Cyclophosphazene Hydrazides as Scaffolds for Multi-Ferrocenyl Assemblies: Synthesis, Structure, and Electrochemistry

Vadapalli Chandrasekhar,*,† Gurusamy Thangavelu Senthil Andavan,†
Selvarajan Nagendran,† Venkatasubbaiah Krishnan,†
Ramachandran Azhakar,† and Raymond J. Butcher‡

*Department of Chemistry, Indian Institute of Technology, Kanpur-208 016, India, and
Department of Chemistry, Howard University, Washington, D.C. 20059*

Received September 12, 2002

Reactions of *N*-methylhydrazine with chlorocyclophosphazenes, $N_3P_3Cl_6$ (**1**), $N_3P_3(OPh)Cl_5$ (**2**), *gem*-$N_3P_3Ph_2Cl_4$ (**3**), *spiro*-$N_3P_3(O_2C_{12}H_8)_2Cl_2$ (**4**), $N_3P_3(OPh)_5Cl$ (**5**), and diphenylphosphinic chloride, $Ph_2P(O)Cl$ (**6**), proceed in a regiospecific manner to afford the products $N_3P_3[N(Me)NH_2]_6$ (**1a**), $N_3P_3(OPh)[N(Me)NH_2]_5$ (**2a**), *gem*-$N_3P_3Ph_2[N(Me)NH_2]_4$ (**3a**), *spiro*-$N_3P_3(O_2C_{12}H_8)_2[N(Me)NH_2]_2$ (**4a**), $N_3P_3(OPh)_5[N(Me)NH_2]$ (**5a**), and $Ph_2P(O)[N(Me)NH_2]$ (**6a**). The terminal NH_2 groups in all of these compounds are reactive and have been used in the condensation reaction involving ferrrocene-2-carboxaldehyde to afford the corresponding hydrazones $N_3P_3[N(Me)N{=}CHC_5H_4FeC_5H_5]_6$ (**1b**), $N_3P_3(OPh)[N(Me)N{=}CHC_5H_4FeC_5H_5]_5$ (**2b**), *gem*-$N_3P_3Ph_2[N(Me)N{=}CHC_5H_4FeC_5H_5]_4$ (**3b**), *spiro*-$N_3P_3(O_2C_{12}H_8)_2[N(Me)N{=}CHC_5H_4FeC_5H_5]_2$ (**4b**), $N_3P_3(OPh)_5[N(Me)N{=}CHC_5H_4FeC_5H_5]$ (**5b**), and $Ph_2P(O)[N(Me)N{=}CHC_5H_4FeC_5H_5]$ (**6b**). The structures of **1**−**6**(**a**,**b**) have been determined by the use of multinuclear NMR, mass spectroscopy, and elemental analysis. X-ray crystal structures of **1b**, **3b**, **4b**, **5b**, and **6b** have also been determined, which confirm their molecular structures. Cyclic voltammetric experiments on the ferrocenyl derivatives **1b**−**6b** reveal an essentially reversible oxidation peak. Further, all of these are electrochemically quite robust and do not decompose on oxidation.

Introduction

In recent years there is a considerable amount of interest in the preparation of multi-metallocenyl assemblies in general and multi-ferrocenyl assemblies in particular.[1] This emanates from the objective of generating novel materials possessing interesting chemical, electric, optical, and magnetic properties. Thus, such compounds possessing electrochemically active groups can be viewed as excellent candidates for multielectron reservoir systems, electron-transfer mediators, redox-active materials for the modification of electrodes, ion sensors, or materials for electronic devices.[2] Among the various classes of compounds that have received attention, dendrimers containing a redox-active periphery of ferrocenes have been most actively investigated.[3] Astruc and co-workers have utilized a benzene type core prepared from (η^5-C_5H_5)Fe(η^6-2,3,5,6-Me_4−C_6H_2) to graft ferrocene moieties in the periphery.[4] Alternate approaches include using ferrocenyl silylation of triallyl benzene derivatives to prepare appropriate dendrons, which have been used in a convergent synthesis to assemble ferrocene dendrimers.[5] Other types of syntheses involving both convergent and divergent methods are known.[6] However, all of these examples involve multistep synthesis with the final yields of the products being low to moderate. Also X-ray crystal structures of these multi-ferrocene compounds are not known.

In an effort to find shorter synthetic methods for the preparation of multi-ferrocene assemblies in good yields, we have chosen *inorganic* alternatives. Chlorocyclophosphazenes such as $N_3P_3Cl_6$ with a reactive periphery and a robust framework provide an excellent choice for supporting redox-active substituents because these

---

† Indian Institute of Technology.

‡ Howard University.

(1) (a) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689. (b) Nguyen, P.; Elipe, P. G.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515.

(2) (a) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, 100, 4248. (b) Astruc, D. *New. J. Chem.* **1992**, *16*, 305. (c) Astruc, D. *Top. Curr. Chem.* **1991**, *160*, 47. (d) Hill, H. A. U.; Page D. J.; Walton, N. J. *J. Electroanal. Chem.* **1987**, *217*, 141. (e) Valério, C.; Fillaut, J.-L.; Ruiz, J.; Guittard, J.; Blais J.-C.; Astruc, D. *J. Am. Chem. Soc.* **1997**, *119*, 2588.

(3) (a) Bard, A. J. *Nature* **1995**, *374*, 13. (b) Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71. (c) Astruc, D. *Acc. Chem. Res.* **2000**, *33*, 287. (d) Nlate, S.; Ruiz, J.; Sartor, V.; Navarro, R.; Blais J.-C.; Astruc, D. *Chem. Eur. J.* **2000**, *6*, 2544. (e) Takada, K.; Díaz, D. J.; Abruña, H. D.; Cuadrado, I.; Casado, C.; Alonso, B.; Morán, M.; Losada, J. *J. Am. Chem. Soc.* **1997**, *119*, 10763.

(4) Valério, C.; Alonso, E.; Ruiz, J.; Blais, J.-C.; Astruc, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 1747.

(5) Nlate, S.; Ruiz, J.; Blais J−C.; Astruc, D. *Chem. Commun.* **2000**, 417.

(6) (a) Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Lobete, F.; García, B.; Ibisate M.; Losada, J. *Organometallics* **1996**, *15*, 5278. (b) Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J.; Belsky, V. *J. Am. Chem. Soc.* **1997**, *119*, 7613. (c) Jutzi, P.; Batz, C.; Neumann. B.; Stammler, H.-G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2118. (d) Turrin, C. O.; Chiffre, J.; Daran, J. C.; de Montauzon, D.; Caminade, A.-M.; Manoury, E.; Balavoine G.; Majoral, J. P. *Tetrahedron* **2001**, *57*, 2521. (e) Turrin, C. O.; Chiffre, J.; de Montauzon, D.; Daran, J. C.; Caminade, A.-M.; Manoury, E.; Balavoine G.; Majoral, J. P. *Macormolecules* **2000**, *33*, 7328.

10.1021/om020760d CCC: $25.00
Publication on Web 02/05/2003

rings are multifunctional and are stable to redox processes. A second advantage of using cyclophosphazenes as supports for multi-ferrocene assemblies is that in most instances the chemistry of these ring systems can be readily extended to the polymeric analogues.[7] However, directly using $N_3P_3Cl_6$ for building fully substituted ferrocenyl-containing compounds has not met with success. Previous efforts at introducing the metallocenyl substituent on the cyclophosphazene ring have involved the reaction of the corresponding lithium salts with fluoro- or chlorocyclophosphazenes.[8] In both instances the reactions are complex, and although interesting products have been isolated, fully substituted derivatives have not been obtained. Recently Allen and co-workers have reported the reactions of *N*-(ferrocenylmethyl)-*N*-methyl amine, 1-ferrocenyl-2-propanol, 2-ferrocenylethanol, or ferrocenylmethanol with $N_3P_3Cl_6$.[9,10] In the reactions of *N*-(ferrocenylmethyl)-*N*-methyl amine substitution of only three chlorines has been achieved with the yields of the bis- and tris-substituted products being very low.[9] In the reactions with ferrocenyl methanol degraded products were observed, while products up to bis substitution were observed in reactions with ferrocenyl ethanol.[10] Togni and co-workers have reported a convergent methodology for preparing phosphine-containing chiral ferrocene-substituted cyclotetraphosphazenes.[11] However, this compound has not been characterized by X-ray crystallography and its electrochemical behavior also has not been reported.

We report an alternate and a more convenient synthetic strategy of using cyclophosphazenes as scaffolds for supporting ferrocenes. Our method consists of first converting chlorocyclotriphosphazenes (**1**−**5**) to the corresponding cyclotriphosphazene hydrazides which contain reactive $-NH_2$ groups (**1a**−**5a**). As a model for the multifunctional cyclophosphazenes we have utilized the monofunctional acyclic phosphorus hydrazide $Ph_2P(O)[N(Me)NH_2]$ (**6a**). These hydrazides are amenable to further reaction with ferrocene carboxaldehyde to afford the corresponding hydrazones (**1b**−**6b**). This strategy allowed us to even synthesize a cyclophosphazene (**1b**) containing six ferrocene units. The ferrocenyl derivatives **1b**−**6b** are electrochemically robust. All of these compounds have been characterized by various spectroscopic techniques. Further, compounds **1b**, **3b**, **4b**, **5b**, and **6b** have also been characterized by X-ray crystallography. These aspects are discussed in the following account.

Experimental Section

Reagents and General Procedures. All operations have been carried out in an inert atmosphere of nitrogen or argon. The solvents and general chemicals were purified and dried according to standard procedures. $Ph_2P(O)Cl$ (**6**) (Lancaster, U.K.), 2,2′-dihydroxybiphenyl (Fluka), and ferrocene (Aldrich) were used as obtained. *N*-Methylhydrazine was obtained as a gift from the Vikram Sarabhai Space Research Centre, Thiruvananthapuram, India. $N_3P_3Cl_6$ (Aldrich) was recrystallized from *n*-hexane before use. Ferrocene carboxaldehyde,[12] $N_3P_3[N(Me)NH_2]_6$ (**1a**),[13] $N_3P_3(OPh)Cl_5$ (**2**),[14] *gem*-$N_3P_3Ph_2Cl_4$ (**3**),[15] *spiro*-$N_3P_3(O_2C_{12}H_8)_2Cl_2$ (**4**),[16] $N_3P_3(OPh)_5Cl$ (**5**),[17] and $Ph_2P(O)[N(Me)NH_2]$ (**6a**)[18] were prepared according to literature procedures.

Instrumentation. Infrared spectra were recorded in Nujol mull or as KBr pellets on a FT-IR Bruker-Vector model. Electronic spectra were recorded on a Perkin-Elmer-Lambda 20 UV−vis spectrometer and on a Shimadzu UV-160 spectrometer using dichloromethane as the solvent. Cyclic voltammetric experiments were carried out on a EG&G Princeton Applied Research model 273A polarographic analyzer utilizing a three-electrode configuration of a platinum working electrode, a commercially available saturated calomel electrode (SCE) as the reference electrode, and a platinum mesh electrode. Half-wave potentials were measured as the average of the cathodic and anodic peak potentials. The voltammograms were recorded in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte and the potential was scanned from −1.5 to +1.5 V at various scan rates. The data obtained from the optical spectra and the cyclic voltammetric experiments were analyzed by the Origin Professional 6.0 program. Elemental analyses of the compounds were obtained from Thermoquest CE instruments CHNS-O, EA/110 model. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV, and the spectra were recorded at room temperature. EI mass spectra were obtained on a JEOL D-300 spectrometer. The $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra were recorded in $CDCl_3$ solutions on a JEOL JNM LAMBDA 400 model spectrometer. Chemical shifts are reported in ppm with respect to TMS (internal reference) for ^{13}C and ^1H chemical shifts and 85% H_3PO_4 (external reference) for the ^{31}P chemical shifts.

X-ray Structure Determination of 1b, 3b, 4b, 5b, and 6b. The crystal data for **1b**, **3b**, and **4b** are given in Table 1 and for **5b** and **6b** in Table 2, respectively. X-ray quality crystals for compound **1b** were obtained by a slow evaporation of a 1:1 dichloromethane and benzene solution of it, and those of **3b** were obtained by a slow evaporation of a solution of it in ethyl acetate and hexane (30:70). In the case of **4b**, **5b**, and **6b** suitable crystals were obtained by vapor diffusing *n*-hexane into their chloroform solutions at room temperature. X-ray diffraction data for **3b** and **6b** were collected using an Enraf Nonius FR590 CAD-4 diffractometer. The structures were solved using WINGX 1.64.03a, a collective crystallographic package.[19] All the hydrogen atoms were included in idealized positions, and a riding model was used. The data for the compounds **1b** and **4b** were collected on a Siemens P4S diffractometer. All structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods

---

(7) Saraceno, R. A.; Riding, G. H.; Allcock H. R.; Ewing, A. G. *J. Am. Chem. Soc.* **1998**, *110*, 7254.

(8) Allcock, H. R.; Desorcie, J.; Riding, G. H. *Polyhedron* **1987**, *6*, 164.

(9) Myer, C. N.; Allen, C. W. *Inorg. Chem.* **2002**, *41*, 60.

(10) Nataro, C.; Myer, C. N.; Cleaver, W. M.; Allen, C. W. *J. Organomet. Chem.* **2001**, *637*−*639*, 284.

(11) Schneider, R.; Köllner, C.; Weber I.; Togni, A. *Chem. Commun.* **1999**, 2415.

(12) Sato, M.; Kono, H.; Shiga, M.; Motoyama, I.; Hata, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 252.

(13) Galliot, C.; Caminade, A.-M.; Dahan, F.; Majoral, J. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1477.

(14) Dell, B.; Fitzsimmons, B. W.; Shaw, R. A. *J. Chem. Soc.* **1965**, 4070.

(15) McBee, E. T.; Okuhara, K.; Morton, C. J. *Inorg. Chem.* **1966**, *5*, 450.

(16) Carriedo, G. A.; Fernander-Catuxo, L.; Garcia Alonso, F. J.; Gomex-Elipe, P.; Gonzealez, P. A. *Macromolecules* **1996**, *29*, 5320.

(17) Selvaraj, I. I.; Reddy, D.; Chandrasekhar, V.; Chandrasekar, T. K. *Heterocycles* **1991**, *32*, 703.

(18) Majoral, J. P.; Kraemer, R.; Navech, J.; Mathis, F. *Tetrahedron* **1976**, *32*, 2633.

(19) (a) Farrugia, L. J. WinGX, Version 1.64.03a; An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-Crystal X-Ray Diffraction Data; Department of Chemistry, University of Glasgow, 1997−2002. (b) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

Table 1. Crystal and Structure Refinement Data for Compounds 1b, 3b, and 4b

parameter	**1b**	**3b**	**4b**
empirical formula	$C_{79}H_{88}Cl_3Fe_6N_{15}OP_3$	$C_{60}H_{62}Fe_4N_{11}P_3$	$C_{49}H_{43}Cl_3Fe_2N_7O_4P_3$
fw	1798	1253.52	1104.86
temperature, K	293(2)	293(2)	293(2)
wavelength, Å	0.71069	0.71069	0.71073
cryst syst	monoclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
unit cell dimens	$a = 24.028(14)$, Å $\alpha = 90.000(9)°$	a = 13.006(5) Å, $\alpha = 112.821(5)°$	$a = 11.222(16)$ Å, $\alpha = 101.260(10)°$
	b =16.329(8) Å, $\beta = 113.04(14)°$	b = 13.888(5) Å, $\beta = 95.174(5)°$	$b = 14.214(2)$ Å, $\beta = 108.595(12)°$
	$c = 22.363(5)$ Å, $\gamma = 90.000(13)°$	c = 17.159(5) Å, $\gamma = 92.084(5)°$	$c = 17.108(5)$ Å, $\gamma = 101.877(13)°$
volume, Å^3, Z	8074(8), 4	2836.5(17), 2	2429.0(6), 2
density(calcd), Mg/m^3	1.479	1.468	1.511
abs coeff, mm^{-1}	1.263	1.138	0.914
F(000)	3708	1296	1132
cryst size, mm	0.32 × 0.47 × 0.43	0.40 × 0.32 × 0.28	0.06 × 0.42 × 0.29
θ range for data collection, deg	2.49 to 25.00	1.61 to 22.48	2.14 to 25.00
limiting indices	$0 \le h \le 23$, $-19 \le k \le 0$, $-26 \le l \le 24$	$0 \le h \le 13$, $-14 \le k \le 14$, $-18 \le l \le 18$	$-13 \le h \le 0$, $-15 \le k \le 16$, $-19 \le l \le 20$
no. of reflns collected	6865	7760	8924
no. of ind reflns	6687 ($R_{int} = 0.1346$)	7369 ($R_{int} = 0.0398$)	8471 ($R_{int} = 0.0360$)
completeness to θ	93.9	99.8	98.9
refinement method	full-matrix least-squares on F^2	full-matrix least-squares of F^2	full-matrix least-squares on F^2
no. of data/restraints/params	6687/0/438	7369/ 0/ 707	8471/0/659
goodness-of-fit on F^2	1.004	0.923	1.048
final R indices [$I > 2\sigma(I)$]	R1 = 0.0938, wR2 = 0.2104	R1 = 0.0507, wR2 = 0.1259	R1 = 0.0610, wR2 = 0.1284
R indices (all data)	R1 = 0.2309, wR2 = 0.2849	R1 = 0.1498, wR2 = 0.1755	R1 = 0.1569, wR2 = 0.1870
largest diff peak and hole, e Å^{-3}	0.753 and −0.528	0.343 and −0.388	0.508 and −0.491

Table 2. Crystal and Structure Refinement Data for Compounds 5b and 6b

parameter	**5b**	**6b**
empirical formula	$C_{42}H_{38}FeN_5O_5P_3$	$C_{24}H_{23}FeN_2OP$
fw	841.53	442.26
temperature, K	93(2)	293(2)
wavelength, Å	0.71073	0.71069
cryst syst	monoclinic	monoclinic
space group	$P2(1)/c$	$P21/c$
unit cell dimens	$a = 10.9501(12)$ Å, $\alpha = 90.000$ °	$a = 11.911$ (5) Å, $\alpha = 90.000(9)°$
	$b = 16.4398(18)$ Å, $\beta = 92.249(2)°$	$b = 8.250(18)$ Å, $\beta = 96.388(14)°$
	$c = 21.431(12)$ Å, $\gamma = 90.000°$	$c = 21.789(5)$ Å, $\gamma = 90.000(13)°$
volume, Å^3, Z	3854.9(7), 4	2127.8(16), 4
density(calcd), Mg/m^3	1.450	1.381
abs coeff, mm^{-1}	0.569	0.801
F(000)	1744	920
cryst size, mm	0.50 × 0.60 × 0.60	0.40 × 0.38 × 0.22
θ range for data collection, deg	1.90 to 24.88	1.72 to 22.45
limiting indices	$-12 \le h \le 12$, $-19 \le k \le 19$, $-25 \le l \le 25$	$-5 \le h \le 12$, $-8 \le k \le 1$, $-23 \le l \le 23$
no. of reflns collected	22 256	2999
no. of ind reflns	6651 ($R_{int} = 0.0737$)	2746 ($R_{int} = 0.0085$)
completeness to θ	99.4%	99.3%
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	6651/0/544	2746/0/354
goodness-of-fit on F^2	1.031	1.147
final R indices [$I>2\sigma(I)$]	R1 = 0.0461, wR2 = 0.1219	R1 = 0.0470, wR2 = 0.1244
R indices (all data)	R1 = 0.0584, wR2 = 0.1310	R1 = 0.0637, wR2 = 0.1453
largest diff peak and hole, e Å^{-3}	0.721 and −0.688	0.531 and −0.514

against F^2 (SHELXL-97).[20] Hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters.

Synthesis of Cyclophosphazene Hydrazides. $N_3P_3(OPh)[N(Me)NH_2]_5$ (2a). To a stirred solution of *N*-methylhydrazine (1.79 g, 39.0 mmol) in chloroform (30 mL) at 0 °C was added dropwise a solution of $N_3P_3Cl_5(OPh)$ (1.05 g, 2.6 mmol) taken in choloroform (30 mL). After the addition was complete the reaction mixture was allowed to come to room temperature and was further stirred for a period of 36 h. At this stage the reaction was stopped and the reaction mixture was filtered to remove *N*-methylhydrazine hydrochloride. Removal of solvent from the filtrate in vacuo afforded a waxy solid. This was chromatographed over a basic alumina column using methanol−ethyl acetate (10:90) as the eluant to afford pure **2a** as a waxy solid. Yield: 0.92 g, 78.3%. ^{1}H NMR: 2.41, 2.75, 2.93 (d, 15H, N(CH_3), $^3J(^1H-^{31}P)$ = 10.5, 10.7, and 11.5 Hz, respectively); 3.07 (s, 10H, −NH_2), 7.26−7.53 (m, 5H, aromatic). ^{31}P NMR: 29.3 (d, P(N(Me)−)$_2$), 22.3 (t, P(N(Me)−)(OPh)), ^2J(P−N−P) = 40.4 Hz. FAB-MS: 453 (M$^+$). Anal. Calcd for $C_{11}H_{30}N_{13}OP_3$: C, 29.14; H, 6.67; N, 40.16. Found: C, 28.95; H, 6.39; N, 39.93.

***gem*-$N_3P_3Ph_2[N(Me)NH_2]_4$ (3a).** The preparation of **3a** was done in the same manner as that of **2a.** The quantities of the reactants involved are *gem*-$N_3P_3Cl_4Ph_2$ (**3**) (5.00 g, 11.6 mmol) and *N*-methylhydrazine (4.81 g, 105.0 mmol). A solid obtained at the end of workup was dissolved in hot benzene (75 mL) and was allowed to cool to 25 °C. To this *n*-hexane (120 mL)

---

(20) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Analysis (release 97-2); University of Göttingen: Göttingen, Germany, 1998.

was added and the solution was kept at 5 °C to obtain a white solid. Yield: 4.33 g, 79.5%. Mp: 112 °C. ^{1}H NMR: 2.80 (d, 12 H, $-$N(C*H*$_3$); $^3J(^1\text{H}-^{31}\text{P}) = 10.8$ Hz), 3.57 (s, 8H, $-$N*H*$_2$), 7.35$-$7.86 (m, 10 H, aromatic). ^{31}P NMR: 28.1 (d, P(N(Me)$-$)$_2$), 20.2 (t, P(Ph)$_2$), ^2J(P$-$N$-$P) = 17.8 Hz. EI-MS: 469 (M$^+$). Anal. Calcd for $C_{16}H_{30}N_{11}P_3$: C, 40.94; H, 6.44; N, 32.82. Found: C, 40.83; H, 6.34; N, 32.76.

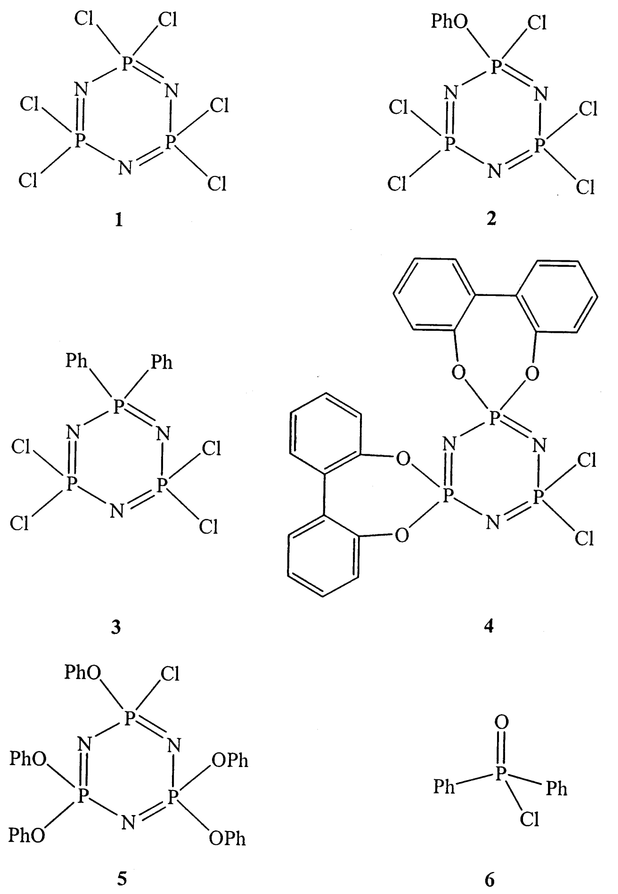
$N_3P_3(O_2C_{12}H_8)_2[N(Me)NH_2]_2$ (4a). The preparation of **4a** was done in the same manner as that of **2a** except that there was no need for a chromatographic separation. The quantities involved were $N_3P_3Cl_2(O_2C_{12}H_8)_2$ (**4**) (6.00 g, 10. 4 mmol) and *N*-methylhydrazine (2.40 g, 52.1 mmol). A solid obtained at the end of workup was dissolved in hot acetonitrile (125 mL) and kept at 5 °C to afford a crystalline product (6.19 g, 88.8%). Mp: 276 °C. ^{1}H NMR: 2.98 (d, 6H, $-$N(C*H*$_3$); $^3J(^1\text{H}-^{31}\text{P}) =$ 11.0 Hz), 3.07 (s, 4H, $-$N*H*$_2$), 7.26$-$7.53 (m, 16 H, aromatic). ^{31}P NMR: 29.3 (t, P(N(Me)$-$)$_2$), 26.6 (d, P($O_2C_{12}H_8$)$_2$), ^2J(P$-$N$-$P) = 58.2 Hz. FAB-MS: 548 (M$^+$ $-$ N(Me)NH$_2$). Anal. Calcd for $C_{26}H_{26}N_7O_4P_3$: C, 52.62; H, 4.42; N, 16.52. Found: C, 52.31; H, 4.42; N, 16.44.

$N_3P_3(OPh)_5[N(Me)NH_2]$ (5a). To a stirred solution of *N*-methylhydrazine (0.77 g, 16.6 mmol) in chloroform (60 mL) at 0 °C was added dropwise a solution of $N_3P_3Cl(OPh)_5$ (4.24 g, 6.67 mmol) taken in choloroform (60 mL). After the addition was complete the reaction mixture was allowed to come to room temperature and was further stirred for a period of 12 h. At this stage the reaction was stopped and filtered to remove the hydrochloride of *N*-methylhydrazine. Removal of the volatiles from the filtrate in vacuo afforded an oil, which was chromatographed over a basic alumina column (eluant: ethyl acetate$-$*n*-hexane, 12:88) to afford pure **5a** as a yellow oil (1.02 g, 80%). ^{1}H NMR: 2.54 (d, 3H, $-$N(C*H*$_3$); $^3J(^1\text{H}-^{31}\text{P}) = 11.\ 5$ Hz), 3. 07 (s, 2H, $-$N*H*$_2$), 6.91$-$7.27 (m, 25H, aromatic). ^{31}P NMR: 20.7 (t, P(OPh)(N(Me)$-$)), 9.4 (d, P(OPh)$_2$), ^2J(P$-$N$-$P) = 71.2 Hz. FAB-MS: 646 (M$^+$). Anal. Calcd for $C_{31}H_{30}N_5O_5P_3$: C, 57. 68; H, 4.68; N, 10.85. Found: C, 57.02; H, 4.36; N, 10.29.

Condensation of the Hydrazides with Ferrocene Carboxaldehyde. $N_3P_3[N(Me)N{=}CHC_5H_4FeC_5H_5]_6$ (1b). To a solution of **1a** (0.41 g, 1.00 mmol) in methanol (60 mL) was added dropwise over a period of 30 min a solution of ferrocene-2-carboxaldehyde (1.35 g, 6.31 mmol) in methanol (60 mL). The reaction mixture was stirred at 25 °C for 12 h. Removal of the solvent in vacuo afforded a solid. This was purified over a basic alumina column. Elution with ethyl acetate$-$*n*-hexane (5:95) removed the unreacted ferrocene-2-carboxaldehyde. Pure **1b** was obtained by elution with ethyl acetate$-$*n*-hexane (40:60). Yield: 1.22 g, 77%. Mp: 104 °C. UV$-$visible (CH_2Cl_2): $\lambda_{\max}$ (ϵ), 442 nm (30 845 mol^{-1} cm^{-1}). ^{1}H NMR: 3.30 (d, 18H, $-$N(C*H*$_3$); $^3J(^1\text{H}-^{31}\text{P}) = 8.6$ Hz), 4.03 (s, 30H, ferrocene), 4.22 (s, 12H, ferrocene), 4.79 (s, 12H, ferrocene), 7.36 (s, 6H, imino). ^{31}P NMR: 16.9 (s). FAB-MS: 1581 (M$^+$). Anal. Calcd for $C_{72}H_{78}N_{15}P_3Fe_6$: C, 54.68; H, 4.97; N, 13.29. Found: C, 53.81; H, 4.67; N, 13.07.

$N_3P_3(OPh)[N(Me)N{=}CHC_5H_4FeC_5H_5]_5$ (2b). Compound **2b** was prepared by adopting a similar protocol as used for **1b** except that ethanol was used as the solvent. The quantities of the reactants are **2a** (0.45 g, 1.00 mmol); ferrocene-2-carboxaldehyde (1.12 g, 5.25 mmol). The workup of the reaction afforded a solid. This was purified over a basic alumina column. After eluting unreacted ferrocene-2-carboxaldehyde using a mixture of ethyl acetate$-$*n*-hexane (5:95) the pure fraction of **2b** was eluted with ethyl acetate$-$*n*-hexane (40:60). The total amount of **2b** obtained was 1.05 g, 73.2%. Mp: 89 °C. UV$-$visible (CH_2Cl_2): $\lambda_{\max}$ (ϵ), 444 nm (30 575 mol^{-1} cm^{-1}). ^{1}H NMR: 3.09, 3.26, and 3.27 (d, 15H, $-$N(C*H*$_3$); $^3J(^1\text{H}-^{31}\text{P})$ = 8.8, 8.5, and 8.8 Hz, respectively); 4.00 (s, 25H, ferrocene), 4.36 (s, 10H, ferrocene), 4.52 (s, 10H, ferrocene), 7.16 (s, 5H, imino), 7.18$-$7.36 (m, 5H, aromatic). ^{31}P NMR: 17.5 (d, P(N(Me)$-$)$_2$), 13.8 (t, P(OPh)(N(Me)$-$)), ^2J(P$-$N$-$P) = 57.7 Hz. FAB-MS: 1434 (M$^+$). Anal. Calcd for $C_{66}H_{70}N_{13}OP_3Fe_5$: C, 55.30; H, 4.92; N, 12.70. Found: C, 54.66; H, 4.41; N, 12.37.

Chart 1

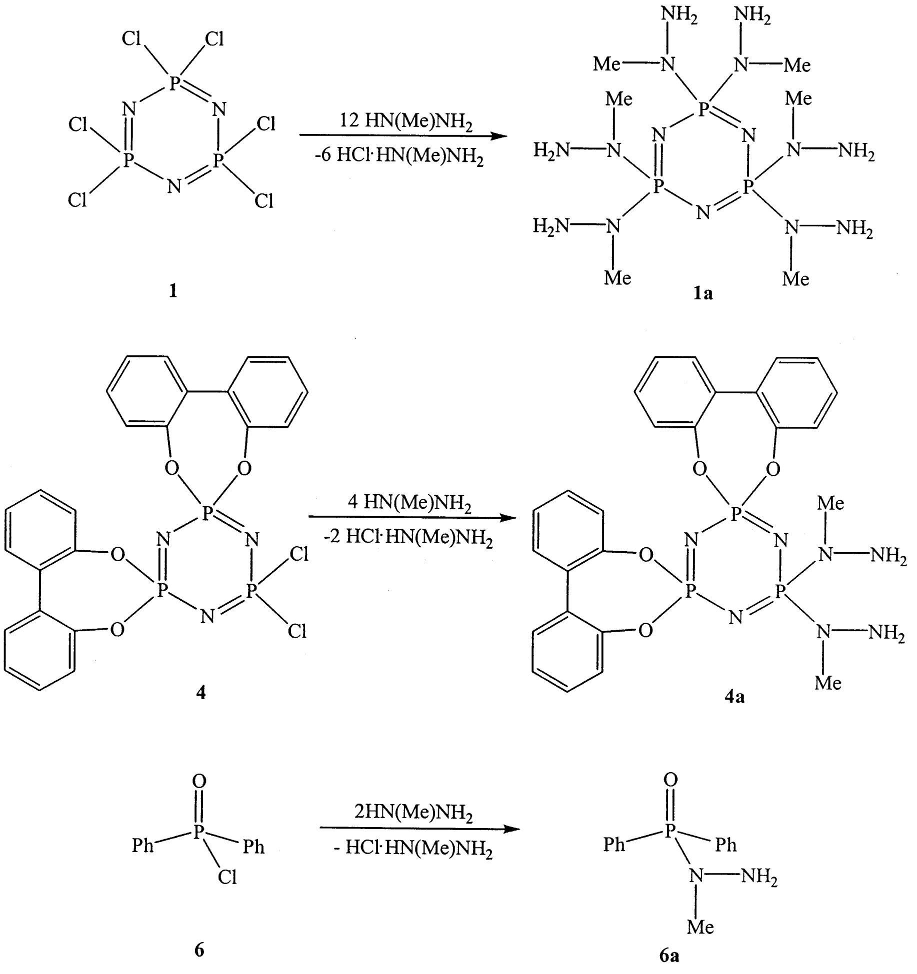


$N_3P_3Ph_2[N(Me)N{=}CHC_5H_4FeC_5H_5]_4$ (3b). Compound **3b** was prepared by adopting a procedure analogous to that used for preparing **1b**. The quantities of the reactants and product are **3a** (0.47 g, 1.0 mmol); ferrocene-2-caboxaldehyde (0.90 g, 4.20 mmol). Yield: 0.99 g, 79%. Mp: 114 °C. UV$-$visible (CH_2Cl_2): $\lambda_{\max}$ (ϵ), 448 nm (19 795 mol^{-1} cm^{-1}). ^{1}H NMR: 3.18 (d, 12H, $-$N(C*H*$_3$); $^3J(^1\text{H}-^{31}\text{P}) = 8.8$ Hz), 4.07 (s, 20H, ferrocene), 4.20 (s, 8H, ferrocene), 4.54 (s, 8H, ferrocene), 7.34 (s, 4H, imino), 7.35$-$8.01 (m, 10H, aromatic). ^{31}P NMR ($CDCl_3$): 15.1 (d, P(N(Me)$-$)$_2$), 20.2 (t, PPh$_2$), ^2J(P$-$N$-$P) = 24.2 Hz. FAB-MS: 1253 (M$^+$). Anal. Calcd for $C_{60}H_{62}N_{11}P_3Fe_4$: C, 57.49; H, 4.99; N, 12.29. Found: C, 57.12; H, 4.89; N, 12.16.

$N_3P_3(O_2C_{12}H_8)_2[N(Me)N{=}CHC_5H_4FeC_5H_5]_2$ (4b). This compound was prepared in the same manner as described for **1b** except that one of the reactants, **4a**, was taken in dichloromethane (50 mL), while ferrocene-2-carboxaldehyde was taken in ethanol. The quantities of the reactants are **4a** (2.38 g, 4.00 mmol) and ferrocene-2-carboxaldehyde (1.75 g, 8.2 mmol). The product **4b** precipitates from the reaction medium and is purified by washing with ethanol (2 × 25 mL) (6.19 g, 88.8%). Mp: 260 °C. UV$-$visible (CH_2Cl_2): $\lambda_{\max}$ (ϵ) 449 nm (11 995 mol^{-1} cm^{-1}). ^{1}H NMR: 3.29 (d, 6H, $-$N(C*H*$_3$); $^3J(^1\text{H}-^{31}\text{P}) = 8.8$ Hz), 4.07 (s, 10H, ferrocene), 4.22 (s, 4H, ferrocene), 4.57 (s, 4H, ferrocene), 7.28$-$7.53 (m, 8H, aromatic and imino). ^{31}P NMR: 18.8 (t, P(N(Me)$-$)$_2$), 26.2 (d, P($O_2C_{12}H_8$)$_2$), ^2J(P$-$N$-$P) = 71.2 Hz. FAB-MS: 985 (M$^+$). Anal. Calcd for $C_{48}H_{42}N_7O_4P_3Fe_2$: C, 58.50; H, 4.30; N, 9.95. Found: C, 57.97; H, 4.11; N, 9.49.

$N_3P_3(OPh)_5[N(Me)N{=}CHC_5H_4FeC_5H_5]$ (5b). To a solution of **5a** (1.29 g, 2.0 mmol) in methanol (35 mL) was added dropwise ferrocene-2-carboxaldehyde (0.45 g, 2.1 mmol) in methanol (40 mL) at 25 °C and stirred for 8 h. Removal of

Scheme 1



solvent from the reaction mixture in vacuo afforded an oil. This was chromatographed over a basic alumina column. Ethyl acetate–*n*-hexane (5:95) was used to elute unreacted ferrocene-2-carboxaldehyde, while elution with ethyl acetate–hexane (25:75) afforded the title compound in a pure state. This was recrystallized from a mixture of dichloromethane and *n*-hexane (1:2) at 5 °C to afford a shiny crystalline compound (1.35 g, 80%). Mp: 94 °C. UV–visible (CH_2Cl_2): λ_{max} (ϵ), 448 nm (4770 mol^{-1} cm^{-1}). ^1H NMR: 2.54 (d, 3H, $-N(CH_3)$; $^3J(^1H-^{31}P) = 9.5$ Hz), 3.91 (s, 5H, ferrocene), 4.07 (s, 2H, ferrocene), 4.10 (s, 2H, ferrocene), 7.12 (s, 1H, imino), 6.85–7.08 (m, 25 H, aromatic). ^{31}P NMR: 14.1 (t, $P(OPh)(N(Me)-)_2$), 9.1 (d, $P(OPh)_2$), $^2J(P-N-P) = 76.0$ Hz. FAB-MS: 841 (M^+). Anal. Calcd for $C_{42}H_{38}N_5O_5P_3Fe$: C, 59.94; H, 4.55; N, 8.32. Found: C, 59.38; H, 4.39; N, 8.11.

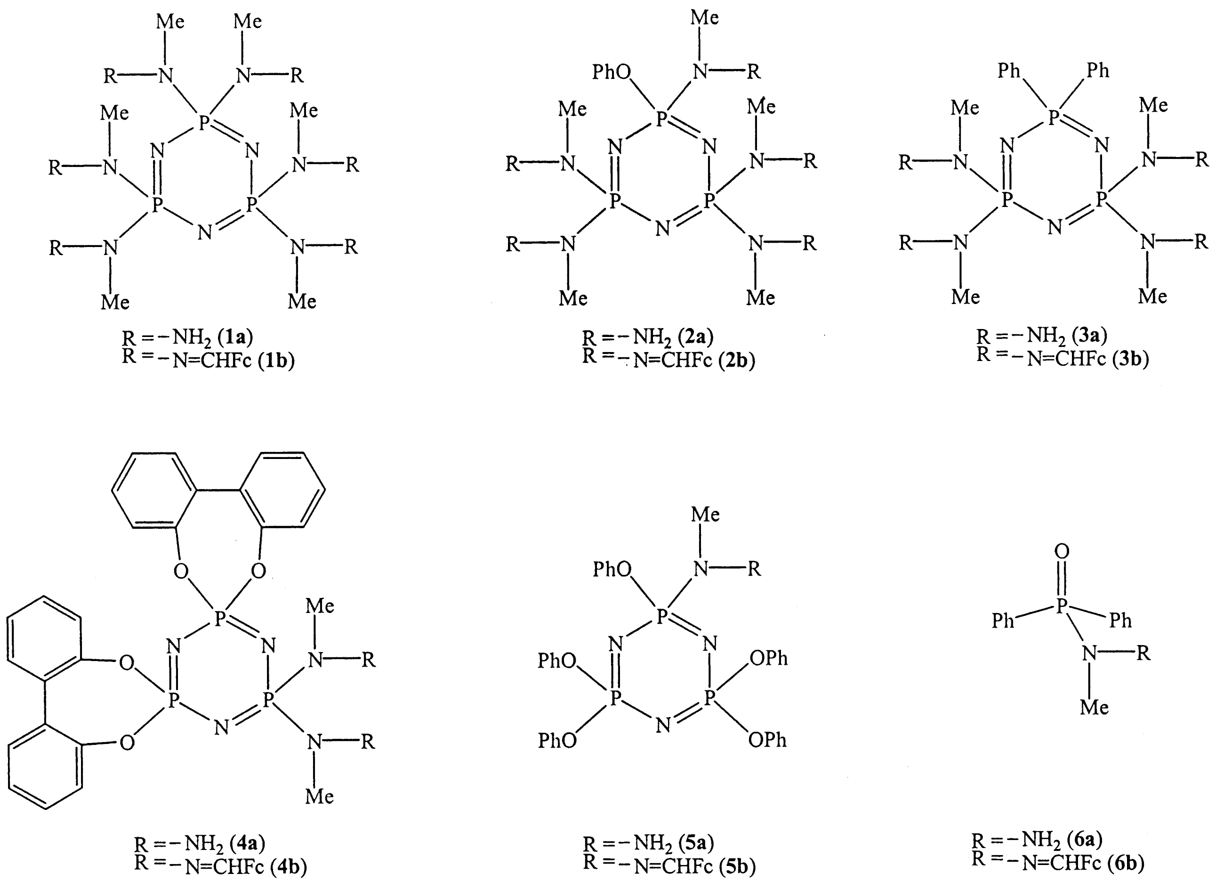
$Ph_2P(O)[N(Me)N=CHC_5H_4FeC_5H_5]$ (6b). This was prepared by a procedure analogous to that used for **1b.** The quantities of the reactants are **6a** (0.98 g, 4.00 mmol); ferrocene-2-carboxaldehyde (0.90 g, 4.2 mmol). Pure **6b** was obtained by elution with ethyl acetate–*n*-hexane, 30:70. Yield: 1.5 g, 84.9%. Mp: 142 °C. UV–visible (CH_2Cl_2): $\lambda_{max}(\epsilon)$: 448 nm (4675 mol^{-1} cm^{-1}). ^1H NMR: 3.20 (d, 3H, $-N(CH_3)$; $^3J(^1H-^{31}P) = 7.2$ Hz), 4.02 (s, 5H, ferrocene), 4.21 (s, 2H, ferrocene), 4.37 (s, 2H, ferrocene), 7.38 (s, 1H, imino), 7.44–7.85 (m, 10H, phenyl). ^{31}P NMR: 31.1 (s). FAB-MS: 442 (M^+). Anal. Calcd for $C_{24}H_{23}N_2OPFe$: C, 65.18; H, 5.24; N, 6.33. Found: C, 65.01; H, 5.17; N, 6.11.

Results and Discussion

Synthetic and Spectroscopic Aspects. We have chosen various chlorocyclophosphazenes (**1**–**5**) containing from six reactive chlorines to one as the starting materials (Chart 1). As a model for these compounds, the acyclic phosphorus derivative $Ph_2P(O)Cl$ (**6**) was chosen. These were reacted with *N*-methylhydrazine to afford the corresponding hydrazides **1a**–**6a** (Scheme 1, Chart 2). In all of these reactions *N*-methylhydrazine was also used to scavenge the liberated hydrogen chloride, obviating the need for an additional base. All of these reactions are regiospecific; the *N*-methyl end of the difunctional reagent reacts with the phosphorus compound, leading to products containing reactive terminal $-NH_2$ groups (Scheme 1, Chart 2). Another notable feature of these reactions is the complete absence of cross-linked products and the isolation of the products **1a**–**6a** in excellent yields. Condensation of the hydrazides **1a**–**6a** with stoichiometric amounts of ferrocene carboxaldehyde occurs at room temperature to afford the corresponding hydrazones **1b**–**6b** in quantitative yields (Schemes 2 and 3, Chart 2). Thus by the use of a mild reaction pathway involving the extrusion of water as the byproduct we have assembled cyclophosphazenes supporting from six ferrocenes to one.

The compounds **1a**–**6a** and **1b**–**6b** show prominent parent ion peaks in their mass spectra. The proton NMR spectra of these compounds are characterized by a doublet for the N-CH_3 protons. The compounds **2a** and **2b** show three resonances for the N-CH_3 resonances. The second-order effect of *virtual coupling* is seen for N-CH_3 resonance arising out of the $=P[N(CH_3)NH_2]_2$

Chart 2


R = –NH$_2$ (**1a**)
R = –N=CHFc (**1b**)

R = –NH$_2$ (**2a**)
R = –N=CHFc (**2b**)

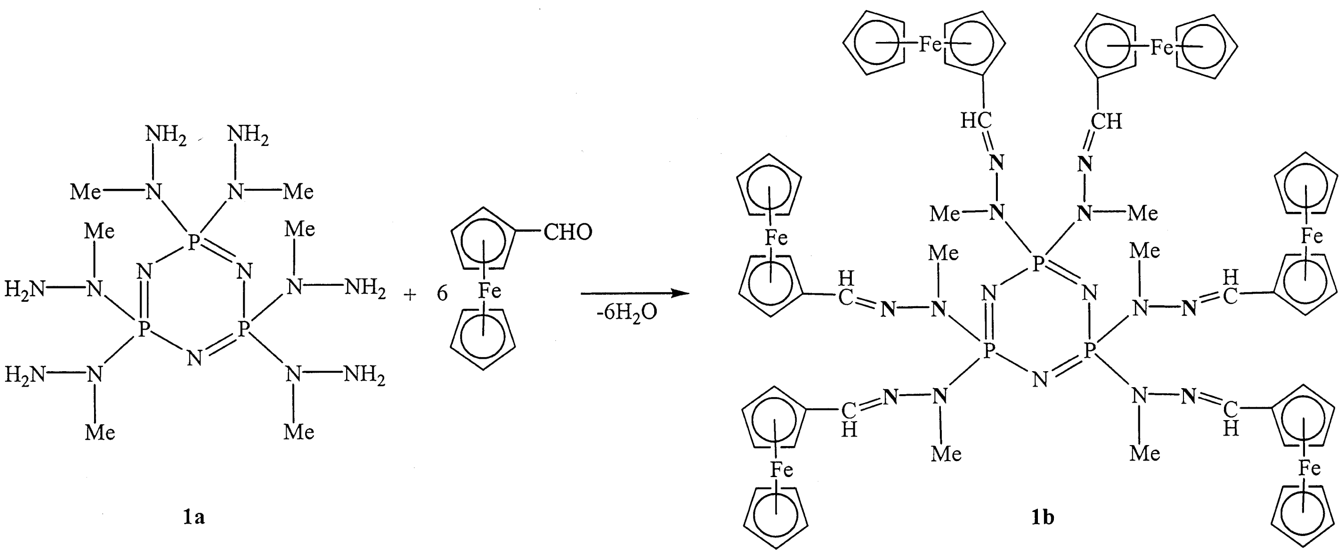
R = –NH$_2$ (**3a**)
R = –N=CHFc (**3b**)

R = –NH$_2$ (**4a**)
R = –N=CHFc (**4b**)

R = –NH$_2$ (**5a**)
R = –N=CHFc (**5b**)

R = –NH$_2$ (**6a**)
R = –N=CHFc (**6b**)

Scheme 2



1a

1b

group (**1a**–**3a**, **5a**) and the =P(N(C*H*$_3$)N=CHC$_5$H$_4$-FeC$_5$H$_5$)$_2$ group (**1b**–**3b**, **5b**). The N-C*H*$_3$ resonance for all the compounds (**1a**–**6a**) moves downfield upon conversion to the corresponding hydrazones (**1b**–**6b**); simultaneously the ^3J*(P–H) value decreases (Table 3). The ^{31}P{^{1}H} NMR spectra of **1a** and **1b** as well as **6a** and **6b** are single lines. The others show an AX$_2$ or A$_2$X type of first-order spectra. The ^{31}P{^{1}H} NMR data show some interesting trends. First, reaction of the chloro derivatives (P–Cl) to afford the hydrazides {P[N(CH$_3$)-NH$_2$]} results in the chemical shift of the corresponding phosphorus center to move downfield. Conversion of the latter to the hydrazone {P(N(CH$_3$)N=CHC$_5$H$_4$FeC$_5$H$_5$)} reverses the change in chemical shift and moves it upfield. This is illustrated in the conversion of N$_3$P$_3$Cl$_6$ (+19.5 ppm) to N$_3$P$_3$[N(Me)NH$_2$]$_6$ (+29.4 ppm) and N$_3$P$_3$-[N(Me)N=CHC$_5$H$_4$FeC$_5$H$_5$]$_6$ (+16.9 ppm).

The optical absorption spectra of **1b**–**6b** recorded under similar concentration conditions reveal the presence of an absorption band centered in the range 448–458 nm (Figure 1). Earlier studies by Gray and co-workers[21] and more recent work by Thomas et al.[22]

Scheme 3

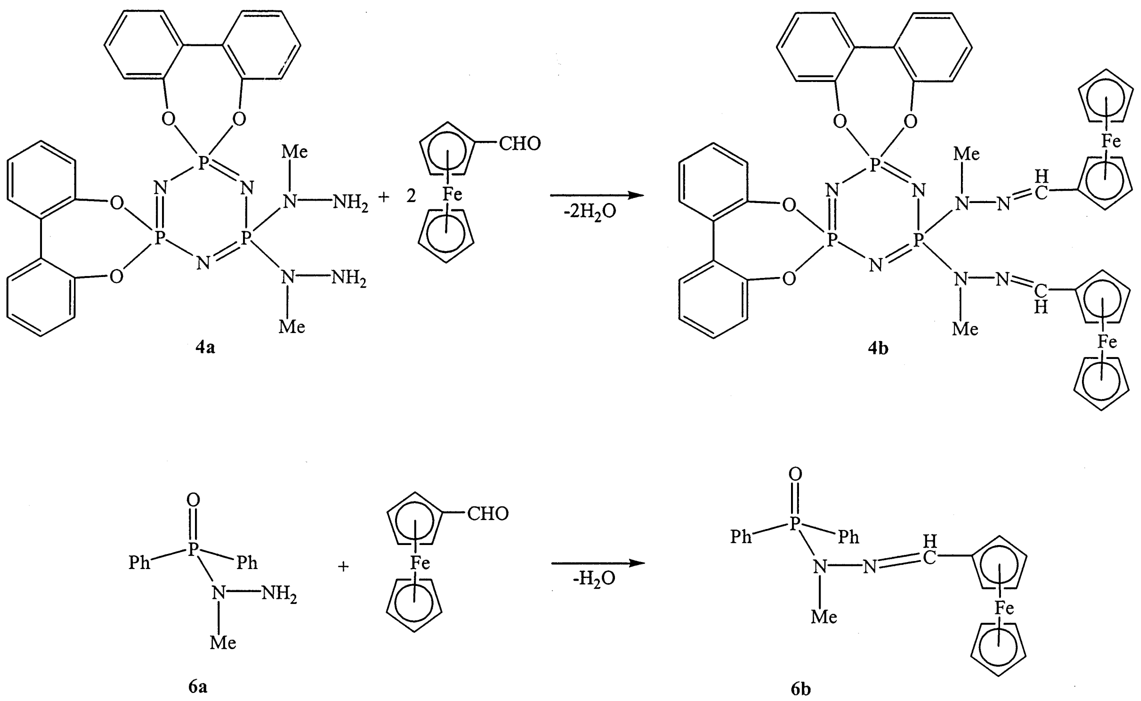


Table 3. ^{1}H and ^{31}P NMR Data for the Compounds 1a−6a and 1b−6b

	^{1}H		$^{31}P^{a}$			
compound	(P−N−CH_3) δ	^{3}J*(P−H)[b] Hz	P[N(Me)R]$_2$ δ	P[{N(Me)R}R^1]$_2$ δ	P(R^{2}R^3)$_2$ δ	^{2}J(P−N−P)
$N_3P_3[N(Me)NH_2]_6$ (**1a**)	2.80	11.2	29.4			
$N_3P_3[N(Me)N{=}CHC_5H_4FeC_5H_5]_6$ (**1b**)	3.30	8.6	16.9			
$N_3P_3(OPh)[N(Me)NH_2]_5$ (**2a**)	2.93	11.5	29.3	22.3[c]		40.4
	2.75	10.7				
	2.41	10.5				
$N_3P_3(OPh)[N(Me)N{=}CH{-}\ C_5H_4FeC_5H_5]_5$ (**2b**)	3.27	8.8	17.5	13.8[c]		57.7
	3.26	8.5				
	3.09	8.8				
gem-$N_3P_3Ph_2[N(Me)NH_2]_4$ (**3a**)	2.80	10.8	28.1		20.2[d]	17.8
gem-$N_3P_3Ph_2[N(Me)N{=}CH{-}\ C_5H_4FeC_5H_5]_4$ (**3b**)	3.18	8.8	15.1		20.2[d]	24.2
gem-$N_3P_3(O_2C_{12}H_8)_2[N(Me)NH_2]_2$ (**4a**)	2.98	11.0	29.3		26.6[e]	58.2
gem-$N_3P_3(O_2C_{12}H_8)_2[N(Me)N{=}CH\ C_5H_4\text{-}FeC_5H_5]_2$ (**4b**)	3.29	8.8	18.8		26.2[e]	71.2
$N_3P_3(OPh)_5[N(Me)NH_2]$ (**5a**)	2.54	11.5		20.7[c]	9.4[f]	71.2
$N_3P_3(OPh)_5[N(Me)N{=}CH{-}\ C_5H_4FeC_5H_5]$ (**5b**)	2.65	9.5		14.1[c]	9.1[f]	76.0
$Ph_2P(O)[N(Me)NH_2]$ (**6a**)	2.79	10.4		32.3[g]		
$Ph_2P(O)[N(Me)N{=}CH\ C_5H_4FeC_5H_5]$ (**6b**)	3.20	7.2		31.1[g]		

[a] The phosphorus chemical shifts of the corresponding chloro derivatives are as follows: $N_3P_3Cl_6$, 19.5 ppm; $N_3P_3(OPh)Cl_5$: δPCl_2, 22.5; $\delta P(OPh)(Cl)$, 12.3; *gem*-$N_3P_3Ph_2Cl_4$: δPCl_2, 18.3; $N_3P_3(O_2C_{12}H_8)_2Cl_2$: δPCl_2, 19.6; $N_3P_3(OPh)_5Cl$: $\delta P(OPh)Cl$, 22.2; $Ph_2P(O)Cl$, 44.9 ppm. [b] This value represents the apparent coupling constant in view of "virtual coupling" found in many of these compounds [c] R^1 = OPh. [d] $R^2 = R^3$ = Ph. [e] $R^2 = R^3$ = 2,2′-biphenoxy. [f] $R^2 = R^3$ = OPh. [g] Single phosphorus

allow this absorption to be assigned as arising due to a d−d transition. The increase in the number of ferrocenyl arms leads to a linear increase in the ϵ values. Thus **1b** shows the highest ϵ value of 30 845 mol^{-1} cm^{-1}, while **5b** and **6b** with only one ferrocenyl arms show low ϵ values (4770 and 4675 mol^{-1} cm^{-1}, respectively).

X-ray Crystal Structures of 1b and 3b−6b. The DIAMOND[23] diagram of **1b** is given in Figure 2. The ORTEP diagrams of **3b**−**6b** are given in Figures 3−7. Selected metric parameters for these compounds are given in Tables 4 and 5.

The X-ray crystal structure of the hexaferrocenyl derivative **1b** (Figure 2) reveals that the cyclotriphosphazene ring is perfectly planar. The molecular structure of **1b** represents the first structural characterization of a completely substituted cyclophosphazene containing ferrocenyl arms. The six ferrocenyl pendant groups are arranged in a symmetric manner about the cyclophosphazene ring; each side of the ring contains three ferrocenyl pendant groups. The overall arrangement is an approximate cyclic array of the ferrocenyl groups about the cyclophosphazene framework. The average endocyclic P−N bond length within compound **1b** is 1.579 Å, while the average N−P−N and P−N−P

---

(21) Sohn, Y. S.; Hendrickson, D. A.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.

(22) (a) Thomas, K. R. J.; Lin, J. T.; Wen, Y. S. *Organometallics* **2000**, *19*, 1008. (b) Thomas, K. R. J.; Lin, J. T.; Lin, K. J. *Organometallics* **1999**, *18*, 5285.

(23) Brandenburg, K. *Diamond*, Version 2.1c; Crystal Impact GbR, 1996−1999.

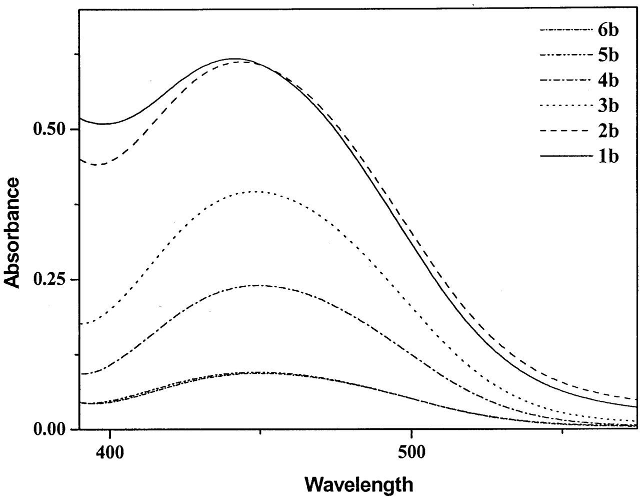


Figure 1. UV–visible spectra for the ferrocenyl derivatives (**1b**–**6b**) recorded using 2 × 10^{-5} M dichloromethane solution.

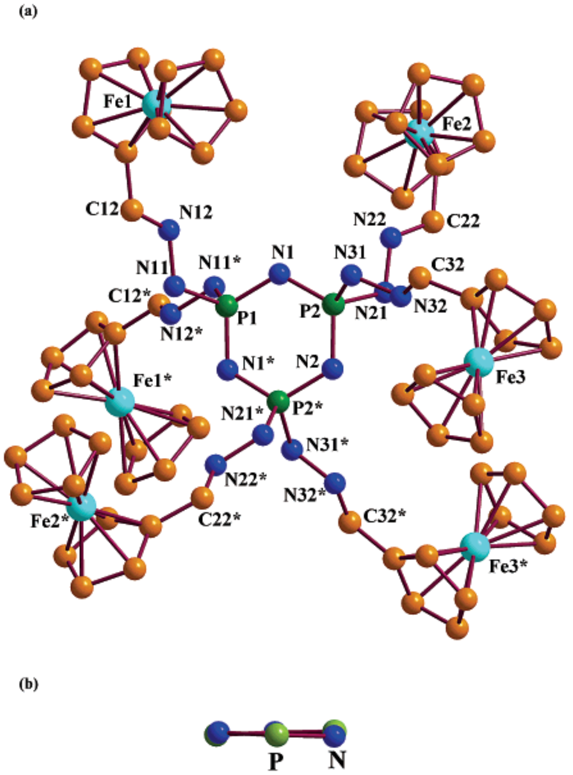


Figure 2. (a) DIAMOND picture of hexaferrocenyl assembly **1b**. Methyl groups on the imino carbon atoms are omitted for clarity. (b) Cyclophosphazene ring of **1b**.

bond angles are 118.6° and 121.2°, respectively. The average exocyclic P–N bond length is 1.665 Å, while the average exocyclic N–P–N bond angle is 106.8°. These values are analogous to those observed for other hexakisaminocyclophosphazenes.[24] The metric parameters related to the ferrocenyl moiety in **1b** and **3b**–**6b** are unexceptional (Supporting Information).

The molecular structure of the tetraferrocenyl derivative **3b** shows that the cyclophosphazene ring is slightly nonplanar (Figure 3b).[25] The atoms P1 and P2 deviate from the mean plane by 0.17 and 0.12 Å, while the atom N3 moves away in the opposite direction by 0.20 Å. The P–N distances flanking the P(Ph)$_2$ unit are nearly similar: P1–N1, 1.612(7) Å, and P1–N3, 1.599(8) Å. The average value of the other four P–N bond distances is 1.579 Å, which is similar to what was observed for **1b**. The average values of the ring N–P–N and P–N–P bond angles are 117.4° and 118.5°, respectively. The exocyclic P–N bond distance is slightly longer (av 1.741 Å).

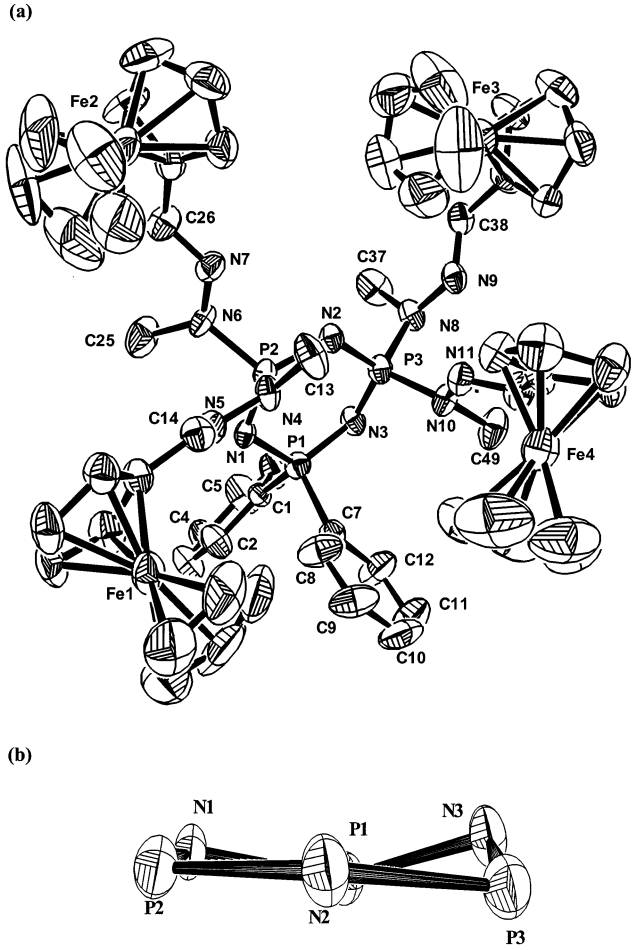


Figure 3. (a) ORTEP diagram of tetraferrocenyl assembly **3b**. The thermal ellipsoids are drawn at the 50% probability level. (b) Cyclophosphazene ring of **3b**.

The crystal structure of the diferrocenyl derivative **4b** (Figure 4) shows that the six-membered cyclophosphazene ring is only very slightly nonplanar. Thus, the maximum deviation from the mean plane of the ring is observed for P1 (0.10 Å). The P–N bond distances within the ring are nonequivalent, as expected for compounds of the type *gem*-$N_3P_3X_2Y_4$. Three types of bond distances are observed. The long bond distances of 1.589(5) and 1.592(5) Å are observed for P1–N1 and P1–N3, respectively, while the short bond distances of 1.557(5) and 1.565(5) Å are found for P2–N1 and P3–N3. These trends are consistent with bond length variations in substituted cyclophosphazenes.[24] The bond angle at P1 is the smallest at 115.5°, while at P2 and P3 they enlarge to 118.0° and 119.1°, respectively. In contrast, the bond angles at nitrogen are larger. The

---

(24) Chandrasekhar, V.; Thomas, K. R. J. *Struct. Bond.* **1993**, *81*, 41.

(25) PRAST in WinGX, Version 1.64.031 (release Nov. 1999): Nardelli, M. *J. Apply. Crystallogr.* **1995**, *28*, 659.

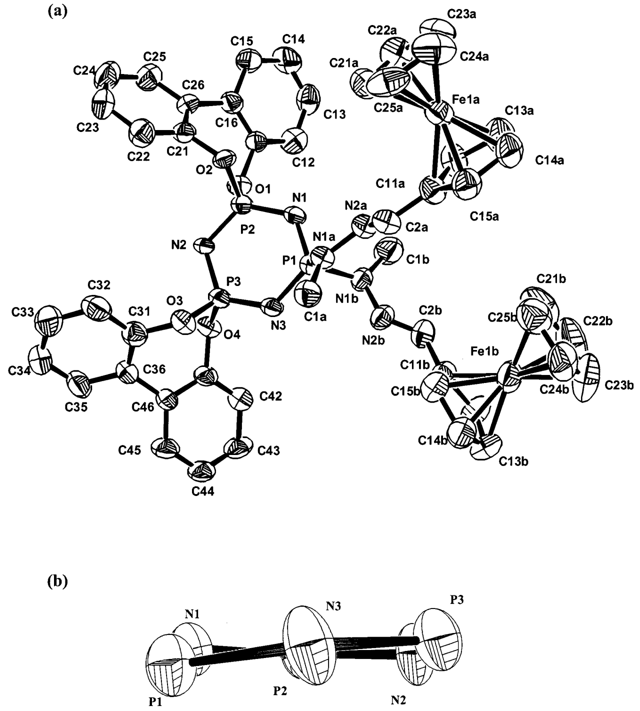


Figure 4. (a) ORTEP diagram of diferrocenyl assembly **4b**. The thermal ellipsoids are drawn at the 50% probability level. (b) Cyclophosphazene ring of **4b**

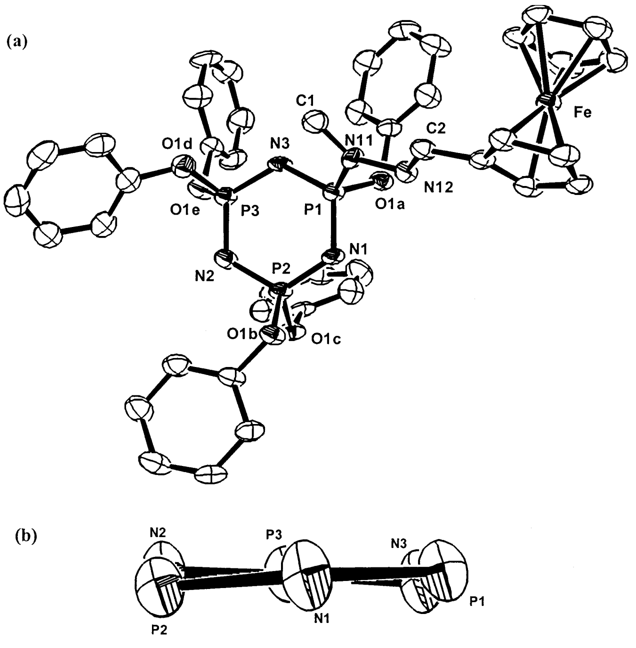


Figure 5. (a) ORTEP diagram of monoferrocenyl derivative **5b**. The thermal ellipsoids are drawn at the 80% probability level. (b) Cyclophosphazene ring of **5b**.

exocyclic P–O bond angles are smaller than normal tetrahedral angles. Within the biphenyldioxy group, the individual phenyl rings are at an angle of 44° to each other.

The X-ray crystal structure of the monoferrocenyl cyclophosphazene derivative **5b** is shown in Figure 5. This is the only example where the phosphorus atom containing the ferrocenyl pendant group also has a different substituent (OPh). Similar to **1b** the N_3P_3 ring in compound **5b** is also perfectly planar. The ring P–N distances flanking the P(OPh)(N(Me)N=CHC_5H_4–Fe–C_5H_5) segment are equal (1.593(2) Å). This value is longer than those observed in previous instances as discussed above. The other metric parameters are normal.

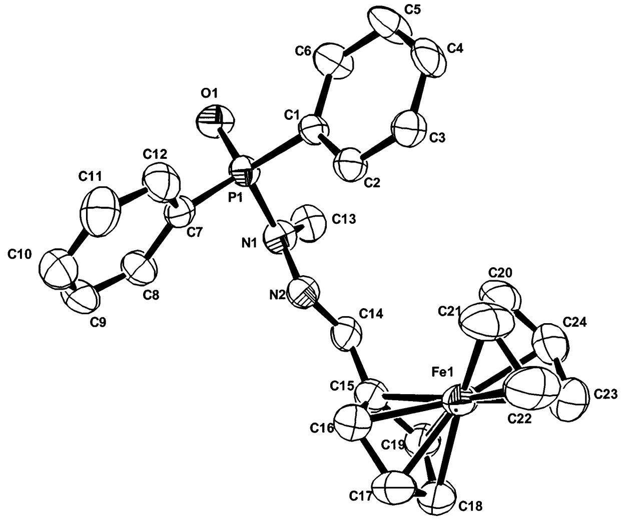


Figure 6. ORTEP diagram of monoferrocenyl derivative **6b**. The thermal ellipsoids are drawn at the 50% probability level.

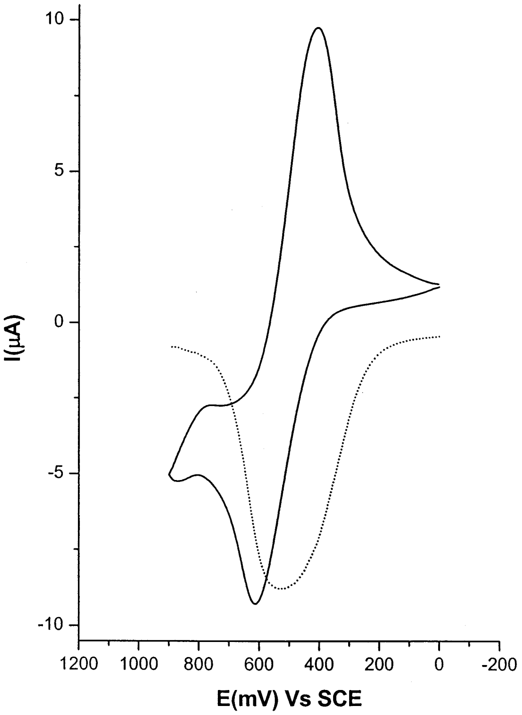


Figure 7. Cyclic voltammogram (solid line) of **1b** at 25 mV s^{-1}, showing a single essentially reversible oxidation peak; the dotted line shows the differential pulse voltammogram of **1b**.

The crystal structure of **6b** is an interesting example and serves as a reference for the other ferrocenyl compounds discussed above. This structure shows a tetrahedral arrangement around the phosphorus. The P–O bond distance of 1.468(3) Å is consistent with P=O bond distances observed in the literature.[26] The latter is sensitive to the substituents on phosphorus. Thus the

---

(26) Vilkov, L. V.; Sadova, N. I.; Zilberg, I. Y. *Zh. Strukt. Khim.* **1967**, *8*, 528.

Table 4. Selected Bond Lengths (Å) for Compounds 1b−6b

1b		**3b**		**4b**		**5b**		**6b**	
P(1)−N(1)	1.569(8)	P(1)−N(1)	1.612(6)	P(1)−N(1)	1.589(5)	P(1)−N(1)	1.593(2)	P(1)−O(1)	1.468(3)
P(2)−N(1)	1.578(8)	P(1)−N(3)	1.599(6)	P(1)−N(3)	1.592(5)	P(1)−N(3)	1.592(2)	P(1)−N(1)	1.680(3)
P(2)−N(2)	1.589(6)	P(2)−N(1)	1.564(6)	P(2)−N(1)	1.566(5)	P(2)−N(1)	1.580(2)	P(1)−C(1)	1.799(4)
P(1)−N(11)	1.658(8)	P(2)−N(2)	1.578(6)	P(2)−N(2)	1.578(5)	P(2)−N(2)	1.588(2)	P(1)−C(7)	1.786(4)
P(2)−N(21)	1.663(5)	P(3)−N(3)	1.584(6)	P(3)−N(3)	1.557(5)	P(3)−N(3)	1.575(2)	N(1)−N(2)	1.383(5)
P(2)−N(31)	1.673(4)	P(3)−N(2)	1.591(6)	P(3)−N(2)	1.580(5)	P(3)−N(2)	1.578(2)	N(2)−C(14)	1.276(5)
$N{-}N_{avg}$	1.387	P(1)−C(1)	1.666(6)	P(1)−N(1A)	1.677(6)	P(1)- N(11)	1.662(2)		
$N{=}C_{avg}$	1.280	P(1)−C(7)	1.664(5)	P(1)−N(1B)	1.667(5)	P(1)- O(1a)	1.5962(18)		
		P(2)−N(4)	1.687(4)	P(2)−O(2)	1.591(4)	P(2)−O(1b)	1.5881(19)		
		P(2)−N(6)	1.671(5)	P(2)−O(1)	1.585(5)	P(2)−O(1c)	1.5981(18)		
		P(3)−N(8)	1.798(5)	P(3)−O(3)	1.592(5)	P(3)−O(1d)	1.5937(19)		
		P(3)−N(10)	1.808(5)	P(3)−O(4)	1.596(5)	P(3)−O(1e)	1.5859(19)		
		$N{-}N_{avg}$	1.367	$N{-}N_{avg}$	1.392	N(11)−N(12)	1.399(3)		
		$N{=}C_{avg}$	1.271	$N{=}C_{avg}$	1.270	N(12)−C(2)	1.280(3)		

Table 5. Selected Bond Angles (deg) for Compounds 1b−6b

1b		**3b**		**4b**		**5b**		**6b**	
N(1)*−P(1)−N(1)	117.8(5)	N(1)−P(1)−N(3)	116.6(3)	N(1)−P(1)−N(3)	115.5(3)	N(1)−P(2)−N(2)	117.43(12)	O(1)−P(1)−N(1)	110.01(17)
N(1)−P(2)−N(2)	118.9(5)	N(1)−P(2)−N(2)	119.1(3)	N(1)−P(2)−N(2)	118.5(3)	N(3)−P(3)−N(2)	118.67(12)	C(7)−P(1)−C(1)	108.40(17)
P(1)−N(1)−P(2)	122.1(5)	N(3)−P(3)−N(2)	117.1(3)	N(3)−P(3)−N(2)	119.1(3)	N(3)−P(1)−N(1)	117.79(12)	O(1)−P(1)−C(1)	110.64(17)
P(2)−N(2)−P(2)*	119.7(7)	P(2)−N(1)−P(1)	119.1(4)	P(2)−N(1)−P(1)	122.1(3)	P(2)−N(1)−P(1)	121.80(14)	O(1)−P(1)−C(7)	114.66(18)
N(11)−P(1)−N(11)*	108.3(3)	P(2)−N(2)−P(3)	119.1(3)	P(2)−N(2)−P(3)	120.2(3)	P(3)−N(2)−P(2)	121.64(13)	N(1)−P(1)−C(7)	104.66(17)
N(31)−P(2)−N(21)	105.2(3)	P(3)−N(3)−P(1)	116.6(4)	P(3)−N(3)−P(1)	122.2(3)	P(3)−N(3)−P(1)	121.20(14)	N(1)−P(1)−C(1)	108.06(17)
		C(1)−P(1)−C(7)	106.1(4)	N(1a)−P(1)−N(1b)	106.4(3)	O(1a)−P(1)−N(11)	104.47(10)	N(2)−C(14)−C(15)	120.3(4)
		N(6)−P(2)−N(4)	105.2(3)	O(1)−P(2)−O(2)	102.5(2)	O(1b)−P(2)−O(1c)	98.42(10)	N(2)−N(1)−C(13)	121.7(4)
		N(8)−P(3)−N(10)	102.9(3)	O(3)−P(3)−O(4)	103.0(2)	O(1e)−P(2)−O(1d)	104.18(11)		

Table 6. Cyclic Voltammetric Data for Compounds 1b−6b along with Some Multi-Ferrocene Assemblies[a,b]

compound	$E_{1/2}$ (V)	ΔE_p (mV)	ref
$N_3P_3[N(Me)N{=}CHC_5H_4FeC_5H_5]_6$ (**1b**)	+0.51	205	this work[c]
$N_3P_3(OPh)[N(Me)N{=}CH{-}C_5H_4FeC_5H_5]_5$ (**2b**)	+0.51	206	this work[c]
gem-$N_3P_3Ph_2[N(Me)N{=}CH{-}C_5H_4FeC_5H_5]_4$ (**3b**)	+0.51	154	this work[c]
gem-$N_3P_3(O_2C_{12}H_8)_2[N(Me)N{=}CH{-}C_5H_4FeC_5H_5]_2$ (**4b**)	+0.55	140	this work[c]
$N_3P_3(OPh)_5[N(Me)N{=}CH{-}C_5H_4FeC_5H_5]$ (**5b**)	+0.53	108	this work[c]
$Ph_2P(O)[N(Me)N{=}CH{-}C_5H_4FeC_5H_5]$ (**6b**)	+0.58	91	this work[c]
$C_5H_5FeC_5H_4CHO$	+0.87	142	this work[c]
$[(C_5H_5)FeC_6\{(CH)_2(C_5H_4FeC_5H_5)\}_6]PF_6$	+0.44	55	30[c]
$[C_6\{(CH_2)_5(Fc)\}_6]$	+0.45	-	30[c]
$[C_5H_5)FeC_6\{(CH_2)C_6H_4OC(O)C_5H_4FeC_5H_5\}_6]PF_6$	+0.78	60	31[c]
$[C_6\{(CH_2)_2C_6H_4OC(O)(C_5H_4FeC_5H_5)\}_6]$	+0.88	120	31[c]
$[\{BuSn(O)OC(O)(C_5H_4FeC_5H_5)\}_6]$	+0.72	128	32[c]
$C_5H_5FeC_5H_4CH_2(Me)NH$	+0.54	92	9[d]
$N_3P_3Cl_5[N(Me){-}CH_2{-}C_5H_4FeC_5H_5]$	+0.54	80	9[d]
trans-$N_3P_3Cl_4[N(Me){-}CH_2{-}C_5H_4FeC_5H_5]_2$	+0.52	100	9[d]
gem-$N_3P_3Cl_4[N(Me){-}CH_2{-}C_5H_4FeC_5H_5]_2$	+0.51	74	9[d]
trans-$N_3P_3Cl_3[N(Me){-}CH_2{-}C_5H_4FeC_5H_5]_3$	+0.53	73	9[d]
gem-$N_3P_3Cl_3[N(Me){-}CH_2{-}C_5H_4FeC_5H_5]_3$	+0.49	82	9[d]
$N_3P_3Cl_4[N(Me){-}CH_2{-}C_5H_4FeC_5H_5][O(CH_2)_4CMeCH_2]$	+0.51	93	9[d]
$N_3P_3Cl_3[N(Me){-}CH_2{-}C_5H_4FeC_5H_5]_2[O(CH_2)_4CMeCH_2]$	+0.50	78	9[d]

[a] Versus SCE. [b] The I_c/I_a and the $E_{1/2}$ for ferrocene (under these experimental conditions) are 1.08 and 0.51 V, respectively. [c] Potential at the scan rate of 25 mV s^{-1}. [d] Potential at the scan rate of 100 mV s^{-1}.

shortest value observed is for $P(O)Br_3$, viz., 1.41 Å. In $Ph_2P(O)NMe_2$, a compound that is structurally related to **6b**, the P−O bond distance is 1.47 Å. In **6b** the P1−N1 distance is 1.680(4) Å and is very close to the P−N single bond distance of 1.70 Å.[27]

Electrochemical Studies. Electrochemical studies on ferrocenyl-substituted cyclophosphazenes are quite limited. Allcock and co-workers have investigated the electrochemical behavior of a few compounds where the ferrocene is directly attached to the cyclophosphazene such as in *ansa*-$N_3P_3F_4(C_5H_4{-}Fe{-}C_5H_4)$.[28] Recently Allen and co-workers have investigated the preparation and electrochemical behavior of some *N*-(ferrocenylmethyl)-*N*-methylaminocyclotriphosphazenes[9] and a ferrocenyl alcohol derivative, $N_3P_3Cl_5OCH_2CH_2C_5H_4$-$FeC_5H_5$.[10]

Cyclic and differential pulse voltammetric studies have been carried out on compounds **1b**−**6b.** The electrochemical data for these compounds along with some related derivatives are summarized in Table 6, and the cyclic voltammogram of **1b** recorded at 25 mV s^{-1} has been shown as a representative example (Figure 7). A single essentially reversible oxidation peak is observed for all the compounds. The observation of a single oxidation peak for **1b**−**4b** suggests that *all* the pendant ferrocene moieties present in these compounds have equivalent redox potentials. It has been noted earlier that in order for a mediator to be effective in electron-transfer process all the redox centers present

---

(27) Wingerter, S.; Pfeiffer, M.; Murso, A.; Lustig, C.; Stey, T.; Chandrasekhar, V.; Stalke, D. *J. Am. Chem. Soc.* **2001**, *123*, 1381.

(28) Saraceno, R. A.; Riding, G. H.; Allcock, H. R.; Ewing, A. G. *J. Am. Chem. Soc.* **1988**, *110*, 7259.

should be equivalent.[29−32] In compounds such as **1b**−**4b**, although the ferrocenyl moieties present therein are physically well separated from each other, all of them are oxidized at the same potential. Such an equivalence of multiple ferrocene units arranged at the periphery of dendrimeric structures has been observed earlier.[3]

The $E_{1/2}$ values are shifted to less positive numbers with an increase in the number of ferrocene arms. Thus the $E_{1/2}$ value is lowest for **1b**, containing six ferrocene arms, and is the highest for **5b** and **6b**, containing only one ferrocene arm. However, all the oxidation potentials are lower than those observed for ferrocene carboxaldehyde (0.87 V). The electrochemical behavior of **1b**−**6b** is reproducible, indicating that these compounds or their oxidized products are perfectly stable and robust. This has been verified up to 10 continuous electrochemical cycles. Further evidence for the electrochemical stability of **1b**−**6b** comes from the observation that the peak potential does not vary with scan rate (10−200 mV s^{-1}).

Conclusion

In conclusion, cyclophosphazene hydrazides are excellent synthons for the preparation of multi-ferrocenyl assemblies. The advantage of this method is the convenience it affords in terms of varying the ferrocene units systematically from one to six. The X-ray crystal structures of these cyclophosphazene-supported ferrocenyl derivatives including $N_3P_3[N(Me)N{=}CH{-}C_5H_4\text{-}FeC_5H_5]_6$ show the adaptability of the cylophsophazene ring in supporting the ferrocene units without any steric congestion. The cyclophosphazene ring itself undergoes a slight puckering in some situations. The electrochemical behavior of these ferrocenyl derivatives shows that all of them show a single reversible oxidation wave. The observation of this even in multi-ferrocenyl derivatives suggests the electrochemical equivalence of the ferrocene moieties.

Acknowledgment. We are thankful to the Council of Scientific and Industrial Research (New Delhi) for financial support. GTS, S.N., and V.K. also thank this organization for the award of a Senior Research Fellowship.

Supporting Information Available: Tables (S1−S25) giving atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters for **1b** and **3b**−**6b**. The CIF files for all these compounds are also presented. These materials are available free of charge via the Internet at http://pubs.acs.org.

OM020760D

---

[29] Myer, C. N.; Allen, C. W. *Polym. Prepr.* **2000**, *41*, 558.

[30] Fillaut, J.-L.; Lineares, J.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2460.

[31] Fillaut, J.-L.; Astruc, D. *Chem. Commun.* **1993**, 1320.

[32] Chandrasekhar, V.; Nagendran, S.; Bansal, S.; Kozee, M. A.; Powell, D. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 1833.