Articles

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Quaternized Cyclic and High Polymeric Phosphazenes and Their Interactions with Tetracyanoquinodimethane

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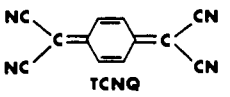
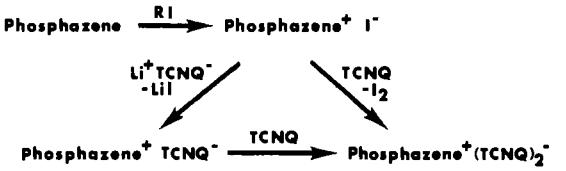
Small-molecule cyclotri- or cyclotetraphosphazenes and their linear high polymeric analogues bearing amino, phosphino, or organohalogeno side groups have been quaternized by treatment with methyl iodide or triphenylphosphine. Quaternization occurred at the side-group sites except with the piperidino derivatives, where the reactive sites were the skeletal nitrogen atoms. The quaternized species reacted with lithium 7,7,8,8-tetracyanoquinodimethane (LiTCNQ) to generate TCNQ "simple salts", and these (or their onium precursors) reacted with neutral TCNQ to generate the "complex salts". The electrical conductivities of the cyclic trimeric phosphazene complex salts (10^{-3}–10^{-2} Ω^{-1} cm^{-1}) were higher than those of their high polymeric counterparts.

This work forms part of a general investigation of the way in which different side-group structures affect the chemical and physical properties of ring systems and high polymers based on a phosphazene skeleton.[1-3] In earlier studies we have explored the influence of simple alkoxy, aryloxy, or amino side groups,[4,5] biologically active side groups, such as steroidal,[6] amino acid ester,[7] procaino,[8] or heparin units,[9] metalloporphyrin structures,[10] and, most recently, transition-metal organometallic units.[11,12] In this paper we describe an extension of these general principles to the quaternization of a variety of cyclic and high polymeric phosphazenes and to the use of the resultant onium derivatives for salt formation with 7,7,8,8-tetracyanoquinodimethane (TCNQ).[13-23]

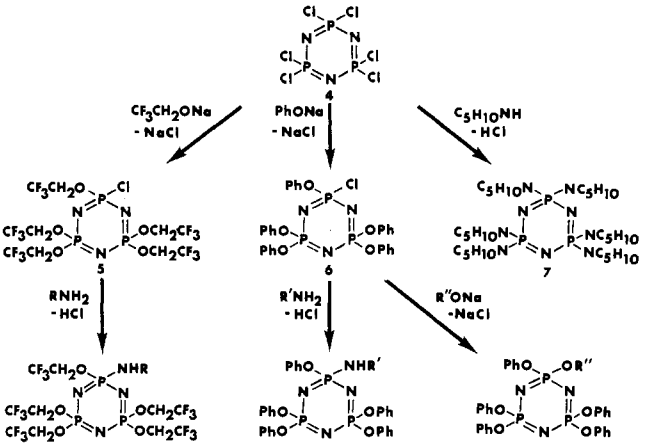


TCNQ forms two series of crystal-stacked, salt-like, electroactive complexes. In the first, TCNQ accepts an electron from a metal or organic donor to yield so-called "simple" salts of formula $M^{n+}(TCNQ^{-})_n$.[24] The TCNQ radical anions form electrically conducting stacks in the crystal structure. Such simple salts generally have low to intermediate level electrical conductivities (10^{-12}–10^{-4} Ω^{-1} cm^{-1}). The second class consists of the so-called "complex" salts formed by the addition of neutral TCNQ to the simple-salt structures, to give species of formula $M^{+n}(TCNQ^{-})_n(TCNQ)$. Many complex salts have high electrical conductivities (10^{-3}–10^{2} Ω^{-1} cm^{-1}).[25]

Scheme I



Scheme II



Our objective was to investigate the influence of the attachment of TCNQ units on the behavior of rigid cyclophosphazene molecules (**2**) (which might themselves be induced to stack in a

(1) Allcock, H. R. *ACS Symp. Ser.* **1983**, *No. 232*, 49.
(2) Allcock, H. R. *Sci. Prog. (Oxford)* **1980**, *66*, 355.
(3) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.
(4) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(5) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1016.
(6) Allcock, H. R.; Fuller, T. J. *Macromolecules* **1980**, *13*, 1338.
(7) Allcock, H. R.; Fuller, T. J.; Mack, D. P.; Matsumura, K.; Smeltz, K. M. *Macromolecules* **1977**, *10*, 824.
(8) Allcock, H. R.; Austin, P. E.; Neenan, T. X. *Macromolecules* **1982**, *15*, 689.
(9) Neenan, T. X.; Allcock, H. R. *Biomaterials* **1982**, *3*, 2, 78.
(10) Allcock, H. R.; Greigger, P. P.; Gardner, J. E.; Schmutz, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 606.
(11) Allcock, H. R.; Lavin, K. D.; Tollefson, N. M.; Evans, T. L. *Organometallics* **1983**, *2*, 267.
(12) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Suszko, P. R.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2337.
(13) Goodings, E. P. *Chem. Soc. Rev.* **1976**, 95.
(14) Herman, A. M.; Yen, S. P. S.; Rembaum, A.; Landel, R. F. *J. Polym. Sci., Polym. Lett. Ed.* **1971**, *9*, 627.
(15) Watanabe, M.; Tschikura, A.; Kamiya, T.; Shinohara, I. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 331.
(16) Lupinski, J. H.; Kopple, K. D.; Hertz, J. J. *J. Polym. Sci., Part C* **1967**, *16*, 1561.
(17) Hadek, V.; Noguchi, H.; Rembaum, A. *Macromolecules* **1974**, *4*, 494.
(18) Ciesielski, W.; Kryszewski, M. *Rocz. Chem.* **1976**, *50*, 947.
(19) Kamiya, T.; Goto, K.; Shinohara, I. *J. Polym. Sci., Chem. Ed.* **1979**, *17*, 561.
(20) Goodings, E. P. *Discuss. Faraday Soc.* **1971**, *51*, 157.
(21) Pittman, C. U.; Surnarayanan, B. *J. Am. Chem. Soc.* **1974**, *96*, 7916.
(22) Pittman, C. U.; Surnarayanan, B.; Sakasaki, Y. *Adv. Chem. Ser.* **1976**, *No. 150*, 46.
(23) Hertler, W. R. *J. Org. Chem.* **1976**, *41*, 1412.
(24) Pecherz, J.; Ciesielski, W.; Kryszewski, N. *Macromolecules* **1981**, *14*, 1139.
(25) Melby, L. R.; Harder, P. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1962**, *84*, 3374.

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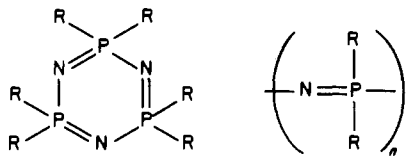
crystalline lattice) and on the properties of high polymeric phosphazenes (**3**) in which the conformational mobility of the



2 **3**

n = 10 000-15 000

polymer chain might be constrained by TCNQ stacking or in which collinear orientation of the long polymer chains might generate a stabilizing framework for TCNQ stacking in a matrix that could be shaped into films and fibers.

Small-molecule and high polymeric phosphazenes are especially appropriate as carrier species for TCNQ because (a) many different cosubstituent groups can be attached to the skeleton, with a known influence on crystal structure, polymer conformation, or conformational mobility and (b) two different salt-forming sites for TCNQ were available—organic side groups and the skeletal nitrogen atoms.

Results and Discussion

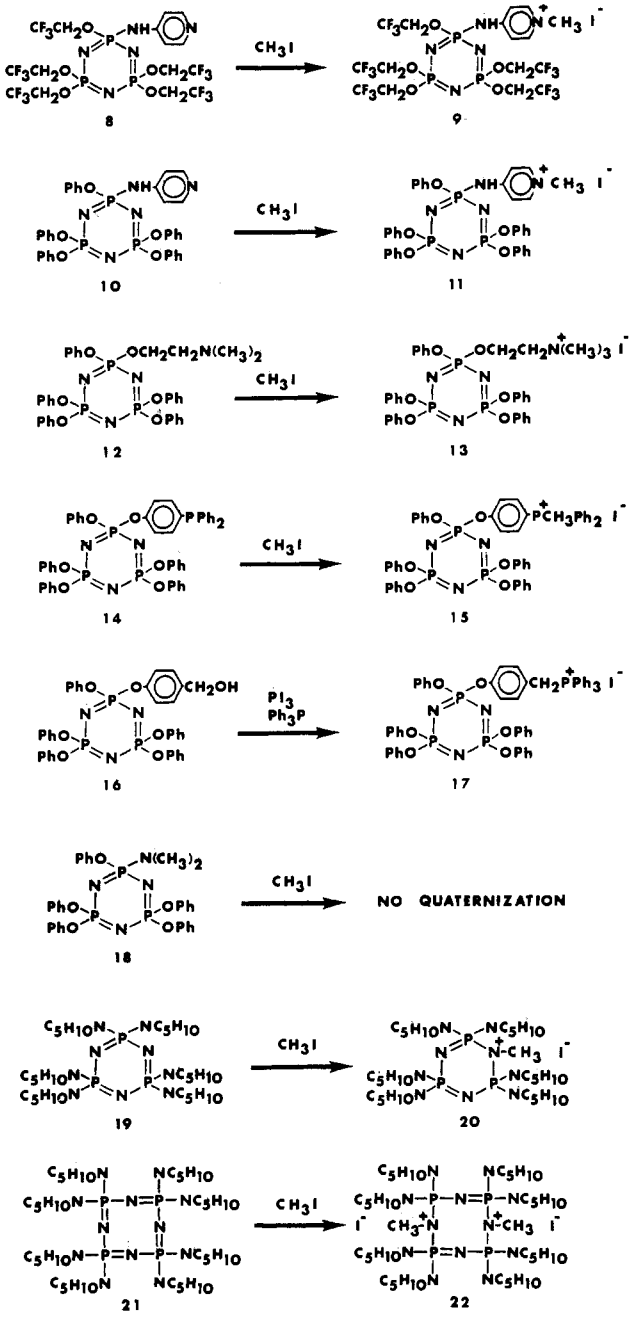
Synthesis of Cyclic Trimers. The synthesis strategy consisted of three parts: (a) preparation of phosphazene-onium iodide salts by quaternization of several cyclic and polymeric phosphazenes (phz) either at side-group sites or at the skeletal nitrogen atoms; (b) reaction of the phosphazene-onium salts with lithium TCNQ to yield simple-salt species of type phz^+ $TCNQ^-$; (c) treatment of phz^+TCNQ^- with neutral TCNQ to yield the complex salts $phz^+TCNQ^-{\cdot}TCNQ$ or direct reaction between the quaternary salts and neutral TCNQ to give the complex TCNQ salts. These routes are illustrated in Scheme I.

The synthesis of the small-molecule phosphazene-onium iodide salts was accomplished, starting from $(NPCl_2)_3$ (**4**), by replacement of five chlorine atoms by CF_3CH_2O or C_6H_5O groups (**5** and **6**) or of six chlorine atoms by piperidine (**7**), as illustrated in Scheme II. Subsequent reaction of **5** or **6** with various functional nucleophiles yielded **8**, **10**, **12**, **14**, **16**, and **18** (Scheme III). Details of these transformations are given in the Experimental Section. Subsequent treatment of these species with methyl iodide or triphenylphosphine yielded **9**, **11**, **13**, **15**, and **17**, quaternized at the side-group nitrogen or pendent phosphorus sites. Treatment of species **19** with methyl iodide resulted in quaternization of one *skeletal* nitrogen atom. The cyclic tetramer (**21**) was quaternized at two distal skeletal nitrogen atoms (**22**), a result that suggests an insight into the behavior of the analogous high polymers. Species **18** could not be quaternized. This last result is of special interest because it illustrates the shielded or deactivated nature of side-group nitrogen atoms linked directly to the phosphazene ring. The choice of the phenoxy cosubstituent group in **10–18** was based on the perceived need to reduce the basicity of the skeletal nitrogen atoms to favor the quaternization at the pendent sites. Some steric shielding of these sites by phenoxy groups was also anticipated.

Structural characterization of the cyclic trimers was by means of elemental microanalysis, infrared and electronic spectroscopy, ^1H and ^{31}P NMR spectroscopy, and electron-impact mass spectrometry (see Table I).

Synthesis of the Polymers. These syntheses followed the pattern established at the small-molecule, cyclic trimer or tetramer level. Specifically, hexachlorocyclotriphosphazene (**4**) was polymerized thermally to linear high molecular weight poly(dichlorophosphazene)[26] (**23**) (Scheme IV). As shown in our earlier

Scheme III



publications,[4,5] this polymer is an excellent macromolecular reactive intermediate that, in solution, serves as a substrate for a wide range of halogen-replacement nucleophile-substitution reactions.[1-5] The resultant poly(organophosphazenes) are stable compounds with numerous uses. A key advantage of this synthesis pathway is that, because many different organophosphazene derivatives can be obtained from one precursor polymer, the resultant poly(organophosphazenes) are similar to each other in average chain length, molecular weight distribution, etc. Only the side groups are different. Hence, it is possible to study the effects of variations in side-group structure on physical properties in a manner that is difficult to accomplish with conventional organic-type polymers.

As shown in Schemes IV and V, the TCNQ–polyphosphazene complexes were prepared via the quaternization of a poly(aminophosphazene) side group, poly(phosphinoorganophosphazene) side groups, or skeletal nitrogen units. It will be noted that, in most cases, the polymers studied were mixed-substituent macromolecules, prepared by sequential replacement of the halogen atoms in poly(dichlorophosphazene) by two different nucleophiles.

(26) Allcock, H. R.; Gardner, J. E.; Smeltz, K. M. *Macromolecules* **1975**, *8*, 36.

Table I. Summary of Characterization Data

(a) Small Molecule Systems

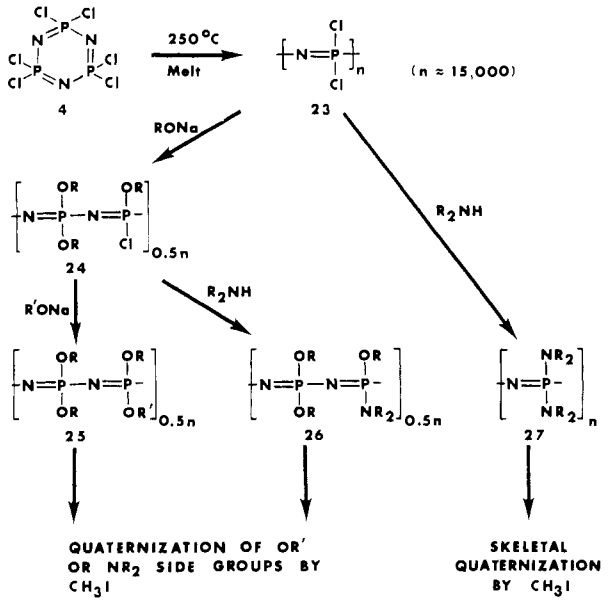
compd	^{1}H NMR,[a] ppm	^{31}P NMR,[b] ppm [J, Hz]	EI,[c] m/e	mp, °C	elem microanal.[f] % calcd C	H	N	P	I	% found C	H	N	P	I
$N_3P_3(OCH_2CF_3)_5Cl$ (**5**)	4.6–4.4 (m)	ν_A = 27.9, ν_B = 15.3 [J_{AB} = 87]	665	oil	18.05	1.51	6.31			18.25	1.28	6.27		
$N_3P_3(OCH_2CF_3)_5NHC_5H_4N$ (**8**)	8.33 (d), 7.03 (d), 4.5–4.3 (m)	ν_A = 15.3, ν_B = 17.1 [J_{AB} = 71]	723	102	24.90	2.07	9.68	12.86		25.57	2.04	10.30	12.75	
$N_3P_3(OC_6H_5)_5NHC_5H_4N$ (**10**)	8.34 (d), 7.3–6.9 (m), 6.77 (d), 4.99 (br)	ν_A = 12.2, ν_b = 8.6 [J_{AB} = 72]	693	123	60.60	4.32	10.10	13.41		60.60	4.08	9.95	13.52	
$N_3P_3(OC_6H_5)_5OCH_2CH_2N(CH_3)_2$ (**12**)	7.3–6.7 (m), 3.73 (t), 2.36 (t), 2.14 (m)	ν_A = 13.9, ν_B = 10.0 [J_{AB} = 65]	688	165–168	59.30	5.08	8.13	13.51		59.71	5.21	8.36	12.48	
$N_3P_3(OC_6H_5)_5OC_6H_4CHO$-*p*	9.93 (s), 7.7–6.9 (m)	9.4 (s)	721	62	61.58	4.16	5.83	12.90		60.28	5.01	5.32	11.46	
$N_3P_3(OC_6H_5)_5OC_6H_4CH_2OH$-*p* (**16**)	7.3–6.9 (m), 4.63 (s)	8.3 (s)	723	58	61.41	4.43	5.81	12.86		58.37	4.00	6.28	14.46	
$N_3P_3(OC_6H_5)_5OC_6H_4CH_2P^+(C_6H_5)_3I^-$-*p* (**17**)	7.9–6.7 (m), 5.23 (d)	24.6 (s), 9.6 (s)		72–75	60.27	4.20	3.84	11.32	11.60	57.86	3.98	3.21	10.71	14.21
$N_3P_3(OCH_2CF_3)_5NHC_5H_4N^+CH_3I^-$ (**9**)	8.24 (d), 7.68 (d), 4.6–4.5 (m), 4.63 (s)	ν_A = 15.7, ν_B = 11.3 [J_{AB} = 73]		154–155	22.20	2.08	8.09	10.75	14.68	22.37	2.31	8.61	10.80	15.88
$N_3P_3(OC_6H_5)_5NHC_5H_4N^+CH_3I^-$ (**11**)	8.32 (d), 7.60 (d), 7.3–6.9 (m), 4.25 (s)	ν_A = 9.8, ν_b = 8.6 [J_{AB} = 28]		125–127	51.74	3.95	8.38	11.14	15.21	55.37	4.85	7.69	10.09	14.08
$N_3P_3(OC_6H_5)_5OCH_2CH_2N^+(CH_3)_3I^-$ (**13**)	7.4–6.8 (m), 3.7–3.6 (m), 3.14 (s)	ν_A = 14.6, ν_B = 10.1 [J_{AB} = 81]		270–274 dec	50.60	4.58	6.75	11.20	15.30	51.46	4.78	6.32	14.68	16.18
$N_3P_3(OC_6H_5)_5OC_6H_4P^+(CH_3)(C_6H_5)_2I^-$-*p* (**15**)	7.9–6.9 (m), 3.26 (s)	23.2 (s), 9.6 (s)		69–72	57.70	4.12	4.12	12.17	12.46	57.78	4.54	3.91	12.08	12.40
$[N_3P_3(NC_5H_{10})_6CH_3]^+I^-$ (**20**)	3.04 (br), 2.78 (t), 1.62 (br)	ν_A = 13.3, ν_B = 20.5 [J_{AB} = 40[d]]		216–217	47.63	8.07	16.13	11.91	16.26	47.63	7.85	15.83	12.01	16.58
$[N_4P_4(NC_5H_{10})_8(CH_3)_2]^{2+}(I^-)_2$ (**22**)	3.73 (t), 3.10 (br), 1.54 (br)	0.9 (s)[d]		238–241	44.37	7.57	14.79		22.36	46.22	7.74	15.14		19.12

(b) Polymers

compd	^{31}P NMR,[b] ppm	elem microanal. % calcd C	H	N	P	I	% found C	H	N	P	I
$[NP(OCH_2CF_3)_{1.7}(NHC_5H_4N)_{0.3}]_n$ (**28**)	−8.5 (s)	24.37	2.03	9.28	12.85		24.60	2.05	9.07	12.76	
$[NP(OCH_6H_5)_{1.82}(NHC_5H_4N)_{0.18}]_n$ (**30**)	−21.0 (s)	61.30	4.25	8.20	13.40		58.45	4.79	8.67	13.14	
$[NP(OC_6H_5)_{1.66}(OCH_2CH_2N(CH_3)_2)_{0.34}]_n$ (**32**)	−20.4 (s), −22.0 (s)	59.24	5.10	8.18	13.51		56.97	5.22	8.67	14.45	
$[NP(OC_6H_5)(OC_6H_4CH_2OH)]_n$ (**40**)	−18 (v, br)	60.23	3.86	5.41	11.97		58.13	3.99	5.74	12.42	
$[NP(OC_6H_5)(OC_6H_4CH_2P^+(C_6H_5)_3I^-)]_n$ (**41**)	22.4 (s), −19.6 (s)[e]	58.77	4.11	2.21	9.79	20.06	56.38	4.08	3.04	11.20	19.43
$[NP(OCH_2CF_3)_{1.7}(NHC_5H_4N)_{0.16}(NHC_5H_4N^+CH_3I^-)_{0.14}]_n$ (**29**)	−8.4 (m)	23.17	2.04	8.58	11.87	6.81	21.52	2.02	7.74	13.21	6.25
$[NP(OC_6H_5)_{1.82}(NHC_5H_4N^+CH_3I^-)_{0.18}]_n$ (**31**)	−19.7 (m)	56.13	4.11	7.42	12.08	8.91	54.14	4.19	7.65	11.33	8.95
$[NP(OC_6H_5)_{1.66}(OCH_2CH_2N^+(CH_3)_3I^-)_{0.34}]_n$ (**33**)	−20.0 (m)	50.41	4.58	6.76	11.17	15.56	47.29	4.85	6.98	11.33	15.75
$[NP(OC_6H_5)_{1.72}(OC_6H_4P^+(CH_3)(C_6H_5)_2I^-)_{0.28}]_n$ (**35**)	21.8 (m), −20.0 (m)	58.24	4.15	4.34	12.31	11.03	57.00	4.20	4.52	12.95	10.85
$[NP(OC_6H_5)_{1.52}(OC_6H_4P^+(CH_3)(C_6H_5)_2I^-)_{0.48}]_n$ (**37**)	21.7 (m), −20.1 (s)	56.49	4.07	3.61	11.84	15.73	55.85	4.34	3.65	11.40	15.58
$[NP(OC_6H_5)_{0.92}(OC_6H_4P^+(CH_3)(C_6H_5)_2I^-)_{1.08}]_n$ (**39**)	22.0 (s), −19.5 (s)[d]	53.59	3.94	2.40	11.06	23.52	49.49	3.97	3.74	11.30	23.78
$[N_{0.58}{}^+P(NC_5H_{10})_2{\cdot}0.13HCl^-{\cdot}0.45CH_3I^-]_n$ (**43**)	13 (v, br), −3 (v, br)[d]	44.52	7.63	14.91		20.29	42.16	6.83	16.02		20.30

[a] $CDCl_3$ solvent. [b] Tetrahydrofuran solvent unless noted otherwise. [c] Electron impact mass spectral parent peaks. [d] CH_3CN solvent. [e] CF_3CH_2OH solvent. [f] Microanalytical discrepancies are often found for polyphosphazenes, especially when salt-type structures are present (see ref 31). Incomplete combustion may explain these results. The iodine analyses generally seem more accurate than carbon–hydrogen analyses, based on comparisons with the NMR data.

Scheme IV



The "inactive" substituent groups were present to permit some chain flexibility, i.e. to offset the tendency of charged side groups to generate dipolar crosslinks that would inhibit the shaping of the polymer into fibers or films. Moreover, the inactive groups served to prevent quaternization of the backbone. We recognize that such a structural arrangement may be detrimental to an enhancement of the electrical conductivity of the polymers, but it constitutes an essential first step in the fundamental exploration of this system. In different polymers the "inactive" substituent groups (CF_3CH_2O– or C_6H_5O–) constituted from 46% to 91% of the total side groups present. Polymer **42** undergoes skeletal quaternization only, and at every other nitrogen atom, a result that is compatible with the behavior of the corresponding cyclic tetramer (**21**). The specific intermediary polymers and their quaternary derivatives are shown as **28**–**43**. The synthetic procedures are given in the Experimental Section.

TCNQ salt formation with the quaternized polymers was accomplished by treatment with a minimum of 1.5 equiv of Li^+TCNQ^- to give the simple salts. Complex salts were obtained by treatment of the simple salts with 1 equiv or less of TCNQ in boiling acetonitrile. This two-stage method permitted a facile variation of the TCNQ salt stoichiometry.

The structural characterization was accomplished by ^1H and ^{31}P NMR spectroscopy, infrared and electronic spectroscopy, and elemental microanalysis. Typical data are shown in Table I.

Electrical Conductivity. The small-molecule phosphazene–TCNQ adducts were found to be several orders of magnitude more conductive than their high polymeric counterparts (Table II). We interpret this to mean that TCNQ stacking can occur in the solid state even when bulky cyclophosphazene molecules form part of the countercation structure. However, it appears that the high polymeric polyphosphazene backbone can interfere with this stacking, at least in the nonoriented samples studied in this work. A second explanation for the higher conductivity of several of the small-molecule systems is that the amount of TCNQ per repeating unit is higher (one for every three repeating units) than in the high polymers.

The simple-salt high polymeric TCNQ compounds (and the iodide salts) were electrical insulators. Treatment of these simple-salt derivatives with TCNQ increased the conductivity into the weak semiconductor range (Table II). Moreover, those polymers with the highest concentrations of bound $TCNQ^-$ required the least additional TCNQ to induce an onset of conduction. This probably reflects the closer average proximity of $TCNQ^-$ sites and the greater opportunities for TCNQ stacking and electron delocalization. The higher conductivities were generally associated with polymers that contained the highest concentrations of $TCNQ^-$ active sites.

Table II. Electrical Conductivities[36,37] (log σ, Ω^{-1} cm^{-1})

(a) Small Molecule Model Compounds

	simple	complex
Side-Group Bound		
$N_3P_3(OC_6H_5)_5OC_6H_4CH_2P^+(C_6H_5)_3$ (from **17**)	−7	−2.5
$N_3P_3(OCH_2CF_3)_5NHC_5H_4N^+CH_3$ (from **9**)	−6	−3
$N_3P_3(OC_6H_5)_5NHC_5H_4N^+CH_3$ (from **11**)	−6.3	−1.5
$N_3P_3(OC_6H_5)_5OCH_2CH_2N^+(CH_3)_3$ (from **13**)	−6	−2.3
$N_3P_3(OC_6H_5)_5OC_6H_4P^+(CH_3)(C_6H_5)_2$ (from **15**)	−9.3	−2
Skeletal Bound		
$N_3{}^+P_3(NC_5H_{10})_6(CH_3)$ (from **20**)	−10.5	−9.3
$N_4{}^{2+}P_4(NC_5H_{10})_8(CH_3)_2$ (from **22**)	−4	−3

(b) Macromolecular Systems

polymer from polymer$^+$–$TCNQ^-$ system	amt of neutral TCNQ dopant required for semiconduction, equiv/$TCNQ^-$	maximum conductivity (with TCNQ dopant level, equiv/$TCNQ^-$)
29	0.4	−10
31	0.4	−8 (1)
35	1.0	>−6.5 (1.2)
37	0.8	>−6 (1.2)
39	0.4	−7 (0.8)
33	0.2	−5.5 (1.2)
43	0.6	>−7 (1.2)
41	0.6	−6.5 (0.8)

Films prepared from these polymer systems (by solution casting) consistently showed higher conductivities than compressed pellets of the same materials. For example, polymer **35** showed an increase in conductivity from 3×10^{-7} Ω^{-1} cm^{-1} for the compressed pellet to 2×10^{-4} Ω^{-1} cm^{-1} for a film of the same material. This may reflect the better opportunities for alignment of the TCNQ stacks during preparation of the films. However, it was not possible to align the polymer chains by the usual film orientation procedures because of the brittleness.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Ethyl Corp.) and octachlorocyclotetraphosphazene (Ethyl Corp.) were purified by vacuum sublimation and recrystallization from heptane. Poly(dichlorophosphazene) was prepared as described previously.[4] Trifluoroethanol (Halocarbon Products Corp.) and *N,N*-dimethylethanolamine (Aldrich) were dried over molecular sieves. Phenol (Aldrich), bromophenol (Aldrich), 4-hydroxybenzaldehyde (Aldrich), and 4-aminopyridine (Aldrich) were purified by vacuum sublimation. Dimethylamine (Matheson) was dried over sodium before use. Piperidine (Aldrich) was dried and distilled from calcium hydride. Sodium hydride (Alfa), as a 50% dispersion in oil, and sodium spheres (Aldrich) were washed with dry heptane before use. 7,7,8,8-Tetracyanoquinodimethane (Aldrich) was recrystallized from acetonitrile. Lithium tetracyanoquinodimethane was prepared by a published method.[26] Tetrahydrofuran (VWR) and dioxane (VWR) were dried and distilled from sodium benzophenone ketyl. Acetonitrile (VWR) and benzene (Fisher) were dried and distilled from calcium hydride. All other reagents and solvents were used as received.

Equipment. Infrared spectra were recorded on a Perkin-Elmer Model 580 grating spectrophotometer. Electronic absorption spectra were obtained for TCNQ salts in acetonitrile solution with the use of a Cary 17 spectrophotometer. ^1H NMR spectra were obtained with the use of a Bruker WP-200 Fourier transform spectrometer. ^{31}P NMR spectra were recorded with a JEOL PS-100 FT NMR spectrometer operated at 40 MHz or a Varian CFT 20 spectrometer operated at 32.2 MHz. Electron-impact mass spectral results were obtained with the use of an AEI MS-902 mass spectrometer. A Waters Associates Preparative LC/System 500 liquid chromatograph was used in the purification of many of the small-molecule model compounds. Microanalytical data were supplied by Galbraith Laboratories, Knoxville, TN.

Synthesis of $N_3P_3(OC_6H_5)_5Cl$ (6). Compound **6** was prepared by the method described previously.[27] Specifically, hexachlorocyclo-

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

triphosphazene was allowed to react with 5 equiv of sodium phenoxide in tetrahydrofuran. The product was purified by recrystallization from heptane.

Synthesis of $N_3P_3(OCH_2CF_3)_5Cl$ (5). Trifluoroethanol (270 g, 2.70 mol) was dissolved in dry diethyl ether (250 mL), and this solution was added to sodium spheres (62.1 g, 2.7 mol) suspended in diethyl ether (200 mL). When the reaction was complete (≃24 h), the solution was added dropwise to a cold (0 °C) solution of hexachlorocyclotriphosphazene (180 g, 0.51 mol) in diethyl ether (1 L). The reaction mixture was stirred for 3 h at 0 °C. The mixture was then extracted with water to remove sodium chloride and excess sodium trifluoroethoxide. The organic layer was dried over magnesium sulfate and filtered. The ether was then removed under reduced pressure. A rapid vacuum distillation (flask to flask) removed excess trifluoroethanol and traces of ether. The product was isolated as a clear, colorless oil. ^{31}P NMR spectroscopy revealed traces of the tetra- and hexasubstituted phosphazenes as impurities. These impurities were removed after subsequent reactions with nucleophiles. Yield: 240 g (69%). Characterization data are listed in Table I.

Synthesis of $N_3P_3(OCH_2CF_3)_5NHC_5H_4N$ (8). 4-Aminopyridine (11.0 g, 0.12 mol) was dissolved in tetrahydrofuran (240 mL). This solution was added to a tetrahydrofuran solution (250 mL) of **5** (40 g, 0.06 mol). The mixture was stirred at reflux for 72 h, during which time a copious precipitate of 4-aminopyridine hydrochloride was formed. A ^{31}P NMR spectrum of the reaction mixture revealed an AB_2 spin system different from that of the starting material, **5**. This indicated that the reaction was complete. The hot solution was filtered, and solvent was removed from the filtrate under reduced pressure to afford a white solid material. The solid residue was purified by column chromatography using silica gel (95%/5% CH_2Cl_2/THF as eluent). Removal of the eluent solvent gave **8** as a white crystalline solid. Yield: 40 g (92%). Characterization data are given in Table I.

Synthesis of $N_3P_3(OC_6H_5)_5NHC_5H_4N$ (10). 4-Aminopyridine (10.0 g, 0.11 mol) was dissolved in tetrahydrofuran (500 mL). This solution was added to a tetrahydrofuran solution (200 mL) of **6** (32 g, 0.05 mol). The mixture was stirred at reflux for 48 h, during which time 4-aminopyridine hydrochloride precipitated from solution. A ^{31}P NMR spectrum of the reaction mixture revealed an AB_2 spin system different from that of the starting material, **6**. This indicated that the reaction was complete. The hot solution was filtered, and solvent was removed from the filtrate under reduced pressure to give a clear oil. The oil solidified on standing. This material was purified by column chromatography using silica gel (75%/25% CH_2Cl_2/THF as eluent). The product was isolated as a white crystalline solid. Yield: 12 g (34%). Characterization data are listed in Table I.

Synthesis of $N_3P_3(OC_6H_5)_5OCH_2CH_2N(CH_3)_2$ (12). *N,N*-Dimethylethanolamine (11.2 g, 0.12 mol) was dissolved in dioxane (100 mL), and this solution was added to sodium hydride (5.0 g, 0.12 mol) suspended in dioxane (100 mL). After completion of the reaction, additional dioxane (100 mL) was added and the reaction mixture was heated to 50 °C. The hot solution was added dropwise to a solution of **6** (40.0 g, 0.063 mol) in dioxane (280 mL). The reaction mixture was stirred for 48 h at reflux temperature. The mixture was then filtered and the solvent removed from the filtrate with a rotary evaporator, affording a clear oil. This oil was purified by HPLC column chromatography using silica gel (95%/5% CH_2Cl_2/THF as eluent). Removal of the eluent gave **12** as a clear oil, which solidified on standing. Yield: 28 g (65%). See Table I for characterization data.

Synthesis of $N_3P_3(OC_6H_5)_5N(CH_3)_2$ (18). Compound **18** was prepared as described here although other synthetic routes are known. Dimethylamine (25 g, 0.55 mol) was dissolved in tetrahydrofuran (150 mL) at 0 °C. This solution was added to a tetrahydrofuran solution (100 mL) of **6** (5 g, 0.0079 mol). The mixture was stirred at 0 °C for 70 h, during which time a copious precipitate of dimethylamine hydrochloride was formed. A ^{31}P NMR spectrum of the reaction mixture revealed an AB_2 spin system different from that of the starting material, **6**. The cold solution was filtered, and the solvent was removed from the filtrate under reduced pressure to afford a clear oil. The resultant oil was purified by column chromatography using silica gel (90%/10% CH_2Cl_2/THF as eluent). Removal of the solvent gave **18** as a white crystalline solid. Yield: 5.0 g (99%).

Synthesis of $N_3P_3(OC_6H_5)_5OC_6H_4P(C_6H_5)_2$-*p* (14). Compound **14** was prepared by the method described previously.[28] Specifically, $N_3P_3(OC_6H_5)_5OC_6H_4Li$-*p* was synthesized by the metal–halogen exchange reaction of $N_3P_3(OC_6H_5)_5OC_6H_4Br$-*p* with *n*-butyllithium. The lithio derivative was then allowed to react with chlorodiphenylphosphine to give **14**. The product was purified by HPLC column chromatography on silica gel using toluene as the eluent.

(28) Allcock, H. R.; Evans, T. L.; Fuller, T. J. *Inorg. Chem.* **1980**, *19*, 1026.

Synthesis of $N_3P_3(OC_6H_5)_5OC_6H_4CHO$. 4-Hydroxybenzaldehyde (22.5 g, 0.18 mol) was dissolved in tetrahydrofuran (200 mL). This solution was added to a suspension of sodium hydride (7.4 g, 0.18 mol) in tetrahydrofuran (100 mL). A yellow suspension was formed. Tetra-*n*-butylammonium bromide (1.0 g, 0.003 mol) was added to the reaction mixture, which was then heated to 50 °C. To this solution was added rapidly a tetrahydrofuran solution (500 mL) of **6** (90 g, 0.14 mol). The reaction mixture was stirred at reflux temperatures for 72 h. The mixture was then filtered hot and the solvent removed from the filtrate with the use of a rotary evaporator to leave an oil. This was purified by HPLC column chromatography using silica gel (50%/50% CH_2Cl_2/hexane as eluent). Removal of the eluent solvent gave the product as a white solid. Yield: 70 g (70%). Characterization data are listed in Table I.

Synthesis of $N_3P_3(OC_6H_5)_5OC_6H_4CH_2OH$ (16). The species $N_3P_3(OC_6H_5)_5OC_6H_4CHO$ (24 g, 0.03 mol) was dissolved in tetrahydrofuran/ethanol (100 mL, 90/10 (v/v)). This solution was added to a solution of sodium borohydride (1.26 g, 0.033 mol) in tetrahydrofuran (50 mL). The reaction mixture was stirred for 24 h at room temperature after which time the mixture was pink in color. This mixture was added dropwise to dilute HCl (10 mL, 3N). A white solid precipitated and was collected and washed to neutrality with ethanol. Compound **16** was purified by recrystallization from ethanol. Yield: 21 g (88%). Characterization data are given in Table I.

Synthesis of $N_3P_3(OC_6H_5)_5OC_6H_4CH_2P^+(C_6H_5)_3I^-$ (17). Compound **16** (5.5 g, 0.0076 mol) was dissolved in tetrahydrofuran (200 mL). To this solution was added phosphorus triiodide (3.5 g, 0.0085 mol), and the mixture was stirred at room temperature for 18 h. Triphenylphosphine (2.2 g, 0.0084 mol) was dissolved in tetrahydrofuran (50 mL) and was added to the phosphazene solution. The solution was stirred for an additional 24 h after which the crude reaction mixture was concentrated. The concentrate was then added dropwise to hexane to precipitate the product. Compound **17** was collected and reprecipitated from tetrahydrofuran into hexane and was finally washed with diethyl ether. Yield: 5.3 g (64%). Characterization data are listed in Table I.

Synthesis of $N_3P_3(NC_5H_{10})_6$ (19). Compound **19** was prepared in a manner similar to that described previously.[29] Specifically, hexachlorocyclotriphosphazene was allowed to react with a large excess of piperidine in benzene. The product was purified by filtration of a methylene chloride solution of **19** through silica gel.

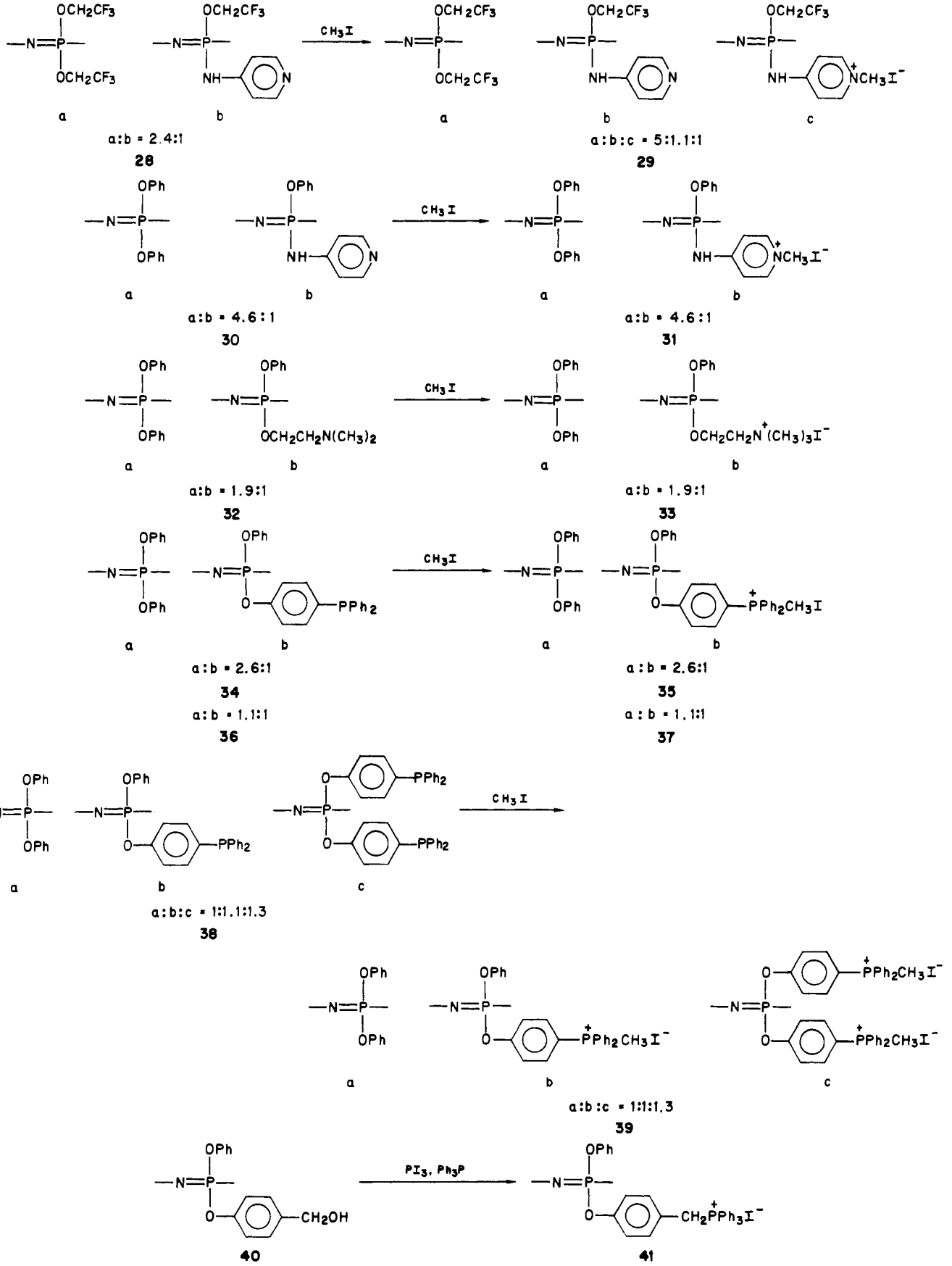
Synthesis of $N_4P_4(NC_5H_{10})_8$ (21). Compound **21** was prepared by the interaction of octachlorocyclotetraphosphazene with piperidine by the method reported previously.[30] The product was purified in a manner similar to that described for **19**.

Synthesis of $[NP(OCH_2CF_3)_{1.70}(NHC_5H_4N)_{0.30}]_n$ (28). Sodium trifluoroethoxide was prepared by the addition of a solution of trifluoroethanol (43.3 g, 0.43 mol) in tetrahydrofuran (100 mL) to a stirred suspension of sodium hydride (17.3 g, 0.43 mol) in tetrahydrofuran (100 mL). After 4 h, the reaction mixture was heated to reflux temperature and was then Schlenk-filtered. The filtrate was added to a stirred solution of poly(dichlorophosphazene) (29.6 g, 0.25 mol) in tetrahydrofuran (1 L). The reaction mixture was stirred at reflux for 48 h and was then added to a solution of 4-aminopyridine (36 g, 0.38 mol) in tetrahydrofuran (500 mL) that had previously been heated to reflux. The polymer precipitated from solution within 0.5 h of the addition. Dimethyl sulfoxide (550 mL) was added to resolubilize the polymer. The reaction mixture was heated slowly to 90 °C and maintained at that temperature for 48 h. The solution was then concentrated, and the concentrate was added to water to precipitate the polymer. The product was washed with additional water, dissolved in tetrahydrofuran, and reprecipitated into water. The reprecipitation procedure was carried out twice more from tetrahydrofuran into hexane. Yield: 14 g (23%). Characterization data are given in Table I.

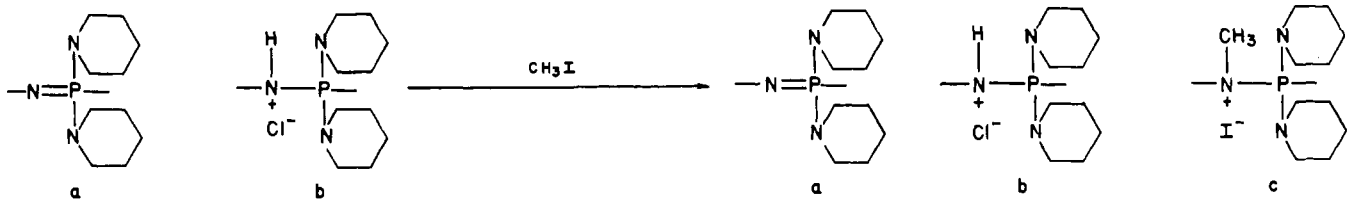
Synthesis of $[NP(OC_6H_5)_{1.82}(NHC_5H_4N)_{0.18}]_n$ (30). Sodium phenoxide was prepared by the addition of a solution of phenol (69 g, 0.73 mol) in dioxane (250 mL) to a stirred suspension of sodium hydride (29.3 g, 0.73 mol) in dioxane (100 mL). After 4 h, the reaction mixture was heated to reflux temperature and filtered. The filtrate was added to a stirred solution of poly(dichlorophosphazene) (50 g, 0.43 mol) in dioxane (1 L). The reaction mixture was stirred at reflux for 48 h and was then added to a solution of 4-aminopyridine (74 g, 0.74 mol) in dioxane (500 mL) that had previously been heated to reflux. The polymer precipitated from solution within 0.5 h of the addition. Dimethyl sulfoxide (350 mL) was added to resolubilize the polymer. The reaction mixture was heated to 80 °C for 48 h and was then concentrated by means of a rotary evaporator. The concentrate was added to water, and the precipitated polymer

(29) Bode, H.; Butow, K.; Lienau, G. *Chem. Ber.* **1948**, *81*, 547.
(30) John, K.; Moeller, T.; Audrieth, L. F. *J. Am. Chem. Soc.* **1961**, *83*, 2608.

Scheme V. Component Repeating Units in the Poly(organophosphazenes)[a]



Scheme V (Continued)



[a] All reactions are given in the form initial polymer $\xrightarrow{X}$ quaternized polymer.

was washed with additional water. The polymer was redissolved in tetrahydrofuran and reprecipitated into water. The reprecipitation procedure was carried out twice more from tetrahydrofuran into hexane. Yield: 32 g (32%). Characterization data are listed in Table I.

Synthesis of $[NP(OC_6H_5)_{1.66}(OCH_2CH_2N(CH_3)_2)_{0.34}]_n$ (32). The phenoxychlorophosphazene was prepared in the same way as described in the preceding procedure. It was then added to a refluxing solution of the sodium salt of *N,N*-dimethylethanolamine. This sodium salt was prepared by the reaction of *N,N*-dimethylethanolamine (57 g, 0.60 mol) and sodium hydride (24 g, 0.60 mol) in refluxing dioxane (500 mL). After the addition of the polymer solution, the reaction mixture was stirred at reflux for an additional 48 h and concentrated with the use of a rotary evaporator, and the concentrate was added to water. The precipitated polymer was collected, washed with ethanol, redissolved in tetrahydrofuran, and reprecipitated into water. The reprecipitation procedure was carried out from tetrahydrofuran into water once again, then from tetrahydrofuran into ethanol, and, finally, from tetrahydrofuran into hexane. Yield: 53 g (54%). Characterization data are given in Table I.

Synthesis of $[NP(OC_6H_5)_{1.72}(OC_6H_5P(C_6H_5)_2)_{0.28}]$ (34). Polymer **34** was synthesized by the method described previously.[31] The approach involved the lithiation of $[NP(OC_6H_5)_{1.72}(OC_6H_4Br)_{0.28}]_n$ with *n*-butyllithium followed by reaction of the lithio intermediate with chlorodiphenylphosphine. Additional polymers (**36**, **38**) were prepared from phenoxy–bromophenoxy copolymers with various stoichiometries in a similar manner.

Synthesis of $[NP(OC_6H_5)_{1.00}(OC_6H_4CHO)_{1.00}]_n$. This polymer was prepared by the reactio of poly(dichlorophosphazene) with 1 equiv of sodium phenoxide followed by displacement of the remaining chlorine atoms with the sodium salt of 4-hydroxybenzaldehyde as described previously.[32]

Synthesis of $[NP(OC_6H_5)_{1.00}(OC_6H_4CH_2OH)_{1.00}]_n$ (40). A solution of the aldehydic precursor (25 g, 0.09 mol) in tetrahydrofuran/methanol (1.6 L, 15/1 (v/v)) was prepared. To this solution was added powdered sodium borohydride (3 g, 0.08 mol). The reaction mixture was stirred for 48 h at room temperature. This mixture was then added slowly to water (12 L) containing HCl (10 mL concentrated). The polymer precipitated from solution and was collected. The polymer was reprecipitated a total of five times from tetrahydrofuran into water. Yield: 21 g (89%). Characterization data are listed in Table I.

Synthesis of $[NP(OC_6H_5)_{1.00}(OC_6H_4CH_2P^+(C_6H_5)_3I^-)_{1.00}]_n$ (41). Polymer **41** (21 g, 0.08 mol) was dissolved in tetrahydrofuran (1 L). Phosphorus triiodide (25 g, 0.06 mol) was added rapidly to the solution, and the mixture was stirred under an atmosphere of dry nitrogen. This converted the alcohol functionality to iodide. The reaction solution became orange in color, and the polymer initially appeared to precipitate from solution. However, the polymer redissolved after the reaction mixture had been stirred for 24 h. This polymer was not isolated, but instead was allowed to react in situ with triphenylphosphine (16.5 g, 0.05 mol) in tetrahydrofuran (100 mL). Following the rapid addition of the triphenylphosphine solution, the resultant mixture was stirred for 24 h at room temperature. The polymer precipitated slowly from solution over this period and was collected by filtration. The product (**41**) was then washed with water (5 L). Yield: 21 g (43%). Characterization data are summarized in Table I.

Synthesis of $[NP(NC_5H_{10})_2]_n$ (42). Polymer **42** was prepared by the method described previously.[5] Specifically, poly(dichlorophosphazene) was allowed to react with an excess of piperidine in benzene at reflux temperature. ^{31}P NMR spectroscopy and elemental microanalysis suggested that hydrogen chloride was associated with 13% of the skeletal nitrogen atoms.[35]

Quaternization Reactions. General Data. Cyclophosphazene model compounds **8**, **10**, **12**, **14**, **19**, and **21** were quaternized with iodomethane to yield compounds **9**, **11**, **13**, **15**, **20**, and **22**, respectively. All the reactions were carried out in a similar manner, and the following procedure is typical. Tetrahydrofuran was used as the reaction solvent for the quaternization of **8**, **10**, **12**, and **14**, but acetonitrile was employed for **19** and **21**. Similarly, high polymers **28**, **30**, **32**, **34**, and **42** were quaternized with iodomethane to give **29**, **31**, **33**, **35**, and **43**, respectively. Tetrahydrofuran was used as the reaction solvent in all cases except for the quaternization of **42** for which acetonitrile was employed. An example of the general quaternization procedure is also given.

Synthesis of $N_3P_3(OC_6H_5)_5NHC_5H_4N^+CH_3I^-$ (11). $N_3P_3(OC_6H_5)_5NHC_5H_4N$ (**10**) (5 g, 0.007 mol) was dissolved in tetrahydrofuran (150 mL). An excess of iodomethane (5 mL, 0.077 mol) was added to the solution. The reaction mixture was stirred at 25 °C for 48 h, after which time the solution was concentrated with the use of a rotary evaporator, and the concentrate was added slowly to hexane. The resultant precipitate was collected, redissolved in tetrahydrofuran, and reprecipitated into hexane. The product was collected and dried under vacuum. ^1H NMR spectroscopy indicated quantitative conversion to the pyridinium salt. Yield: 5.9 g (98%). See Table I for characterization data.

Synthesis of $[NP(OC_6H_5)_{1.72}(OC_6H_4P^+(CH_3)(C_6H_5)_2I^-)_{0.28}]_n$ (35). $[NP(OC_6H_5)_{1.72}(OC_6H_4P(C_6H_5)_2)_{0.28}]_n$ (**34**) (10 g, 0.035 mol) was dissolved in tetrahydrofuran (500 mL). An excess of iodomethane (20 mL, 0.310 mol) was added to the solution. The polymer slowly precipitated from solution following the addition. The mixture was stirred at 25 °C for 8 h, after which time the precipitated polymer was isolated by centrifugation, purified by Soxhlet extraction with acetone, and then dried under vacuum. ^{31}P NMR spectroscopy indicated quantitative conversion to the phosphonium salt. Yield: 8.8 g (77%). Characterization data are summarized in Table I.

Reactions of Side Group and Skeletal Phosphazene-Bound Iodide Salts with Li^+TCNQ^- and TCNQ. General Data. The small-molecule phosphazenes with side-group or skeletal-bound iodide salt residues were allowed to react with Li^+TCNQ^- in boiling tetrahydrofuran or acetonitrile/ethanol to yield the simple TCNQ salts. The iodide salts also were allowed to react with TCNQ in boiling acetonitrile, toluene, or toluene/tetrahydrofuran to afford the complex TCNQ salts. These model compound reactions were performed in a similar manner and only one example of a simple and complex TCNQ salt synthesis is presented.

The high polymeric complex salts were also prepared by a two-stage method. Simple TCNQ salts were first prepared by reactions of the quaternary iodide-containing polymers with Li^+TCNQ^- in boiling acetonitrile/ethanol. The complex salts were then synthesized by treatment with neutral TCNQ in boiling acetonitrile. One typical example of the

(31) Allcock, H. R.; Fuller, T. J.; Evans, T. L. *Macromolecules* **1980**, *13*, 1325.
(32) Allcock, H. R.; Austin, P. E. *Macromolecules* **1981**, *14*, 1616.
(33) Valdes, L. B. *Proc. IRE* **1954**, *42*, 420.
(34) The conductivity was calculated from the formula

$$\sigma\ (\Omega^{-1}\ \mathrm{cm}^{-1}) = \frac{1.8}{2\pi(0.0635\ \mathrm{cm})}\frac{I}{V}\ (\Omega^{-1})$$

See ref 33 and 37.

(35) The chloride ions in **42** were subsequently displaced by a metathetical exchange with Li^+TCNQ^-, as indicated by the chlorine analysis.
(36) The appearance of conductivity maxima at dopant levels greater than 1 equiv of TCNQ per unit of simple salt is presumably a consequence of a slight steric inhibition of complex salt formation. This effect was detected for polymers with low loadings of sterically crowded cations or for polymers with high loadings of uncrowded cations.
(37) The data presented in Table II were obtained for compressed pellets since not all the polymers could be converted to high-quality films.

preparation of a polymeric simple and complex TCNQ salt is given.

Infrared, electronic absorption, and ^1H NMR spectroscopies were used to characterize the TCNQ salts.

Synthesis of $N_3^+P_3(NC_5H_{10})_6{\cdot}CH_3(TCNQ)^-$. $N_3^+P_3(NC_5H_{10})_6{\cdot}CH_3I^-$ (**20**) (2 g, 0.0026 mol) was dissolved in boiling acetonitrile (75 mL). Li^+TCNQ^- (0.72 g, 0.0034 mol) was dissolved in boiling ethanol (50 mL) and then rapidly added to the phosphazene solution. The boiling reaction mixture was stirred for 1 h, and the solvent was then removed with the use of a rotary evaporator. Lithium iodide and excess Li^+TCNQ^- were extracted from the residue with methanol (2 L). The product was washed with diethyl ether (200 mL) until the washings were colorless. The dark green salt was then vacuum-dried. Yield: 1.3 g (66%).

Synthesis of $N_3P_3(OC_6H_5)_5NHC_5H_4N^+CH_3(TCNQ)_2^-$. TCNQ (0.82 g, 0.004 mol) was dissolved in boiling acetonitrile (100 mL). $N_3P_3(OC_6H_5)_5NHC_5H_4N^+CH_3I^-$ (**11**) (5 g, 0.006 mol) was dissolved in boiling acetonitrile (20 mL) and then added rapidly to the TCNQ solution. The boiling mixture was stirred for 0.5 h after which the stirring was stopped and the system cooled to room temperature. After 28 h, the precipitated product was collected and washed with cold acetonitrile (5 mL). The black crystals were then vacuum-dried. Yield: 0.6 g (27%).

Synthesis of $[NP(OC_6H_5)_{1.72}(OC_6H_4P^+(CH_3)(C_6H_5)_2(TCNQ)^-)_{0.28}]_n$. $[NP(OC_6H_5)_{1.72}(OC_6H_4P^+(CH_3)(C_6H_5)_2I^-)_{0.28}]_n$ (**35**) (1.0 g; 0.0009 mol of I^-) was dissolved in boiling acetonitrile (75 mL). Li^+TCNQ^- (0.39 g, 0.0018 mol) was dissolved in boiling ethanol (50 mL) and added to the polymer solution. The hot reaction mixture was stirred for 0.5 h, and then the solvent was removed with the use of a rotary evaporator. The residue was purified by Soxhlet extraction with methanol and then dried in vacuum. Yield: 0.95 g (89%).

Synthesis of $[NP(OC_6H_5)_{1.72}(OC_6H_4P^+(CH_3)(C_6H_5)_2(TCNQ)_2^-)_{0.28}]_n$. $[NP(OC_6H_5)_{1.72}(OC_6H_4P^+(CH_3)(C_6H_5)_2(TCNQ)^-)_{0.28}]_n$ (0.3 g; 0.00024 mol of $TCNQ^-$) was dissolved in hot acetonitrile (100 mL). TCNQ (0.05 g, 0.00024 mol) was dissolved in boiling acetonitrile (5 mL) and added to the polymer solution. After the hot reaction mixture was stirred for 0.5 h, the solvent was removed with the use of a rotary evaporator and the polymer residue was dried under vacuum. Yield: 0.3 g (86%).

Conductivity Measurements. Electrical conductivities of the TCNQ salts in the form of pressed pellets were measured by a standard in-line probe technique with pressure contacts.[33] Samples (70 mg) were compacted under 10 tons of pressure to give pellets of dimensions 0.5 mm × 13 mm diameter. Conductivity measurements also were obtained for some of the polymeric samples in the form of thin films (solution cast) on a glass substrate. Room-temperature measurements were obtained with the use of a commercial probe (Alessi Industries Model ATP test probe fixture fitted with a A4P four point probe) with 0.635-mm probe spacings. Conductivities were corrected for finite sample thickness, and no correction was considered necessary for boundary effects.[34] Currents were imposed with a Keithley Model 225 current source and voltages were measured with a Keithley Model 614 electrometer.

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Registry No. **4**, 940-71-6; **5**, 55975-53-6; **6**, 5032-39-3; **8**, 102260-03-7; **9**, 102260-09-3; $9^+{\cdot}TCNQ^-$, 102260-18-4; $(9^+{\cdot}TCNQ^-){\cdot}TCNQ$, 102260-28-6; **10**, 102260-04-8; **11**, 102260-10-6; $11^+{\cdot}TCNQ^-$, 102260-20-8; $(11^+{\cdot}TCNQ^-){\cdot}TCNQ$, 102260-29-7; **12**, 102260-05-9; **13**, 102260-11-7; $13^+{\cdot}TCNQ^-$, 102260-22-0; $(13^+{\cdot}TCNQ^-){\cdot}TCNQ$, 102260-30-0; **15**, 102260-12-8; $15^+{\cdot}TCNQ^-$, 102260-24-2; $(15^+{\cdot}TCNQ^-){\cdot}TCNQ$, 102260-31-1; **16**, 101671-98-1; **17**, 102260-06-0; $17^+{\cdot}TCNQ^-$, 102260-16-2; $(17^+{\cdot}TCNQ^-){\cdot}TCNQ$, 102260-27-5; **18**, 13848-66-3; **20**, 102260-13-9; $20^+{\cdot}TCNQ^-$, 102260-08-2; $(20^+{\cdot}TCNQ^-){\cdot}TCNQ$, 102260-32-2; **22**, 102260-14-0; $22^+{\cdot}TCNQ^-$, 102260-26-4; $(22^+{\cdot}TCNQ^-){\cdot}TCNQ$, 102260-33-3; F_3CCH_2OH, 75-89-8; $(CH_3)_2N(CH_2)_2OH$, 108-01-0; $(CH_3)_2NH$, 124-40-3; $4\text{-}HOC_6H_4CHO$, 123-08-0; $(CH_3)_2N(CH_2)_2ONa$, 37616-36-7; Li^+TCNQ^-, 1283-90-5; 4-aminopyridine, 504-24-5; $N_3P_3(OC_6H_5)_5OC_6H_4PCHO$, 101671-97-0.

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Four- and Five-Coordinate Platinum Complexes of Divinylphenylphosphine

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A series of platinum(II) complexes of the type L_2PtX_2 (L = divinylphenylphosphine; X = Cl, Br, I) have been prepared and characterized by elemental analyses, physical properties, conductance measurements, infrared spectroscopy, and ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, $^{13}C\{^1H,^{31}P\}$, $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectroscopy. All complexes are nonelectrolytes, and most possess the cis geometry in solution as well as in the solid state. However, L_2PtI_2 slowly isomerizes from cis to trans in $CDCl_3$ solution. Variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy and conductance studies of the equilibrium $L_2PtX_2 + L \rightleftharpoons L_3PtX_2$ have been analyzed in terms of intra- and intermolecular equilibria of the pentacoordinate species L_3PtX_2. The formation of L_3PtX_2 is enthalpy-driven. The crystal structures of dichlorobis(1-phenyl-3,4-dimethylphosphole)platinum(II) (**1**) and dichlorobis(divinylphenylphosphine)platinum(II) (**2**) have been determined from three-dimensional X-ray data collected by counter methods. Compound **1** crystallizes in space group $P2_1/c$ with a = 11.285 (2) Å, b = 11.269 (2) Å, c = 19.386 (3) Å, β = 92.36 (1)°, and Z = 4. Compound **2** crystallizes in space group $P\bar{1}$, with a = 7.861 (2) Å, b = 16.783 (5) Å, c = 8.804 (3) Å, α = 107.59 (2)°, β = 94.93 (2)°, γ = 101.56 (2)°, and Z = 2. Both structures were refined by least-squares methods with R = 0.028 for **1** and R = 0.033 for **2** for 3327 and 3446 reflections with $I/\sigma(I) > 3.0$ for **1** and **2**, respectively. The molecular structures are remarkably similar to one another and contain cis-four-coordinate platinum(II) with no unusual bond distances or internuclear contacts. Detailed comparisons of these structures together with the solution NMR data for the L_3PtX_2 complexes suggest that steric rather than electronic factors are dominant in determining the thermodynamic stability of the pentacoordinate complexes. These conclusions are strengthened by analysis of the infrared data in the CO stretching region for the complexes $LMo(CO)_5$ (L = divinylphenylphosphine, 1-phenyl-3,4-dimethylphosphole). Cotton–Kraihanzel force field analyses and Graham σ- and π-bonding parameters suggest that the phosphole is both a better σ-donor and π-acceptor than the phosphine toward Mo(0). All the data for the platinum complexes suggest that toward Pt(II) these two ligands have similar donor abilities.

Introduction

Recent studies in this laboratory have shown that pentacoordinate species play significant roles in the geometrical isomerizations of square-planar platinum(II) and palladium(II) complexes.[1] Our previous studies concentrated on 1-substituted 3,4-dimethylphospholes as ligands because these ligands have been shown[2] to be reasonably good π-acceptors and sterically small,

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(1) MacDougall, J. J.; Nelson, J. H.; Mathey, F. *Inorg. Chem.* **1982**, *21*, 2145.

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