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Isolation and X-ray Crystal Structure of a Phosphazene Anion

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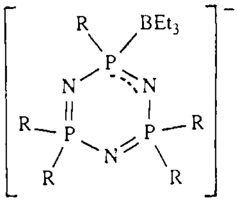
In recent years phosphazene anions **1** have played an important role in phosphazene chemistry as reactive intermediates of considerable synthetic utility.[1-6] Their importance arises from the possession of a nucleophilic skeletal phosphorus(V) atom which, via reaction with a wide variety of organic,[1,2] organometallic,[3] and transition-metal electrophiles,[4-6] allows the introduction of substituents to the phosphazene skeleton which are difficult or impossible to introduce via other methods. This chemistry has been exploited in the synthesis of new cyclotriphosphazene polymerization "monomers"[1,2] and novel polyphosphazenes at the macromolecular level.[6] However, despite their synthetic importance, the electronic structure of phosphazene anions has remained unclear. Indeed, in certain aspects of their chemistry, they appear to possess a phosphorus(III) center.[5] Furthermore, the possibility exists that most of the negative charge resides on skeletal nitrogen atoms. As a resolution of this question, we report the first isolation and X-ray crystal structure determination of a phosphazene anion.



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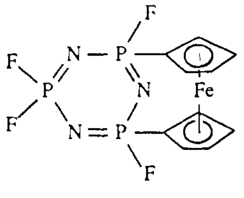

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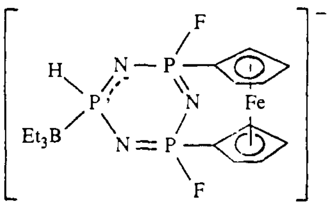

3

Addition of 3 equiv of $Li[BEt_3H]$ in THF to a cooled (ca. 5 °C) solution of the transannular ferrocenylphosphazene **2**[7] in the same solvent resulted in vigorous hydrogen evolution. After 3 h of reaction, ^{31}P NMR[8] provided evidence that **2** had been completely consumed. The major product (ca. 75%)[9] was identified by ^{1}H decoupled and coupled ^{31}P NMR spectroscopy as the phosphazene anion **3**. The ^{1}H decoupled ^{31}P NMR spectrum showed a doublet of doublets at 37.39 ppm ($^{1}J_{PF}$ = 900.8 Hz, $^{2}J_{PNP}$ = 18.5 Hz) assigned to skeletal phosphorus atoms which bear both a fluorine atom and a cyclopentadienyl group, and a broad, low field resonance at 78.1 ppm. The latter resonance split into a doublet in the ^{1}H coupled ^{31}P NMR spectrum ($^{1}J_{PH}$ = 344.2 Hz) and was assigned to a skeletal phosphorus atom bearing hydrogen and triethylborane substituents. Similar broad, low field resonances have been detected for other phosphazene anions.[1] Concentration of the reaction solution and dilution with diethyl ether, followed by slow cooling to −20 °C over 14 days afforded yellow-orange air and moisture-sensitive crystals. On manipulation, the crystals were also found to be sensitive to heat and light. After several unsuccessful attempts, a suitable single crystal was transferred without significant decomposition to an X-ray diffractometer with the probe protected from light and cooled to −50 °C.

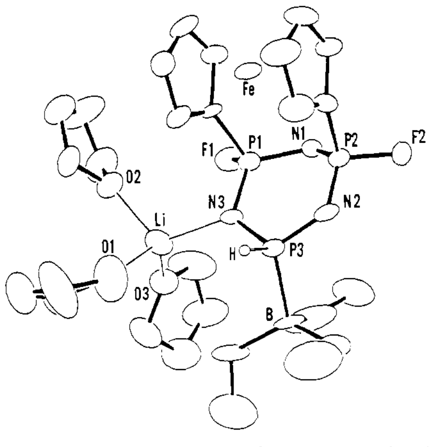

Figure 1. A computer-generated drawing of **3**. Important bond distances (Å) and angles (deg) are as follows: P(1)-N(1) 1.572 (5), N(1)-P(2) 1.588 (6), N(2)-P(3) 1.626 (5), P(3)-N(3) 1.674 (6), N(3)-P(1) 1.592 (6), P(3)-B 1.984 (9), N(3)-Li 2.06 (1), P(3)-H 1.268, P(1)-N(1)-P(2) 110.4 (3), N(1)-P(2)-N(2) 116.5 (3), P(2)-N(2)-P(3) 122.8 (4), N(2)-P(3)-N(3) 112.7 (3), P(3)-N(3)-P(1) 118.7 (3), N(3)-P(1)-N(1) 118.0 (3), N(2)-P(3)-B 115.4 (4), N(3)-P(3)-B 114.3 (3), P(1)-N(3)-Li 113.3 (5), P(3)-N(3)-Li 128.1 (5), B-P(3)-H 106.1.

The molecular structure found for **3** is shown in Figure 1.[10] Two skeletal phosphorus atoms of the phosphazene ring are bonded to both a fluorine atom and a cyclopentadienyl ring of the transannular ferrocenyl group. The remaining skeletal phosphorus atom bears hydrogen and triethylborane substituents. In addition, a skeletal nitrogen atom is coordinated to lithium, which is also bound to three THF solvent molecules. The transannular ferrocene unit and the triethylborane groups are located on opposite sides of the phosphazene ring, presumably for steric reasons. Dramatic differences are found in the bond lengths and angles in the environment of P(3) compared to the situation in **2**.[11] Thus, the lengths of the P(3)-N(3) and P(3)-N(2) bonds are 1.674 (6) and 1.626 (5) Å, respectively, which is appreciably longer than the corresponding value of 1.559 (2) Å for **2**. This bond lengthening is accompanied by a considerable narrowing of the N(2)-P(3)-N(3) bond angle to 112.7 (3)° compared with the value of 120.5 (1)° in **2**. In contrast, the P(2)-N(2)-P(3) angle is widened to 122.8 (4)° with respect to the corresponding angle in **2** of 118.4 (2)°. Surprisingly, the P(3)-N(3)-P(1) angle (118.7 (3)°) is similar to that in **2** (118.1 (1)°) despite the coordination of lithium to N(3). The P(3)-B bond length is 1.984 (9) Å and is consistent with a single bond.[12] The geometry of the phosphazene ring in the environment of P(1), N(1), and P(2) is similar to that found in **2**. Thus, the phosphazene ring shows considerable deviation from planarity, with atom N(1) displaced 0.63 Å from the plane

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(1) Allcock, H. R.; Connolly, M. S.; Whittle, R. R. *Organometallics* **1983**, *2*, 1514-1523.

(2) Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*, 119-157.

(3) Allcock, H. R.; Manners, I.; Mang, M. N.; Parvez, M., unpublished results.

(4) Nissan, R. A.; Connolly, M. S.; Mirabelli, M. G. L.; Whittle, R. R.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1983**, 822-824.

(5) Allcock, H. R.; Mang, M. N.; Riding, G. H.; Whittle, R. R. *Organometallics* **1986**, *5*, 2244-2250.

(6) Allcock, H. R.; Mang, M. N.; McDonnell, G. S.; Parvez, M. *Macromolecules* **1987**, *20*, 2060-2067.

(7) Allcock, H. R.; Lavin, K. D.; Riding, G. H. *Macromolecules* **1985**, *18*, 1340-1345.

(8) ^{31}P NMR spectra were recorded on a Bruker WM-360 instrument and referenced relative to external 85% H_3PO_4.

(9) Two other minor products are also formed, the characterization of which is under investigation.

(10) Crystal data for **3** at 223 K: formula $C_{28}H_{48}BF_2FeLiN_3O_3P_3$ monoclinic, space group $P2_1/c$ with a = 11.363 (3) Å, b = 27.701 (9) Å, and c = 11.667 (5) Å, β = 115.42 (4)°, V = 3316.8 Å^3, Z = 4, 2276 data with $I > 3\sigma(I)$, measured on an Enraf-Nonius CAD4 diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). The structure was solved by direct methods and refined by full-matrix least-squares calculations to R = 0.058, R_w = 0.078.

(11) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Whittle, R. R.; Parvez, M. *Organometallics* **1986**, *5*, 1626-1635.

(12) Bartlett, R. A.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6817-6819.

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defined by the remaining five ring atoms. In **2** the corresponding displacement is 0.62 Å. This type of distortion is attributed to the presence of the transannular ferrocenyl unit.[11]

The coordination of the lithium atom to N(3) in the solid state is consistent with a significant amount of the negative charge in **3** residing on the skeletal nitrogen atoms adjacent to P(3). Interestingly, the NMR spectra for **3** (see above) show that N(3) and N(2) are equivalent, which indicates that the lithium ion either dissociates from N(3) or fluctuates rapidly between N(3) and N(2) in solution at room temperature. These possibilities, together with the reactivity and mechanism of formation of **3**, are under investigation.

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Supplementary Material Available: An ORTEP drawing of **3** and tables of positional and displacement parameters and bond distances and angles (13 pages). Ordering information is given on any current masthead page.

A New Class of Amperometric Biosensor Incorporating a Polymeric Electron-Transfer Mediator

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Typical amperometric glucose electrodes based on glucose oxidase undergo several chemical or electrochemical steps which produce a measurable current that is linearly related to the glucose concentration. In the initial step, glucose converts the oxidized flavin adenine dinucleotide (FAD) center of the enzyme into its reduced form ($FADH_2$). Because these redox centers are located well within the enzyme molecule, direct electron transfer to the surface of a conventional electrode does not occur to any measurable degree. A common method of facilitating this electron transfer is to introduce oxygen into the system since it is the natural electron acceptor for glucose oxidase; the oxygen is reduced by the $FADH_2$ to hydrogen peroxide, which may then diffuse out of the enzyme and be detected electrochemically. Alternatively, one may use a nonphysiological redox couple to shuttle electrons between the $FADH_2$ and the electrode. Sensors based on derivatives of the ferrocene/ferricinium redox couple[2-4] and on electrodes consisting of organic conducting salts such as TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane)[5-9] have recently been reported. In clinical applications, however, sensors based on electron-shuttling redox couples suffer from an inherent drawback: the soluble mediating species can diffuse away from the electrode surface into the bulk solution, which would preclude their use as implantable probes.

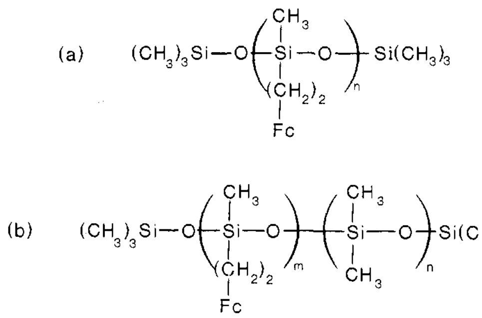

Figure 1. Schematic diagrams of the polymers used in the redox polymer/glucose oxidase/carbon paste electrodes: (a) methyl(ferrocenylethyl)siloxane homopolymer; (b) methyl(ferrocenylethyl)dimethylsiloxane copolymer. Fc refers to $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ or ferrocenyl; n is approximately 35 in the homopolymer; in the copolymer, the m:n ratio is approximately 1:2, with the subunits being randomly distributed (i.e., a random block copolymer).

With this in mind, we have investigated systems where the mediating species is chemically bound to a flexible polymer backbone which allows close contact between the FAD/$FADH_2$ centers of the enzyme and the mediator yet prevents the latter from diffusing away from the electrode surface. The resulting electron-transfer relay system acts in a manner similar to that described by Degani and Heller,[10,11] who chemically attached the electron relays to the enzyme itself. In the present work, however, the necessary electrical communication between the FAD/$FADH_2$ centers and the electrode has been achieved without modifying the enzyme, which can cause a measurable decrease in enzyme activity. The polymers used in this study are shown in Figure 1. The synthesis and characterization of these materials are described elsewhere;[12] the molecular weight of these polymeric materials is approximately 4000. Purification of the polymers was achieved by reprecipitation from chloroform solution, via dropwise addition into a large excess amount of acetonitrile at room temperature. This reprecipitation was repeated 2-3 times to ensure that no low molecular weight species (which could act as freely diffusing electron-transfer mediators) were present. Thin-layer chromatography and high-performance liquid chromatography showed that no oligomeric materials were present in the purified materials.

Figure 2 shows typical cyclic voltammetric results for carbon paste electrodes which were modified with each of the polymeric relay systems in Figure 1 and glucose oxidase. Carbon paste has previously been used for amperometric enzyme electrodes with freely diffusing redox mediators.[13,14] With no glucose present in solution, the voltammetry shows a ferrocene oxidation at approximately 0.3 V (vs the saturated calomel electrode, SCE) for a scan rate of 5 mV/s, while the corresponding reduction of the ferricinium ion occurs at 0.2 V; these values are typical for ferrocene derivatives.[2] Upon addition of glucose, the voltammetry changes dramatically, with a large increase in the oxidation current and a slight lowering of the reduction current. The fact that the reduction current does not increase along with the oxidation current is indicative of the enzyme-dependent catalytic reduction of the ferricinium ion produced at oxidizing potential values. Upon comparison of the voltammograms with and without glucose present, it is apparent that the polymer-bound ferrocene/ferricinium moieties can act as an efficient electron-transfer relay system between the FAD/$FADH_2$ centers of glucose oxidase and the carbon paste electrode.

In order to test the utility of the redox polymer/glucose oxidase/carbon paste electrodes as analytical probes, the catalytic current was measured at a constant applied potential for a large

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(2) Cass, A. E. G.; Davis, G.; Francis, G. D.; Hill, H. A. O.; Aston, W. J.; Higgins, I. J.; Plotkin, E. V.; Scott, L. D. L.; Turner, A. P. F. *Anal. Chem.* **1984**, *56*, 667-671.

(3) Lange, M. A.; Chambers, J. Q. *Anal. Chim. Acta* **1985**, *175*, 89-97.

(4) Iwakura, C.; Kajiya, Y.; Yoneyama, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1019-1020.

(5) Kulys, J. J.; Čėnas, N. K. *Biochim. Biophys. Acta* **1983**, *744*, 57-63.

(6) Albery, W. J.; Bartlett, P. N.; Craston, D. H. *J. Electroanal. Chem.* **1985**, *194*, 223-235.

(7) McKenna, K.; Brajter-Toth, A. *Anal. Chem.* **1987**, *59*, 954-958.

(8) Hale, P. D.; Wightman, R. M. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 269-279.

(9) Hale, P. D.; Skotheim, T. A. *Synth. Met.* **1989**, *28*, 853-858.

(10) Degani, Y.; Heller, A. *J. Phys. Chem.* **1987**, *91*, 1285-1289.

(11) Degani, Y.; Heller, A. *J. Am. Chem. Soc.* **1988**, *110*, 2615-2620.

(12) Inagaki, T.; Lee, H. S.; Skotheim, T. A.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.*, submitted for publication.

(13) Ikeda, T.; Hamada, H.; Senda, M. *Agric. Biol. Chem.* **1986**, *50*, 883-890.

(14) Dicks, J. M.; Aston, W. J.; Davis, G.; Turner, A. P. F. *Anal. Chim. Acta* **1986**, *182*, 103-112.

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