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Synthesis and characterization of ferrocenylalcohol derivatives of hexachlorocyclotriphosphazene. X-ray crystal structure of $N_3P_3Cl_5OCH_2CH_2C_5H_4FeCp$

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Abstract

The preparation of 1-ferrocenyl-2-propanol (**5**) from lithioferrocene and propylene oxide is described. The reaction of lithium diisopropylamide with 2-ferrocenylethanol (**3**) or 1-ferrocenyl-2-propanol (**5**), followed by the addition to hexachlorocyclotriphosphazane (**1**) provides $N_3P_3Cl_{6-n}(OCHRCH_2C_5H_4FeCp)_n$ [R = H, $n = 1$ (**3**) or 2 (**4**); R = CH_3, $n = 1$ (**6**)]. The corresponding reactions with ferrocenylmethanol lead to degradation products via a phosphazene–phosphazene rearrangement. The substitution pattern observed for $N_3P_3Cl_4(OCH_2CH_2C_5H_4FeCp)_2$ (**4**) suggests that the reaction follows a predominantly *cis*-non-geminal pathway. The substituted phosphazene derivatives were characterized by standard means including ^{31}P-NMR, mass spectrometry, elemental analysis and cyclic voltammetry. An X-ray crystal structure of $N_3P_3Cl_5(OCH_2CH_2C_5H_4FeCp)$ (**3**) was obtained.

Keywords: Cyclophosphazene; Ferrocenylalcohols

1. Introduction

Cyclo- and polyphosphazenes have a rich chemical history. Of particular interest is the synthetic diversity of phosphazenes leading to a broad range of cyclophosphazenes which exhibit a variety of different functional groups [1–5]. Typically, substitution is carried out by nucleophilic displacement of halogens on the phosphazene ring. Additional reactions can be carried out on the side groups to further increase the functionality. However, few of these side groups have been studied as redox active centers.

The use of organometallic pendant groups on cyclophosphazenes is relatively recent [4–6]. Organometallic functionality not only furnish sites of additional reactivity, but also provides redox active centers that can be studied electrochemically. In particular, phosphazenes with ferrocene, either directly bound [7] or attached by a saturated carbon chain [8] or organocobalt cluster pendant groups [9] have been studies electrochemically. These studies often focused on the interaction of the phosphazene ring with a redox site generated at the organometallic center.

Currently, we are examining organometallic derivatives in which the phosphazene is insulated from the redox active center. It is anticipated that materials can be prepared which contain multiple redox sites with equivalent or comparable potentials. The electrochemistry of ferrocene has been studied extensively [10], making it an excellent choice for the redox active center in these studies. An assortment of ferrocene derivatives have been prepared providing many different means of attaching the ferrocene to the phosphazene ring. Our work was focused primarily on the substitution of phosphazenes with derivatives of ferrocene containing alcohol and amine [11,12] functionalities. In this paper, we report the synthesis, characterization and electrochemistry of ferrocenylalcohol derivatives of hexachlorocycloptriphosphazene. A preliminary report of some aspects of this work has appeared [12].

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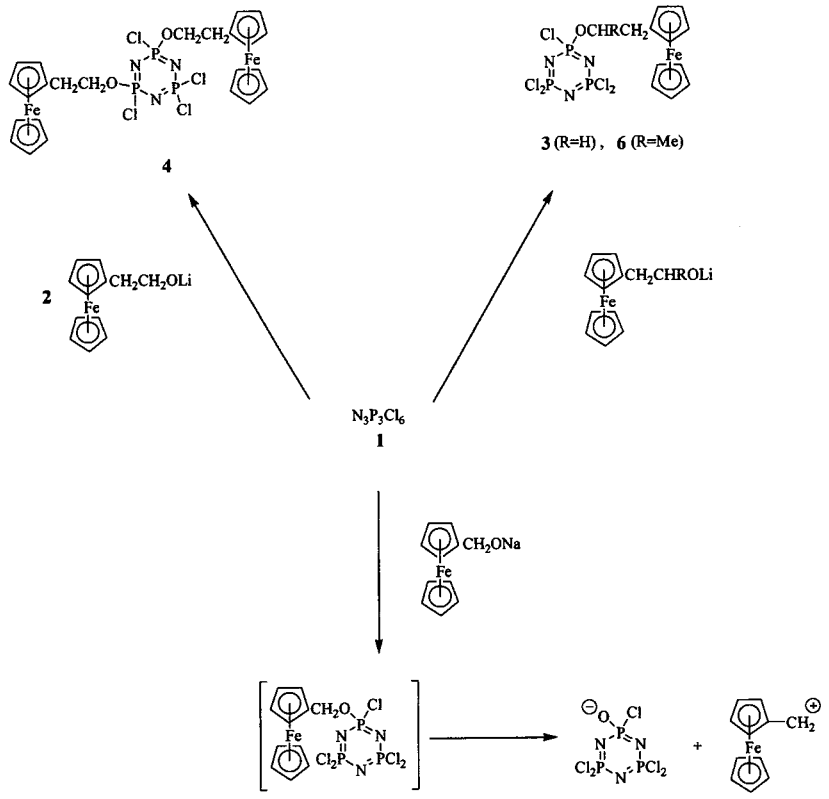

Scheme 1.

2. Results and discussion

2.1. Synthesis and characterization

The synthesis of 1-ferrocenyl-2-propenyl (**5**) was carried out by reacting lithioferrocene with propylene oxide. Other ferrocenyl alcohols were obtained by previously reported procedures. Ferrocenyl alcohol derivatives of cyclotriphosphazenes were prepared by reacting the lithium salt of the alcohol with hexachlorocyclotriphosphazene (**1**) at low temperature (Scheme 1). Yields are typically good ($>45\%$). The degree of ring substitution is controlled by the molar ratio of the reactants. Using one equivalent of 2-ferrocenylethanol (**2**) gave $N_3P_3C1_5(OCH_2CH_2C_5H_4FeCp)$ (**3**) while two equivalents of **2** gave $N_3P_3C1_4(OCH_2CR_2C_5H_4FeCp)_2$ (**4**). Attempts at obtaining compounds with higher than di-substitution were made using up to six equivalents of **2**, but only the di-substituted derivatives were obtained. The reaction of one equivalent of the lithium salt of 1-ferrocenyl-2-propanol (**5**) with **1** gives $N_3P_3C1_5$-$(OCHMeCH_2C_5H_4FeCp)$ (**6**).

By way of contrast, the reaction of the sodium salt of ferrocenylmethanol with **1** leads only to decomposition products which showed IR evidence for phosphorus–oxygen bonds and the blue color characteristic of oxidized ferrocene. The probable pathway for this process is shown in Scheme 1. After the initial presumed formation of the ferrocenylmethanol derivative of **1**, the first (dissociative) step [13] of the phosphazene–phosphazane rearrangement occurs giving rise to the well known ferrocenylmethyl carbocation [14] in which the positive charge is stabilized by interaction with the ferrocene unit. Based on these observations, the phosphazene derivatives of primary ferrocenyl alcohols (**3**, **4**) are expected to be preferable (more stable) than those of secondary ferrocenyl alcohols (**6**).

Compounds **3** and **6** displayed the typical AB_2 pattern expected for a mono-substituted phosphazene in the $^{31}P\{^1H\}$-NMR spectrum. Compound **4** exists as a mixture of *cis*-, *trans*- and *geminal* isomers (Fig. 1) and

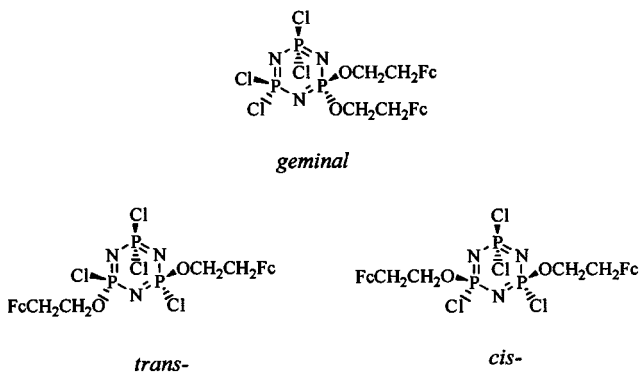

Fig. 1. Geometric isomers of $N_3P_3C1_4(OCH_2CH_2C_5H_4FeCp)_2$ (**4**).

the $^{31}P\{^{1}H\}$ spectrum of **4** shows three separate AB_2 patterns. The *geminal* isomer can be identified based on the unique chemical shift for the $\equiv P(OR)_2$ center and the observed splitting patterns. Though the peaks for the *cis* and *trans* isomers overlap (Fig. 2), a tentative assignment of the *cis* and trans isomers can be made by examining related systems. In the ^{31}P NMR spectra of $N_3P_3Cl_4(OPh)_2$ [15] and $N_3P_3Cl_4(NMe_2)_2$ [16], the *cis* isomer displayed peaks farther upfield than the *trans* isomer. Based on these results, $N_3P_3Cl_4(OCH{=}CH_2)_2$ [17,18] and $N_4P_4Cl_6(OCH{=}CH_2)_2$ [18] have been conditionally assigned as having a *cis* preference in their isomeric distribution. The predominance of the *cis* isomer in $N_3P_3Cl_4(OCH{=}CH_2)_2$ has been confirmed by the ^{1}H NMR spectra of the dimethylaminolysis products $N_3P_3(NMe_2)_4(OCH{=}CH_2)_2$ [19]. In the ^{31}P NMR spectrum of **4**, the more intense peak of the *cis*/*trans* mixture is farther upfield, so the prevailing isomer is tentatively assigned as *cis*. The ratio of isomers is 1:3.4:6.4 (*geminal*/*trans*/*cis*) based on the integration of the peaks. The NMR parameters for each isomer were estimated from the complex mixture and used to simulate the individual spectra. The individual spectra were then combined to give a composite spectrum that was matched to the obtained spectrum by estimating the concentration of each component (Fig. 2). Attempts at separating the di-substituted isomers were unsuccessful.

Factors controlling the regio and stereochemical pathways in the reactions of oxyanions with cyclophosphazenes are unclear. For example, early work on the trifluoroethoxide ion [20] showed dominance of the *trans* non-geminal isomer which recalls the behavior of the well understood reactions of secondary amines with **1** [3,4]. However, more recent work ranging from the examples cited above to the recent remarkable report of a *cis* stereospecific reaction in the reaction of the sodium salts of alkoxy poly(ethyleneglycols) with **1** [21], add credibility to the proposed *cis* perference in **4**. The *cis* perference along with the large steric demands of the ferrocenyl alcohols may explain why the reactions do not proceed effectively past the stage of di-substitution. A similar reluctance to provide higher degrees of substitution has been noted in the reactions of *N*-ferrocenylmethyl–*N*-methylamine with **1** [11,12].

2.2. X-ray structure of 3

A comparison of the pertinent bond lengths and angles for **3** and **2** [22], show that there are no significant structural changes in the ferrocene portion of **3** on going from the free alcohol to the phosphazene derivative. This observation suggests that the ferrocene moiety is isolated electronically from the phosphazene by the saturated ethoxy unit. Few crystal structures of monoorganooxy derivatives of **1** have been reported [3,23]. The variation in the phosphorus–nitrogen bond lengths (Table 1) follow the sequence demonstrated by most other mixed substituent cyclophosphazenes [3], i.e. the longest bonds are those to the substituted phosphorus center (P_1) the next PN bond is the shortest as the

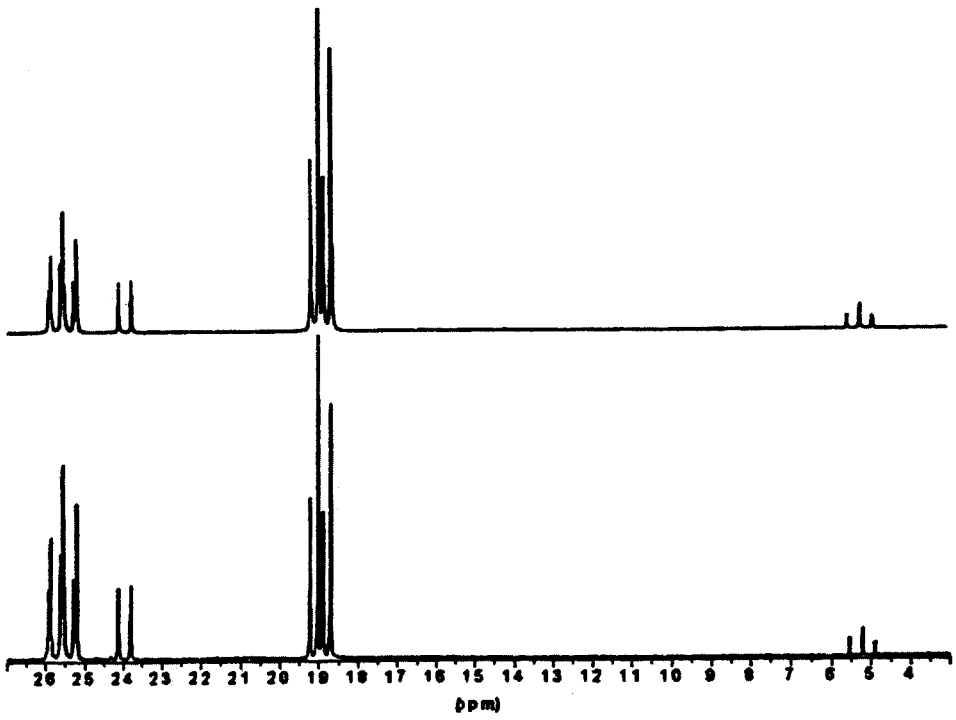

Fig. 2. Observed and simulated ^{31}P NMR spectra of **4**.

remaining bonds in the $-Cl_2PNPCl_2-$ unit are essentially equivalent to those in **1**. Similar bond lengths are observed in $N_3P_3Cl_5OC_6H_4ON_3P_3C1_5$ [24] and $N_3P_3Cl_5$-($OC_6H_4^tBu$-2,4,6) [25] and in all three cases the differences in the endocyclic bond lengths are small due to the similar electronegativities in the Cl and OR substituents [3]. The phosphazene ring is planar. The root mean square (RMS) deviation from the plane was calculated to be 0.025 Å. The RMS deviation from the plane for **1** was calculated based on the published crystallographic data [26] and determined to be 0.021 Å. The ORTEP diagram (Fig. 3) shows the large steric demands of the ferrocenylalcohol portion of **3** and lends credence to the proposal that the difficulty in achieving higher degrees of substitution results from the inaccessibility of the remaining $/PCl_2$ centers.

Table 1
Selected bond lengths (Å) and bond angles (°) for $N_3P_3C1_5(OCH_2CH_2C_5H_4FeCp)$ (**3**)

Bond lengths			
C_{12}–O	1.454(8)	P_2–N_3	1.575(9)
C_{Cp}–C_{Cp} (avg.)	1.394	P_3–N_1	1.562(8)
Fe–C_{Cp} (avg.)	2.030	P_1–Cl	1.989(3)
C_{10}–C_{11}	1.503(9)	P_2–$C1_2$	1.993(3)
C_{11}–C_{12}	1.497(15)	P_2–$C1_3$	1.994(3)
P_1–N_1	1.594(8)	P_3–$C1_4$	1.992(3)
P_1–N_2	1.592(5)	P_3–$C1_5$	1.972(4)
P_2–N_2	1.586(6)		
Bond angles			
P_1–N_1–P_3	121.2(4)	N_1–P_3–N_3	119.1(4)
P_1–N_2–P_2	120.4(4)	$C1_1$–P_1–O	104.4(2)
P_2–N_3–P_3	120.9(5)	$C1_2$–P_2–$C1_3$	100.5(1)
N_1–P_1–N_2	118.2(4)	$C1_4$–P_3–$C1_5$	101.2(2)
N_2–P_2–N_3	119.8(3)		

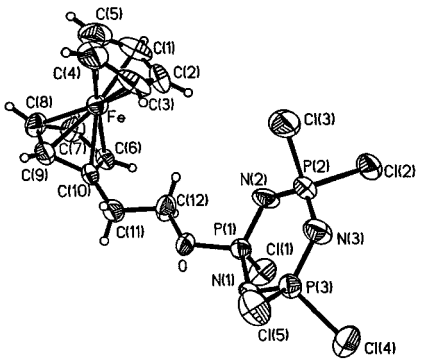

Fig. 3. Thermal ellipsoid drawing of $N_3P_3Cl_5(OCH_2CH_2C_5H_4FeCp)$ (**3**) showing the atom numbering scheme (50% thermal ellipsoids).

Table 2
Electrochemical data for ferrocenylalcohol derivatives of **1** (in CH_2Cl_2)

Compound	$E_{1/2}$ (mV)
$CpFeC_5H_4CH_2CH_2OH$ (**2**)	−54 [a]
$N_3P_3C1_5(OCH_2CH_2C_5H_4FeCP)$ (**3**)	−24 [b]
$N_3P_3C1_4(OCH_2CH_2C_5H_4FeCP)_2$ (**4**)	−4 [b]

[a] Ref. [22].
[b] Glass carbon electrode, Ag | AgCl reference electrode.

2.3. Electrochemistry

Electrochemical data provided by cyclic voltammetry for compounds **3** and **4** are presented in Table 2 and the cyclic voltammogram of **4** is presented in Fig. 4. The compounds exhibit electrochemically reversible one-electron oxidations at the metal center. Compound **2** has previously been characterized electrochemically, and E_2 was determined to be −54 mV relative to Cp_2Fe [22]. There is a +30 mV change in the potential of **3** compared to **2** and +51 mV change in **4**. The observed potential changes reflect the change in electron withdrawing ability of the X unit of $XO(CH_2)_2C_5H_4FeCP$ on going from **2** to **3** to **4**. In the case of **4**, both iron centers are oxidized at indistinguishable potentials. This suggests that there is no electronic communication between the two ferrocene centers through the cyclophosphazene.

3. Experimental

3.1. General procedures

All preparative reactions and chromatography were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Hexachlorocyclotriphosphazene (**1**, Nippon Soda Company, Ltd.) was purified by a process of sublimation, recrystallization from hexane, and farther sublimation. THF (Baker) was distilled over sodium benzophenone under N_2 prior to use. $CDCl_3$ was purchased from Cambridge Isotopes and used without any further purification. Bulk hexanes and CH_2Cl_2 were used as purchased. Lithium diisopropylamide (LDA), 1.5 M in hexanes, and *t*-butyl lithium, 1.7 M in pentane, were purchased from Aldrich. Literature procedures were followed for the preparation of ferrocenylethanol (**2**) [22] and ferrocenylmethanol [27].

All NMR spectra were obtained using a Bruker ARX-500 spectrometer. The H NMR spectra were recorded on compounds dissolved in $CDCl_3$ solution with residual $CHCl_3$ as the internal reference. ^{31}P NMR spectra were obtained in $CDCl_3$ with H_3PO_4 as the external reference. The $^{31}C\{^1H\}$ NMR spectra were recorded in $CDCl_3$ using the solvent as the reference. Mass spectra were determined on a Finnegan 4610 spectrometer operating at 70 eV and data are reported as monoisotopic peaks based on ^{35}Cl. Elemental analyses were performed by Carlson Microlit Labs. Infrared spectra were recorded on a Perkin Elmer Series 2000 FT-IR. NMR spectral simulations were performed us-

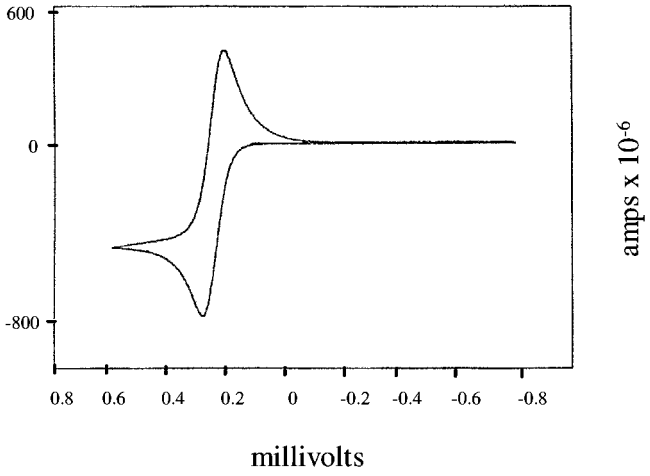

Fig. 4. Cyclic voltammogram of **3** in CH_2Cl_2 at 100 ms at glassy carbon electrode with Ag | AgCl reference electrode.

ing WIN-DAISY version 4.0 from Bruker. Entering atomic coordinates determined by X-ray crystallography into Chem 3D Pro version 4.0 from CambridgeSoft allowed for the RMS deviations from the plane to be calculated.

3.2. Preparation of $N_3P_3Cl_5OCH_2CH_2C_5H_4FeC_5H_5$ (3)

In a typical reaction, 0.1852 g (0.8 mmol) of **2** were placed in a flask with a stir bar and degassed. THF (10 ml) was added and the solution was cooled to − 78 °C. LDA (0.51 ml, 0.76 mmol) was added dropwise with stirring. The reaction stirred for 30 min while maintaining the temperature at − 78 °C. In a separate flask with a stir bar, **1** (0.2794 g, 0.8 mmol) was dissolved in 10 ml of the THF. The solution of **1** was cooled to − 20 °C and the ferrocenylethoxide solution was added dropwise with stirring to the solution of **1** while maintaining the temperature at − 20 °C. The reaction was allowed to slowly warm to room temperature (r.t.) and was stirred overnight. The solvent was removed in vacuo. The residue was dissolved in a minimal amount of dichloromethane and submitted to flash chromatography. Elution with hexanes removed any unreacted **1**. A yellow–orange band was eluded using a 5:1 (v/v) mixture of hexanes/methylene chloride. The solvent was removed in vacuo leaving an orange oil. The oil was dissolved in hexanes. Slow evaporation of the hexanes afforded **3** (0.2209 g, 50.7%) as orange crystals. Mass Spec. (CI): m/z 540.9 ([M^+], 1.90%), 505.9 (2.45, [M − Cl]), 248.9 (39.09, $CpFeC_5H_4CH_2CH_2Cl$), 213.0 (100, $CpFeC_5H_4CH_2CH_2$), 93.0(8.70, $C_5H_4CH_2CH_2$). ^1H NMR: δ 4.29 (2H, dt, $^3J(HP) = 9.68$, $^3J(HH) = 7.03$ Hz, $-OCH_2CH_2-$), 4.12 (5H, 5, Cp), 4.11, 4.09 (4H, AB pattern, C_5H_4), 2.79 (2H, t, $^3J(HH) = 7.03$ Hz, $-OCH_2CH_2-$). ^{13}C NMR: δ 69.60 (d, $^2J(Cp) = 8.34$ Hz, $-OCH_2CH_2-$) 68.70 (s, C_5H_4), 68.42 (s, Cp), 67.82 (s, C_5H_4), 67.71 (s, C_5H_4), 30.02 (s, $-OCH_2CH_2-$). ^{31}P NMR: δ 23.19 (d, $^2J(PP) = 62.19$ Hz, $-PCl_2-$), 15.44 (tt, $^2J(PP) = 61.91$ Hz, $^3J(HP) = 9.65$ Hz, $-PClOR-$). $^{31}P\{^1H\}$ NMR: δ 23.19 (d, $^2J(PP) = 61.89$ Hz, $-PCl_2-$), 15.44 (t, $^2J(PP = 61.92$ Hz, $-PClOR-$). Anal. Found: C, 26.96; H, 2.65; N, 7.52. Calc. for $C_{12}H_{13}Cl_5FeN_3OP_3$: C, 26.63; H, 2.42; N, 7.76%.

3.3. Preparation of $N_3P_3Cl_4(OCH_2CH_2C_5H_4FeC_5H_5)_2$ (4)

A 0.2936 g (1.27 mmol) sample of **2** was dissolved in THF (10 nml) and cooled to − 78 °C. LDA (0.85 ml, 1.27 mmol) was added dropwise and the reaction stirred for 30 min while maintaining the temperature at − 78 °C. In a separate flask, **1** (0.2240 g, 0.64 mmol) was dissolved in 10 nml of THF. The $N_3P_3Cl_6$ solution was cooled to − 20 °C. The procedure used for the preparation of **3** was then followed. Elution with hexanes removed any unreacted **1**. A small yellow–orange band of **3** was eluded using a 5:1 (v/v) mixture of hexanes/methylene chloride. An orange band was eluded using a 1:1 (v/v) mixture of hexanes/methylene chloride. Solvent was removed in vacuo giving **4** as an orange oil (0.2254 g, 48.3%). All attempts at crystallizing **4** were unsuccessful. Mass Spec. (CI) m/z 736.0 ([M^+], 0.12%), 248.9 (19.17, $CpFeC_5H_4CH_2CH_2Cl$), 213.0 (55.34, $CpFeC_5H_4CH_2CH_2$). ^1H NMR: δ 4.28 (2H, M, $-OCH_2-$). $^{13}C\{^1H\}$ NMR: δ 69.03 (s), 68.62(s), 68.34(s), 67.68 (s), 29.93 (s), 14.07 (s). $^{31}P\{^1H\}$ NMR: δ 25.61 (t, $^2J(PP) = 65.29$ Hz, *trans*-), 25.54 (t, $^2J(PP) = 66.38$ Hz, *cis*-), 23.97 (d, $^2J(PP) = 64.14$ Hz, *gem*-), 19.06 (d, $^2J(PP) = 65.35$ Hz, *trans*-), 18.86 (d, $^2J(PP) = 66.39$ Hz, *cis*-), 5.20 (t, $^2J(PP) = 64.04$ Hz, *gem*-). Anal. Found: C, 39.22; H, 3.57; N, 5.27. Calc. for $C_{24}H_{26}Cl_4Fe_2N_3O_2P_3$: C, 39.94; H, 3.65; N, 5.43%.

3.4. Preparation of 1-ferrocenyl-2-propanol (5)

A 250-ml flask was fitted with an addition funnel and was charged with 10.0 g (53.8 mmol) of ferrocene in 100 ml of THF. The solution was cooled to 0 °C and 27 ml of 1.7 M *t*-butyllithium in pentane (45.9 mmol) was added dropwise. This reaction was stirred for 20 min and then 2.5 ml of propylene oxide (35.7 mmol) was added rapidly. The reaction was allowed to warm to r.t. and stirred for 1 h. The reaction was quenched by carefully adding isopropanol until evolution of gas had stopped. The solvent was evaporated and the solids redissolved in diethyl ether and washed with 0.01 M HCl. The crude product was then purified by column chromatography using a silica gel column and 78/22 (v/v) diethyl ether/petroleum ether as an eluent. Solvent was removed in vacuo giving **5** (1.74 g, 20%). Mass Spec. (CI): m/z 224 [M^+]. ^1H NMR: δ 4.1 (9H, m, Cp), 3.7 (2H, m, CH_2), 2.4 (1H, m, $-CH$), 2.2 (1H, br S,

–O*H*), 1.1 (3H, d, ^3J(HH) = 6 Hz, CH_3). ^{13}C{^{1}H} NMR: δ 85.3 (s), 69.3 (s), 69.2 (s), 69.5 (s), 68.5 (s), 68.3 (s), 40.4 (s), 23.4 (s). IR (cm^{-1}): 3352 (OH), 2966 (CH); 1609 (C=C).

3.5. Preparation of $N_3P_3C1_5OCH(CH_3)CH_2C_5H_4FeC_5H_5$ (6)

To a round bottom flask 0.670 g of **5** was added to 10 ml of THF. This solution was cooled to −78 °C and LDA (0.17 ml, 2.5 mmols) was syringed in slowly. The reaction was allowed to stir for 25 min and then transferred to a flask with 1.07 g of **1** in 5 ml of THF cooled to −7 °C. After stirring for 10 min, the flask was allowed to warm to r.t. and react for 2 more h. The solvent was evaporated to an orange oil which was purified by column chromatography using a silica gel column and 96/4 (v/v) petroleum ether/diethyl ether. The solvent was removed giving **6** (1.05 g, 63%). Mass Spec. (CI):*m*/*z* 555 [M +]. ^{1}H NMR: δ 4.6 (1H, m, CB), 4.2–4.0 (9H, m, Cp), 2.8 (2H, dd, ^2J(HH) = 14, ^3J(HH) = 6Hz, CH_2), 2.7 (2H, dd, ^2J(HH) = 14 Hz, ^3J(HH) = 7 Hz, CH_2), 1.4 (3H, d, ^3J(HH) = 6 Hz, CH_3). ^{31}P NMR: δ 22.7 (complex d), 13.7 (td, ^2J(PP) = 62 Hz, ^3J(PH) = 12 Hz). ^{31}P{^{1}H} NMR: δ 22.7 (d, ^2J(PP) = 62 Hz), 13.7 (t, ^2J(PP) = 62 Hz). ^{13}C{^{1}H} NMR: δ 80.9 (d, ^3J(PC) = 8 Hz), 82.7(s), 70.1(s), 69.4(s), 68.8(s), 38.7 (d, ^3J(PC) = 6 Hz), 21.3 (d, ^3J(PC) = 4 Hz). IR (cm^{-1}) 1687 (C=C), 1221 (PN str), 1202 (PN str). Anal. Found: C, 28.32; H, 2.72; N, 7.57. Calc. for $C_{13}H_{15}C1_5FeN_3OP_3$: C, 28.12; H, 2.72; N, 7.57%.

3.6. Attempted preparation of $N_3P_3Cl_5OCH_2C_5H_4FeC_5H_5$

A solution of the sodium salt of ferrocenylmethanol was prepared by dissolving 0.51 g (2.37 mmol) of the alcohol in 15 ml THF. Sodium pieces (0.05 g, 2.17 mmol) were added to this flask and hydrogen gas was visibly evolved. The reaction was allowed to proceed for about 2 h at which time it was transferred by cannula to an addition funnel over a solution of 0.81 g (2.33 mmol) of **1** in 15 ml THF. Addition of the sodium salt proceeded slowly and upon completion the vessel was heated at 45 °C for 48 h. The mixture was then washed twice with aqueous saturated sodium chloride. The aqueous layer was a deep green–blue and the organic layer was orange. The THF layer was dried with magnesium sulfate and evaporated under reduced pressure. The compound was an orange oil that when dissolved in chloroform slowly decomposed and turned blue. IR: 1215 (PN stretch); 1100 (PO); 1040 (PO).

3.7. Crystal structure determination of 3

A crystal of **3** suitable for X-ray analysis was prepared by slow evaporation of a solution of **3**, in hexanes. A 0.5 × 0.2 × 0.1 orange crystal of **3** was mounted on a glass fiber and transferred to a Simens R3m/v diffractometer. The cell constants were determined from a random search routine. Data was collected using Mo–K$_\alpha$ (λ = 0.71073 Å) radiation. The structure was solved by direct methods and refined using full-matrix least-squares analysis. Hydrogen atoms were treated as riding atoms.

3.8. Crystal data and structure of refinement

$C_{12}H_{13}C1_5FeN_3OP_3$, M = 541.3, monoclinic, a = 10.411(2) Å, c = 12.955(2) Å, β = 106.44(1)°, V = 1006.6(3) Å^3, D_{calc} (g cm^{-1}) = 1.786, T = 298 K, space group $P2_1$, Z = 2, μ(Mo–K$_\alpha$) + 1.659 mm^{-1}, F(000) = 540, 1972 reflections measured, 1655 unique (R_{int} = 0.0710), which were used in all calculations. The final unweighted and weighted $\omega R(F^2)$ were 0.0470 and 0.0586, respectively. Goodness-of-fit was 0.67.

3.9. Electrochemistry

Electrochemical experiments were performed in CH_2Cl_2 using a PAR Model 273 potentiostat/galvanostat. A three-electrode configuration was used. The working electrode was a Pt disk (diameter 0.250 mm) sealed in glass. The reference electrode was an Ag wire with electrochemically deposited AgCl inside of a fritted glass tube. The counter electrode was a Pt wire inserted into the solution. Potentials were calibrated against Cp^*_2Fe. The experiments were carried out under a moisture free N_2 atmosphere using NBu_4PF_6 as the supporting electrolyte. Electrochemical data for compounds **3** and **4** are listed in Table 2.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 151298 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] H.R. Allcock, Phosphorus–Nitrogen Compounds, Academic Press, New York, 1972.
[2] H.R. Allcock, in: J.E. Marks, H.R. Allcock, R. West (Eds.), Inorganic Polymers, Ch. 3, Prentice Hall, Englewood Cliffs, NJ, 1991.
[3] C.W. Allen, in: I. Haiduc, D.B. Sowerby (Eds.), The Chemistry of Inorganic Homo- and Heterocycles, Ch. 20, vol. 2, Academic Press, London, 1987.
[4] C.W. Allen, Chem. Rev. 91 (1991) 119.
[5] C.W. Allen, Coord. Chem. Rev. 130 (1994) 137.
[6] H.R. Allcock, J.L. Desorcie, G.H. Riding, Polyhedron 6 (1987) 164.
[7] R.A. Saraceno, G.H. Riding, H.R. Allcock, A.G. Ewing, J. Am. Chem. Soc. 110 (1988) 7254.
[8] A.L. Crumbliss, D. Cooke, J. Castillo, P. Wisian-Neilson, Inorg. Chem. 32 (1993) 6088.
[9] C.W. Allen, M. Bahadur, J. Inorg. Organomet. Polym. 8 (1998) 23.
[10] W.E. Geiger, J. Organomet. Chem. Lib. 22 (1990) 142.
[11] C.N. Myer, C.W. Allen, Polym. Preprints 41 (2000) 558.
[12] C.W. Allen, C.N. Myer, Phosphorus, Sulfur Silicon Relat. Elem. 124–125 (1997) 431.
[13] R.F. Hayes, C.W. Allen, Phosphorus, Sulfur Silicon 93-94 (1994) 209.
[14] W.E. Watts, J. Organomet. Chem. Lib. 7 (1979) 399.
[15] E.T. McBee, K. Okuhara, C.J. Morton, Inorg. Chem. 5 (1966) 450.
[16] R. Keat, R.A. Shaw, M. Woods, J. Chem. Soc. Dalton Trans. (1976) 1582.
[17] K. Ramachandran, C.W. Allen, Inorg. Chem. 22 (1985) 1445.
[18] D.E. Brown, C.W. Allen, Inorg. Chem. 26 (1987) 934.
[19] C.W. Allen, D.E. Brown, S.D. Worley, Inorg Chem. 39 (2000) 810.
[20] J.L. Schmutz, H.R. Allcock, Inorg. Chem. 14 (1975) 2433.
[21] S.B. Lee, S.-C. Song, J.-I. Jin, Y.S. Sohn, J. Am. Chem. Soc. 122 (2000) 8315.
[22] C. Nataro, W.M. Cleaver, C.C. Landry, C.W. Allen, Polyhedron 18 (1999) 1471.
[23] (a) All phosphazene structures determined by X-ray diffraction are summarized in yearly reviews of the literature in this area: C.W. Allen, Organophosphorus Chemistry, vols. 16–28, Royal Society of Chemistry, London, 1986–1997;
(b) J.C. van de Grampel, Organophosphorus Chemistry, vols. 29–31, Royal Society of Chemistry, London, 1998–2000.
[24] (a) K. Brant, A.P. Jekel, A. Meetsma, J.C. van de Grampel, Inorg. Chim. Acta 157 (1989) 251;
(b) D.A. Murashov, V.I. Sokol, V.I. Moiseev, M.A. Porackoshits, I.A. Rozanov, A.I. Gusev, Russ. J. Inorg. Chem. 33 (1988) 203 (Engl. Transl.).
[25] A. Kilic, S. Begec, B. Centinkaya, T. Hokelek, Z. Kilic, N. Gunduz, M. Yildiz, Heteroatom Chem. 7 (1996) 249.
[26] G.J. Bullen, J. Chem. Soc. (A) (1971) 1450.
[27] G.D. Broadhead, J. Chem. Soc. (1958) 655.