including for instance $[Fe(TPP)(H_2O)_2]^+$, which has a distance of 2.09 Å.[1] It is also longer than the 2.0-Å value assumed in sperm whale aquometmyoglobin.[15] The Fe-N(imidazole) distance of 2.132 Å is, however, similar to the corresponding distance in aquometmyoglobin and in horse hemoglobin.[15] An out-of-plane displacement of Fe of some 0.4 Å has been reported for the myoglobin structure whereas the present "in-plane" structure would support the reservations expressed by Scheidt and Reed[1] concerning the probable overestimation of such a displacement.

The high-spin ground state for the present complexes generally mirrors that of the aquomethemes although the zero-field splittings are less than those deduced for $MetHb(H_2O)$ from Mössbauer,[36] ESR,[37] and susceptibility measurements,[38] viz. $D \sim 10\ cm^{-1}$. Such differences in detail are perhaps not surprising in view of the relative ligand field symmetries and strengths of the Schiff-base and porphyrin systems. The similarity of the quadrupole splittings in the Mössbauer spectra of the protein and of the present compounds suggests, nevertheless, a not too dissimilar overall ligand field environment around the Fe atom.

Acknowledgment. This work was supported by grants from the Australian Research Grants Scheme and the Monash University Special Research Grants Fund. The authors are grateful to Dr. J. D. Cashion and students in the Physics Department at Monash University for generous help with Mössbauer measurements.

Registry No. 1, 95674-15-0; 2, 95674-17-2; 3, 95674-20-7; 4, 95674-22-9; Fe(3-MeO-salen)Cl, 62945-14-6; Fe(3-EtO-salen)Cl, 95674-23-0.

Supplementary Material Available: Listings of atom coordinates, anisotropic thermal parameters, and observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Organophosphazenes. 18. Friedel-Crafts Phenylation Reactions of Alkyl- and (Dimethylamino)fluorocyclotriphosphazenes[1]

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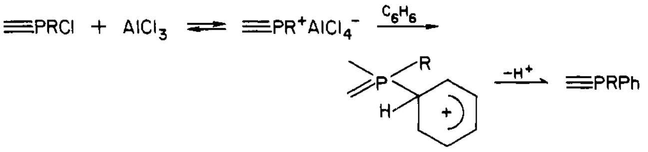
Received August 8, 1984

The (dimethylamino)- and butylpentafluorocyclotriphosphazenes, $N_3P_3F_5R$ ($R = N(CH_3)_2$, n-C_4H_9, t-C_4H_9), undergo the Friedel-Crafts phenylation reaction to yield $N_3P_3F_4(C_6H_5)R$. A geminal configuration was assigned to each of the phenyl derivatives on the basis of the NMR (^1H, ^{13}C, ^{31}P) spectroscopic data. The crystal and molecular structures of $N_3P_3F_4(C_6H_5)(t$-$C_4H_9)$ have been determined; the crystals are orthorhombic, space group *Pmma*, with $a = 7.264$ (1) Å, $b = 12.204$ (2) Å, $c = 17.028$ (3) Å, $V = 1509.5$ (7) Å^3, and $Z = 4$. The final refinement gave $R = 0.042$ and $R_w = 0.054$ for 1087 observed reflections. The molecule, which has a crystallographically imposed mirror plane of symmetry, has the predicted geminal arrangement of organic groups and P-N distances of 1.618 (1), 1.527 (2), and 1.565 (1) Å. The central P-N ring is planar within 0.007 Å. Bond angles are as follows: C-P-C = 108.9 (1)°; F-P-F = 96.36 (9)°; N-P-N = 114.1 (1), 120.91 (9)°; P-N-P = 122.58 (9), 118.9 (1)°. The observation of Friedel-Crafts phenylation of the alkylphosphazenes demonstrates that π donation from an exocyclic substituent is not a necessary prerequisite for this reaction.

Introduction

Friedel-Crafts arylation is a classic reaction[3] in phosphazene chemistry dating back to the pioneering studies of Bode and Bach.[4] The reaction can be used to produce geminal aryl groups in chloro[4,5] and fluorocyclophosphazenes.[6] The observation that the reaction usually yields geminal di-, tetra-, and hexaarylphosphazenes but not mono-, tri-, or pentasubstituted derivatives leads to the suggestion that a $\equiv PPhCl$ center is more reactive than a $\equiv PCl_2$ center. Aminochlorophosphazenes also undergo the Friedel-Crafts arylation reaction, which allows for conversion of a $\equiv PClNR_2$ center to a $\equiv P(Ph)NR_2$ center.[7] Depending on the nature of the amine, side reactions may also become significant. The phosphazo substituent also promotes Friedel-Crafts arylation at a $\equiv PCl(N{=}PPh_3)$ center.[8]

In spite of the synthetic utility of this reaction, little is known about the mechanism. The first step of the reaction is often assumed to be the formation of a phosphonium ion arising from halide abstraction by the Lewis acid:



Definitive evidence on this point has yet to become available. The addition compounds of aluminum tribromide with halocyclotriphosphazenes, $N_3P_3X_6{\cdot}nAlBr_3$ ($X = Cl$, $n = 1$; $X = Br$, $n = 1, 2$) are believed to have the aluminum tribromide entity coor-

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dinated to an endocyclic nitrogen atom.[9] Related addition compounds of $SbCl_5$ and $TiCl_4$ apparently involve the phosphonium ion.[10] Once the phosphonium ion forms, attack on the solvent (benzene) could lead to a cationic σ complex and deprotonation to the observed arylphosphazene. The assumption is implicitly or explicitly made that the facility of the Friedel–Crafts reaction at a $\equiv PXR$ (R = aryl, amino; X = F, Cl) center is due to stabilization of the positive charge (or developing positive charge) on the phosphorus atom by the electron-donating substituent, R.

In this paper, we wish to explore the nature of some of the electronic factors involved in the proposed stabilization of the positive charge on the phosphorus center and expand the range of systems that undergo the Friedel–Crafts arylation reaction.

Experimental Section

Materials and Methods. Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (Firestone Corp.), was converted to hexafluorocyclotriphosphazene,[11] which was in turn converted to (dimethylamino)pentafluorocyclotriphosphazene, $N_3P_3F_5N(CH_3)_2$,[12] (*n*-butyl)pentafluorocyclotriphosphazene, $N_3P_3F_5CH_2(CH_2)_2CH_3$,[13] and (*tert*-butyl)pentafluorocyclotriphosphazene, $N_3P_3F_5C(CH_3)_3$,[13] by previously reported procedures. Diethyl ether was distilled from sodium–benzophenone. Benzene[14] was distilled from sodium. Other reagents and solvents were obtained from standard sources and used without further purification. NMR spectra (in $CDCl_3$) were recorded on a Bruker WM250 spectrometer operating at 250.1 (^1H), 62.9 (^{13}C), and 101.2 MHz (^{31}P). Tetramethylsilane, Me_4Si (for ^1H and ^{13}C), was used as an internal reference. For ^{31}P NMR, 85% H_3PO_4 was used as an external reference. Chemical shifts upfield of the reference are assigned a negative sign. ^{13}C and ^{31}P NMR spectra were recorded under conditions of broad-band decoupling. Mass spectra were recorded on a Finnegan 4610 mass spectrometer operating at 80 eV. Elemental analyses were performed by Integral Microanalytical Laboratories.

Preparation of $N_3P_3F_4[N(CH_3)_2]C_6H_5$ (1). A solution of 2.65 g (0.01 mol) of $N_3P_3F_5N(CH_3)_2$ in 12 mL of benzene was added to a solution of triethylamine (2.8 g, 0.03 mol) and anhydrous aluminum chloride (9.3 g, 0.07 mol) in 50 mL of benzene.[14] The reaction mixture was allowed to stir at reflux for 5 days. The mixture was hydrolyzed over acidified ice water, and the layers were separated. The benzene layer was washed sequentially with saturated sodium bicarbonate solution and distilled water and then dried over anhydrous sodium sulfate and decolorized. After removal of the solvent, the yellow liquid was distilled at reduced pressure (0.02 mmHg) to yield 1.0 g (31.3% of theory) of a colorless oil, bp 60 °C (0.02 mmHg). Anal. Calcd for $N_4P_3F_4C_8H_{11}$: C, 28.92; H, 3.31; mol wt, 332. Found: C, 28.93; H, 3.49; mol wt, 332 (mass spectrum[15]). ^1H NMR:[16] $\delta_{N(CH_3)_2} = 2.6$ (d, 6 H), $^3J_{PH} = 12.9$; $\delta_{C_6H5\text{-}m,p} = 7.5$ (m, 3 H); $\delta_{C_6H_5\text{-}o} = 7.8$ (q, 2 H), $^3J_{PH} = 13.8$. ^{13}C NMR:[16] $\delta_{N(CH_3)_2} = 35.6$ (d), $^2J_{PC} = 3.5$; $\delta_{ArC_2} = 131.2$ (d), $^2J_{PC} = 10.7$; $\delta_{ArC_3} = 128.8$ (d), $^3J_{PC} = 14.9$; $\delta_{ArC_4} = 132.7$ (d), $^4J_{PC} = 3.1$. ^{31}P NMR: $\delta_{\equiv PF_2} = 10.2$ (m, 2 P), $^1J_{PF} = 916.0$;[17] $\delta_{\equiv PN(CH_3)_2C_6H_5} = 29.5$ (m, 1 P), $^2J_{PP} = 63.7$.

Preparation of $N_3P_3F_4[CH_2(CH_2)_2CH_3]C_6H_5$ (2). The procedure was identical with that described for the preparation of **1** except that $N_3P_3F_5CH_2(CH_2)_2CH_3$ was used in place of $N_3P_3F_5N(CH_3)_2$. In a typical experiment, the following quantities were allowed to react for 5 days: $N_3P_3F_5CH_2(CH_2)_2CH_3$ (2.00 g, 0.007 mol), triethylamine (2.52 g, 0.02 mol), and aluminum chloride (7.45 g, 0.06 mol). Distillation yielded a colorless oil whose ^{31}P NMR spectrum consisted of largely the unreacted starting material, small amounts of $N_3P_3F_4[CH_2(CH_2)_2CH_3]C_6H_5$ (less than 10%), and traces of other unidentified materials. Careful fractionation (35 °C at 0.02 mmHg) yielded an impure sample of the desired product. Anal. Calcd for $N_3P_3F_4C_{10}H_{14}$: C, 34.78; H, 4.06; mol wt, 345. Found: C, 29.43; H, 4.50; mol wt, 345 (mass spectrum[15]). ^1H NMR:[16] $\delta_{CH_2(CH_2)_2CH_3} = 1.9$ (m, 2 H); $\delta_{CH_2CH_2CH_2CH_3} = 1.5$ (m, 4 H); $\delta_{(CH_2)_3CH_3} = 0.9$ (m, 3 H); $\delta_{C_6H_5\text{-}m,p} = 7.5$ (m, 3 H); $\delta_{C_6H_5\text{-}o} = 7.8$ (q, 2 H), $^3J_{PH} = 13.3$. ^{13}C NMR: $\delta_{C_\alpha} = 33.6$ (m), $^1J_{PC} = 98.1$; $\delta_{C_{\beta,\gamma}} = 23.2$ (m, 2 C), $\delta_{C_\Delta} = 13.5$ (s); $\delta_{ArC_2} = 130.0$ (d), $^2J_{PC} = 11.0$; $\delta_{ArC_3} = 128.8$ (d), $^3J_{PC} = 12.9$; $\delta_{ArC_4} = 132.6$ (d), $^4J_{PC} = 3.4$. ^{31}P NMR (approximate): $\delta_{\equiv PF_2} = 7.1$, $^1J_{PF} = 883$;[17] $\delta_{\equiv P(C_4H_9)C_6H_5} = 37.8$, $^2J_{PP} = 36$.

Table I. Crystallographic Data

formula	$C_{10}H_{14}F_4N_3P_3$
fw	345.16
cryst syst	orthorhombic
space group, molecules/cell	*Pnma*, 4
a, Å	7.264 (1)
b, Å	12.204 (2)
c, Å	17.028 (3)
V, Å^3	1509.5 (7)
reflcns used for unit cell; 2θ range, deg	25; 24–37
calcd density, g cm^{-3}	1.52
F(000)	704
reflcns scanned, obsd	1529, 1087
2θ range of reflcns scanned, deg	2–50
μ(Mo Kα), cm^{-1}	4.2
final *R*, R_w	0.042, 0.054
max shift in final cycle (σ)	0.09
max peak (final diff map), e Å^{-3}	0.36
goodness of fit	2.36
parameters refined, parameter/reflcn ratio	122, 8.9

Preparation of $N_3P_3F_4[C(CH_3)_3]C_6H_5$ (3). The procedure was identical with that described above except that $N_3P_3F_5C(CH_3)_3$ was used as the phosphazene starting material. In a typical experiment, the following quantities were allowed to react for 5 days: $N_3P_3F_5C(CH_3)_2$ (3.80 g, 0.013 mol), triethylamine (4.10 g, 0.04 mol), and aluminum chloride (13.5 g, 0.10 mol). The yellow solid remaining after removal fo the benzene was sublimed to yield 1.78 g (39.0% of theory) of a milk white solid, mp 102–103 °C. Anal. Calcd for $N_3P_3F_4C_{10}H_{14}$: C, 34.78; H, 4.06; mol wt 345. Found: C, 35.05; H, 3.68; mol wt, 345 (mass spectrum[15]). ^1H NMR:[16] $\delta_{C(CH_3)_3} = 1.1$ (d, 9 H), $^3J_{PH} = 17.7$; $\delta_{C_6H_5\text{-}m,p} = 7.5$ (m, 3 H); $\delta_{C_6H_5\text{-}o} = 7.8$ (q, 2 H), $^3J_{PH} = 12.0$. ^{13}C NMR: $\delta_{C(CH_3)} = 33.9$ (m); $\delta_{ArC_2} = 131.9$ (d), $^2J_{PC} = 10.1$; $\delta_{ArC_3} = 128.2$ (d), $^3J_{PC} = 12.9$; $\delta_{ArC_4} = 132.5$ (d), $^4J_{PC} = 3.4$. ^{31}P NMR: $\delta_{\equiv PF_2} = 9.2$, $^1J_{PF} = 885.1$;[17] $\delta_{\equiv PPhC(CH_3)_3} = 46.1$, $^3J_{PP} = 36.1$.

Attempted Friedel–Crafts Reaction of $N_3P_3F_5OCH_2CH_3$. The procedure was identical with that described above except that $N_3P_3F_5OCH_2CH_3$ (prepared from $N_3P_3F_6$ and $LiOCH_2CH_3$) was used as the phosphazene starting material. No phosphazene-containing products were recovered from the benzene layer after hydrolysis.

X-ray Analysis of $N_3P_3F_4(C_6H_5)(t\text{-}C_4H_9)$. Crystals of **3** suitable for X-ray work were obtained by recrystallization from a petroleum ether–CH_2Cl_2 mixture. A colorless crystal of approximate dimensions 0.30 × 0.30 × 0.35 mm, mounted on a glass fiber, was used for data collection on an Enraf-Nonius CAD-4 diffractometer employing graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. A least-squares fit of the diffractometer setting angles for 25 carefully centered reflections (24° < 2θ < 37°) gave the unit cell parameters listed in Table I.

Systematic absences of 0*kl* (*k* + *l* odd) and *hk*0 (*h* odd) indicate the space group *Pna*2$_1$ (No. 33) or *Pnma* (No. 62); the centrosymmetric space group *Pnma* was verified by the refinement. Reflections were measured with use of ω–2θ scans for 2θ from 2 to 50° (*h* = 0–8, *k* = 14–0, *l* = 0–20). The scan range was $(1.00 + 0.35 \tan \theta)°$, and the scan speed varied from 20 to 4°/min. Of the 1529 reflections measured, 1087 had $I > 3\sigma(I)$ and were used in the refinement. Data were corrected for Lorentz and polarization effects, but due to the low linear absorption coefficient and regular shape of the crystal an absorption correction was not made. Periodic measurement of the intensities of three reflections (2,9,0, 4,0,4, 0,5,11) indicated a 28% decline during the 13.2 h of data collection, and intensities were corrected accordingly.

The structure was solved by direct methods (MULTAN80)[18] and refined by full-matrix least-squares techniques. The molecule has a crystallographically imposed mirror symmetry. Hydrogen atoms were located with use of difference Fourier techniques and were included in the refinement. The final cycle of refinement based on $(|F_o| - |F_c|)^2$ included positional and anisotropic thermal parameters for all non-hydrogen atoms and positional parameters for the hydrogen atoms. The isotropic thermal parameter of each hydrogen atom was constrained at a value 20% greater than the B_{eq} value of the carbon atom to which it was attached. The final refinement gave R[19] = 0.042 and R_w[20] = 0.054. The weighting scheme

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(14) Benzene is a known carcinogen and hence should be only used in a well-ventilated hood while appropriate protective gloves are worn.
(15) Mass spectral data are available as supplementary material.
(16) All NMR (^1H, ^{13}C, ^{31}P) coupling constants are in Hz.
(17) Due to considerable second-order character, the $^1J_{PF}$ values are only approximate.
(18) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M.. "MULTAN80-A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", University of York, York, England, and University of Louvain, Louvain, Belgium.
(19) $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.

Table II. Positional Parameters[a]

atom	*x/a*	*y/b*	*z/c*	B_{eq}, Å^2
P1	0.9951 (1)	0.250	0.52490 (5)	3.57 (2)
P2	0.8471 (1)	0.13958 (6)	0.65138 (4)	4.48 (2)
F1	0.6759 (3)	0.0679 (2)	0.6496 (1)	7.04 (4)
F2	0.9549 (3)	0.0696 (2)	0.7091 (1)	7.84 (5)
N1	0.7965 (5)	0.250	0.6928 (2)	5.21 (8)
N2	0.9409 (3)	0.1388 (2)	0.5711 (1)	4.32 (5)
C1	0.8770 (5)	0.250	0.4331 (2)	3.80 (8)
C2	0.8298 (4)	0.1522 (2)	0.3968 (2)	5.11 (7)
C3	0.7363 (5)	0.1539 (3)	0.3267 (2)	7.05 (9)
C4	0.6923 (7)	0.250	0.2920 (3)	7.4 (1)
C5	1.2400 (5)	0.250	0.5068 (2)	4.75 (9)
C6	1.2928 (5)	0.1476 (3)	0.4606 (2)	6.62 (8)
C7	1.3385 (7)	0.250	0.5869 (3)	9.6 (2)
H2*	0.854 (4)	0.085 (2)	0.421 (2)	6
H3*	0.717 (4)	0.103 (3)	0.304 (2)	8
H4*	0.624 (8)	0.250	0.254 (3)	11
H61*	1.233 (4)	0.156 (3)	0.412 (2)	7
H62*	1.422 (5)	0.150 (3)	0.452 (2)	7
H63*	1.251 (4)	0.079 (3)	0.491 (2)	7
H71*	1.480 (8)	0.250	0.571 (4)	11
H72*	1.294 (5)	0.194 (3)	0.625 (2)	11

[a] Atoms marked with an asterisk were refined isotropically.

used was $w = [\sigma^2(F) + 0.03F^2]^{-1}$, where $\sigma(F)$ was derived from counting statistics. The goodness of fit[21] was 2.36. In the final cycle of refinement the maximum shift/error was 0.09. The final difference map has a maximum value of 0.36 e/Å^3. No secondary extinction correction was made. The atomic scattering factors for neutral atoms were those of Cromer and Waber,[22] and the real and imaginary dispersion corrections were those of Cromer.[23] The computer programs used were those provided by the Enraf-Nonius Structure Determination Package.

Results and Discussion

The synthetic results show that a fluorine atom in both alkyl- and (dimethylamino)pentafluorocyclotriphosphazenes can be conveniently replaced by a phenyl group under Friedel–Crafts conditions. Although (dialkylamino)chlorophosphazenes have previously been shown to undergo Friedel–Crafts phenylation,[7] we report the first example of the corresponding reaction in the fluorophosphazene series and the first example of Friedel–Crafts phenylation of an alkylphosphazene. The new compounds (**1**–**3**) have all been characterized by elemental analysis, mass spectrometry, and NMR (^1H, ^{13}C, ^{31}P) spectroscopy. Observations of the stereochemical course of the Friedel–Crafts phenylation of other cyclophosphazenes[4–7] leads to the suggestion of a geminal substitution pattern being followed in the synthesis of **1**–**3**. The observed values of the $^2J_{PCC}$[24] and $^3J_{PCCH}$[25] coupling constants in **1**–**3** are consistent with geminal rather than nongeminal configurations. The ^{31}P NMR spectrum of each of the new compounds shows a large, complex triplet ($J_{PF} \approx$ 883–916 Hz) due to the $\equiv PF_2$ centers and a small ($J_{PP} \approx$ 36 Hz) triplet due to the $\equiv$PR(Ph) center. The lack of a doublet due to a $\equiv$PFR (or $\equiv$PFPh) center confirms the absence of nongeminal products.

The crystal and molecular structures of **3** were determined in order to verify the proposed geminal configuration and to explore the structural consequences of the sterically crowded environment arising from substitution of both a phenyl and *tert*-butyl group on the same phosphorus atom. The final atomic coordinates of all unique atoms are given in Table II. Selected bond lengths and bond angles may be found in Table III, and an ORTEP drawing of the molecule, together with the atom-numbering scheme, is shown in Figure 1. The observed molecular structure of **3** confirms the geminal configuration of organic functions on the phosphazene. The solid-state structure of **3** is such that the phosphazene ring is bisected by a mirror plane containing N1, P1, C1, C4, H4, C5, C7, and H71. The conformations adopted by the phenyl and *tert*-butyl groups lead to the minimum amount of steric interaction between the two groups. A comparison of the structure of **3** with the structue of the previously reported geminal diphenyltetrafluorocyclotriphosphazene 2,2-$N_3P_3F_4(C_6H_5)_2$ (**4**)[26] is of interest. In **4** five of the six phosphazene ring atoms are close to coplanarity, with the phenyl-substituted phosphorus atom 0.20 Å out of this plane. In **3** the central ring is more nearly planar (within 0.007 Å): the P_3N_2 segment which excludes the unique nitrogen atom is planar within 0.001 Å and the N1 atom is displaced only 0.014 (3) Å from this plane. In a comparison of **3** to **4** a small effect of the increased steric demand of the *tert*-butyl group over the phenyl group is seen in the bond angles at the organo-substituted phosphorus atom (C–P–C = 108.9 (1)° for **3** and 107.9 (3)° for **4**; N–P–N = 114.1 (1)° for **3** and 115.3 (3)° for **4**). The phosphorus–nitrogen bond lengths are virtually identical in **3** and **4**, vary in a manner that is typical of asymmetrically substituted phosphazenes, and can be correlated with the relative ability of each phosphorus center to attract nitrogen lone-pair electron density.[26] The small differences in P–N distances of P_2 are consistent with the effect of replacing an sp^2 carbon atom (in **4**) by an sp^3 carbon atom (in **3**), resulting in a decrease of electron-attracting power of the organo-substituted phosphorus atom. Consequently, the lone pair of electrons at N2 is more strongly attracted to P2 in **3** than in **4**. The increased charge density on P2 in **3** results in less charge delocalization from N1 and hence a longer P2–N1 distance in **3** vs. that in **4** (1.565 (1) vs. 1.555 (4) Å).

Table III. Selected Distances (Å) and Angles (deg) for $N_3P_3F_4(C_6H_5)(C_4H_9)$[a]

P1–N2	1.618 (1)	C1–C2	1.387 (2)
P1–C1	1.784 (3)	C2–C3	1.374 (3)
P1–C5	1.806 (3)	C3–C4	1.351 (4)
P2–F1	1.521 (1)	C5–C6	1.526 (3)
P2–F2	1.520 (1)	C5–C7	1.540 (5)
P2–N1	1.565 (1)	C–H (av)	0.93 (9)
P2–N2	1.527 (2)		
N2–P1–N2	114.1 (1)	F2–P2–N2	110.21 (8)
N2–P1–C1	108.04 (7)	N1–P2–N2	120.91 (9)
N2–P1–C5	108.82 (8)	P2–N1–P2	118.9 (1)
C1–P1–C5	108.9 (1)	P1–N2–P2	122.58 (9)
F1–P2–F2	96.36 (9)	P1–C1–C2	120.6 (1)
F1–P2–N1	108.2 (1)	P1–C5–C6	109.6 (2)
F1–P2–N2	110.06 (8)	P1–C5–C7	107.9 (2)
F2–P2–N1	108.3 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

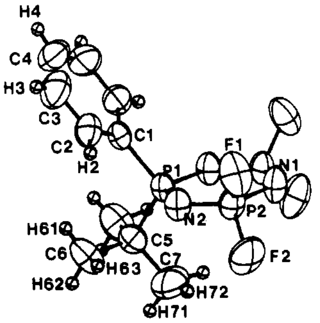

Figure 1. ORTEP drawing (50% probability ellipsoids) of 2,2-$N_3P_3F_4(C_6H_5)(C_4H_9)$ showing the atom-numbering scheme.

One of the goals of this study was to probe substituent electronic effects that may be operative in the Friedel–Crafts phenylation reaction. Since previous investigations have employed exocyclic groups which are potential π donors to the phosphorus center,

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(20) $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

(21) GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

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alkylpentafluorocyclotriphosphazenes were examined in order to clarify differences between σ and π donor substituent effects. The fact that the alkylphosphazenes undergo the phenylation reaction unambiguously demonstrates that π donation from the exocyclic function is not a necessary prerequisite for this reaction to be effective. The significantly higher yield in the reaction of *tert*-butyl vs. the *n*-butyl phosphazene suggests the operation of a mechanism wherein the phoshorus atom undergoing substitution goes to a lower coordinate intermediate (or transition state). This process would be most favorable for the *tert*-butyl derivative, where the maximum relief of steric strain can be obtained. A reasonable model for the Friedel–Crafts phenylation reaction of substituted phosphazenes is one in which the substituted phosphorus atom goes through a three-coordinate phosphorus(V) intermediate which is stabilized by the σ-electron-releasing nature of the substituent. It is possible that, in the phenyl and dialkylamino systems, the σ-electron-releasing effect may be supplemented by a π effect, but conclusive evidence of this has yet to be presented. The reluctance of the ethoxypentafluorocyclotriphosphazene to enter into the Friedel–Crafts reaction is consistent with these proposals since the high electronegativity of the oxygen atom makes it a poor electron-releasing substituent and the small size does not allow for significant relief of steric strain on going to a lower coordinate transition state intermediate.

Acknowledgment. Phosphazene chemistry at the University of Vermont is supported in part by the Office of Naval Research. We wish to thank Firestone Corp. for a generous gift of hexachlorocyclotriphosphazene and Mr. Weglarz for checking certain synthetic results. The X-ray work at Arkansas was supported by the State of Arkansas and the National Science Foundation (EPSCOR Grant ISP801147).

Registry No. 1, 95979-67-2; 2, 95979-68-3; 3, 95979-69-4; $N_3P_3F_5N(CH_3)_2$, 23208-17-5; $N_3P_3F_5CH_2(CH_2)_2CH_3$, 650-08-8; $N_3P_3F_5C(CH_3)_3$, 81095-56-9; $N_3P_3F_5OCH_2CH_3$, 33027-66-6; C_6H_6, 71-43-2.

Supplementary Material Available: Table S1 showing major mass spectral fragments and their intensities, Table S2 showing structure factor amplitudes for $N_3P_3F_4(C_6H_5)(C_4H_9)$, and Table S3 showing anisotropic thermal parameters for $N_3P_3F_4(C_6H_5)(C_4H_9)$ (13 pages). Ordering information is given on any current masthead page.

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Structure and Superconductivity in Lithium-Intercalated Niobium Dichalcogenides

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Received August 11, 1983

The series Li_xNbS_2 ($0 \le x \le 0.50$) and Li_xNbSe_2 ($0 \le x \le 0.67$) have been prepared by high-temperature reaction of Li_2S, Nb, and S or Li_2Se, Nb, and Se. Structures have been determined by analysis of X-ray powder patterns with polytypism observed in the sulfide series. Evidence of staging and Li ordering is reported, and crystal parameters are proposed for a second-staged sample, $Li_{0.2}NbSe_2$. In the series Li_xNbSe_2, T_c exhibits a monotonic decrease with increasing lithium content, falling to less than 2 K by $x = 0.25$. In contrast, in the Li_xNbS_2 series, T_c exhibits a more complicated pattern with T_c plummeting to below 2 K by $x = 0.05$, only to rebound to 3.7 K at $x = 0.33$ and then fall to below 2 K by $x = 0.4$.

Introduction

Among the many unusual properties of the layered transition-metal dichalcogenides, one of the most interesting is the occurrence of moderately high superconducting critical temperatures (6.4 K for NbS_2 and 7.8 K for $NbSe_2$). The superconducting critical temperature, T_c, has been shown to be dependent upon, among other things, the rigidity of the crystal lattice and the density of electronic states, $N(E_F)$, at the Fermi level. If we add electrons to a superconducting material, we expect to see, depending on the shape of the conduction band, either an increase or a decrease in T_c. In many layered materials the Fermi level may be adjusted by the intercalation of alkali metals. Intercalation results in charge transfer from the guest alkali-metal atom to the host dichalcogenide. The intercalate may also alter the structure of the host and may itself form an ordered array within the host. Alkali-metal intercalation of superconducting layered transition-metal dichalcogenides, therefore, promises to yield a host of possible structural and electronic effects, and T_c provides a sensitive tool by which to measure them.

In the present work we have prepared at high temperature two series of alkali-metal intercalated transition-metal dichalcogenides, Li_xNbSe_2 and Li_xNbS_2 ($0 \le x < 1$). We have examined the basic structural parameters, *a* and *c*, and have followed the change in T_c brought on by intercalation.

Experimental Section

For Li_xNbS_2, the starting materials were niobium foil ("Marz" grade, from Materials Research Corp.), Li_2S (99.9%, Cerac, Inc.), and sulfur (99.9999%, Atomergic Chemicals Corp.). X-ray analysis of the commercial Li_2S yielded no evidence of impurities. Amounts of Nb, Li_2S, and S, calculated to give a total sulfur overpressure of 8 atm at the anneal temperature of 750 °C, were added to degassed heavy-walled fused silica tubes in a helium-atmosphere Dri-Lab. After evacuation to 10^{-6} torr, the tubes were sealed and the samples were gradually raised to 950 °C over a period of 8 days. After 1 week at 950 °C, the samples were cooled (at 5 °C/h) to 750 °C, annealed at 750 °C for 4 days, and then quenched into cold water. (Quenching separates the product from the excess sulfur and prevents formation of NbS_3.) All of the samples were then thoroughly ground in the Dri-Lab, resealed with an appropriate amount of sulfur, heated to 950 °C for 1 week, annealed at 750 °C, and quenched.

The products were silvery polycrystalline materials or black finely divided powders. The crystallinity of the samples increased with lithium concentration. It was not possible to make Li_xNbS_2 ($x > 0.50$) samples in this way because of tube attack by the lithium.

Nominally stoichiometric $LiNbS_2$ was obtained by reaction of niobium disulfide with excess *n*-butyllithium in hexane. The mixture was allowed to sit for 10 days (in a nitrogen-atmosphere drybox) and then filtered and rinsed with dry hexane. The product was dried under vacuum and stored, together with all the other samples, in the Dri-Lab. The Li_xNbS_2 samples were found to be only moderately moisture sensitive and could be handled in air for brief periods.

Samples of nominal composition Li_xNbSe_2 ($0 \le x \le 0.67$) were prepared by direct, high-temperature reaction of "Marz" grade niobium foil, Li_2Se (99.9%, Cerac, Inc.), and selenium (99.9999%, Atomergic Chemical Corp.). Samples were prereacted at 400 °C for 1 day and then heated gradually from 600 to 800 °C at 5 °C/h. They were were kept at 800 °C for 1 week, slow-cooled to room temperature, ground in a Dri-Lab, resealed, and heated up to 800 °C again. After a final treatment of 5 days, they were slow-cooled to room temperature. All of the materials were silver-green microcrystalline powders. It was not possible to make Li_xNbSe_2 with $x > 0.67$ this way because of tube attack by lithium. As before, nominally stoichiometric $LiNbSe_2$ was prepared by reaction of $NbSe_2$ with *n*-butyllithium. All of the Li_xNbSe_2 products were moisture sensitive.

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