Anal. Calc. for C₁₅H₂₁NFe; 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, ¹H-NMR: (CDCl₃) δ, 2.28 (t, NCH₂, 4H), 3.25 (s, NCH₂, 2H), 3.52 (t, OCH₂, 4H), 4.02 (s, Cp, 9H); MS (EI) *m/e* (fragment) intensity: 285 (M⁺) 66, 199 (M⁺–NC₄H₈O) 100, 121 (CpFe) 55. Anal. Calc. for C₁₅H₁₉NOFe; 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); ¹H-NMR: (CDCl₃) δ, 2.90 (d, NCH₂ CHCH₂, 4H), 3.33 (s, CpCH₂N, 2H), 3.95 (s, Cp, 9H), 5.00 (m, NCH₂CHCH₂, 4H), 5.65 (m, NCH₂CHCH₂, 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); ¹H-NMR: (CDCl₃) δ, 1.80 (s, NCH₃, 3H), 3.17 (s, PhCH₂, 2H), 3.20 (s, CpCH₂N, 2H), 3.86 (m, Cp, 9H), 7.10 (d, Ph, 5H); MS (EI) *m/e* (fragment) intensity: 319 (M⁺) 42, 243 (M⁺ – C₆H₄) 85, 199 [M⁺ – N(Me)(CH₂Ph)]100, 121 (PhCH₂(Me)NH) 81, 106 (PhCH₂NH) 29, 91 (PhCH₂) 67. Anal. Calc. for C₁₉H₂₁NFe: 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); ¹H-NMR: (CDCl₃) δ, 1.25–1.80 (m, C₆H₁₁, 11H), 2.15 (s, CH₃, 3H), 3.50 (s, CH₂, 2H), 4.15 (s, Cp, 9H); MS (EI) *m/e* (fragment) intensity: 311 (M⁺) 27, 199 [M⁺ – NMe(*c*-C₆H₁₁)]100, 121 (CpFe) 67. Anal. Calc. for C₁₈H₂₅NFe: 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 dissolving about 0.40 g of the amine in 1 ml of CCl₄ and keeping the solution at 30°C for 24 h followed by cooling at 0°C overnight. Orange-red crystals of FeCH₂NH(CH₂CH=CH₂)₂⁺Cl[–] **7** were found to form which were separated by filtration. M.p. 117–118°C, ¹H-NMR: (CDCl₃) δ, 3.45 (d, NCH₂ CHCH₂, 4H), 4.10–4.33 (m, Cp, 9H), 4.39 (s, CpCH₂, 2H), 5.57 (m, NCH₂CHCH₂, 4H), 6.27 (m, NCH₂CHCH₂, 2H). MS (EI) *m/e* (fragment) intensity: 295 (M⁺ – HCl) 56, 234 (FeCH₂Cl) 26, 199 (FeCH₂) 100.

4.5. Reaction of **1** with (ClCN)₂(Cl₂PN) in 4:1 molar ratio

(ClCN)₂(Cl₂PN) (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 [(Me₂N)CN]₂(Cl₂PN) **8** (3.83 g, 85%), m.p. 145°C, ¹H-NMR: (CDCl₃) δ, 3.10 (s, NCH₃, 6H); MS (EI) *m/e* (fragment) intensity; 255 (M⁺) 24. Anal. Calc. for C₆H₁₂N₅PCl₂: 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(C₅H₄CH₂)₂](CH₃)₂N⁺Cl[–] (1.20 g 76%); ¹H-NMR: (CDCl₃) δ, 2.98 (s, NCH₃, 6H), 4.35–4.55 (m,

Cp, C₅H₄, 18H), 4.78 (s, NCH₂, 4H); Anal. Calc. for C₂₄H₂₈Fe₂NCl; 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(Cl₂PN) in 4:1 molar ratio

(ClCN)₂(Cl₂PN) (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 (Et₂NCN)₂(Cl₂PN) **9** (0.66 g, 82%) m.p. 67°C: ¹H-NMR (CDCl₃) δ, 1.15 (t, CH₃, 12H), 3.51 (m, NCH₂, 8H); MS (EI) *m/e* (fragment) intensity; 311 (M⁺) 60, 296 (M⁺ – CH₃) 23, 282 (M⁺ – C₂H₅) 100, 276 (M⁺ – Cl) 30, 268 [NPCI₂NCN(C₂H₅)₂NCNCH₃] 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(Cl₂PN) in 4:1 molar ratio

To a stirred solution of (ClCN)₂(Cl₂PN) (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 [(OC₄H₈N)CN]₂(Cl₂PN) **10** (0.62 g, 85%) m.p. 222°C, ¹H-NMR (CDCl₃) δ, 3.65 (m, NCH₂ and OCH₂): ³¹P-NMR δ, 57.8 (s, PCl₂). MS (EI) *m/e* (fragment) intensity; 339 (M⁺) 100, 309 (M⁺ – CH₂O) 65, 253 [M⁺ – N(CH₂CH₂)₂O] 24, 274 [M⁺ – (CH₂O + Cl)] 43, 86 [N(CH₂CH₂)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(Cl₂PN) in 4:1 molar ratio

(ClCN)₂(Cl₂PN) (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 ¹H- and ³¹P-NMR did not give any evidence for the dialkylamino substituted carbaphosphazene product.

4.9. Reaction of **5** with (ClCN)₂(Cl₂PN) in 4:1 molar ratio

N-Methyl, *N*-benzyl aminomethyl ferrocene (0.61 g, 1.82 mmol) was reacted with (ClCN)₂(Cl₂PN) (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 CCl₄ and kept at 0°C overnight to get a white solid. This was characterized as [(Me)(PhCH₂)NCN]₂(Cl₂PN) **11** (0.17 g, 90%) m.p. 155°C; ¹H-NMR: (CDCl₃) δ, 3.10 (s, NCH₃, 6H), 4.67 (s, NCH₂, 4H), 7.17 (m, C₆H₅, 10H), MS(EI): *m/e* (fragment) intensity; 407 (M⁺) 93, 392 (M⁺ – CH₃) 51, 372 (M⁺ – Cl) 11, 316 (M⁺ – CH₂Ph) 18, 120 [(CH₃)(CH₂Ph)N] 33, 91 (PhCH₂) 100. Anal. Calc. for C₁₈H₂₀N₅PCl₂: 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(Cl₂PN) in 4:1 molar ratio

N-Methyl, *N*-cyclohexylaminomethyl ferrocene (1.89 g, 6.07 mmol) was reacted with (ClCN)₂(Cl₂PN) (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 purified on a silicagel column using a mixture of chloroform and hexane (10:90) as eluant. The major fraction was found to be [(*c*-C₆H₁₁)MeNCN]₂(Cl₂PN) **12** (0.35 g, 60%) m.p. 52–54°C, ¹H-NMR: (CDCl₃) δ, 1.20–1.95 (m, CH₂, 20H), 3.00, 3.10 (NCH₃, 6H), 4.60 (m, br, NCH, 2H); MS (EI): *m/e* (fragment) intensity; 391 (M⁺) 29, 376 (M⁺ – CH₃) 21, 307 (M⁺ – C₆H₁₂) 57, 225 [M⁺ – 2(C₆H₁₁)] 22, 196 [(CN)₂NMe(NPCL₂)] 100. Anal. Calc. for C₁₆H₂₈N₅PCl₂: C, 48.99; H, 7.19; N, 17.86. Found: C, 49.01; H, 7.10; N, 17.75.

Acknowledgements

We thank the Council of Scientific and Industrial Research (CSIR), India and the Department of Science and Technology (DST), India for financial assistance in the form of research grants. NDR thanks UGC India for a research fellowship.

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