DALTON
PERSPECTIVE

Main-group-based rings and polymers

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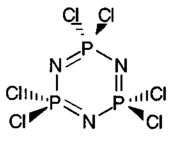
The synthesis and study of heterocycles containing main-group elements have played a pivotal role in the development of inorganic chemistry. Well known 'text-book' classes of inorganic rings include the cyclic phosphazene **1**, which was first prepared by Liebig and Rose[1] in 1834, and borazines such as **2**, the initial example of which was first synthesized by Stock and Pohland[2] in 1926. A further example is provided by sulfanuric chloride **3** which has been known since the 1950s.[3] It is noteworthy that the ring skeletons in phosphazenes **1** and borazines **2** have been shown to be very robust and to permit facile halogen atom replacement reactions.[4] This chemistry has been well studied and has provided much useful information on nucleophilic substitution reactions in inorganic chemistry. The bonding used to describe structures such as **1**–**3** and the possible application of the label 'inorganic benzene' has been the subject of much debate.

Current research continues to uncover fascinating new ring systems which pose intriguing questions with respect to their bonding or which exhibit unexpected reactivity. Some noteworthy examples include 6π-electron gallium-based systems and pseudo aromatic cyclic silylenes,[5,6] novel cyclic tellurium imides,[7] and interesting aluminum–pnicogen heterocycles[8] among others.[9] In addition to these important fundamental questions, a further reason for studying inorganic rings is their potential use as precursors to polymers and solid-state materials.

The synthesis of long chains of atoms of inorganic elements, inorganic polymers, provides a substantial synthetic challenge but is motivated by the possibility of accessing new materials with interesting and useful properties.[10] The most well known and widely used current routes to high molecular weight polysiloxanes **4**,[11] polyphosphazenes **5**,[12] and poly(carbosilanes) **6**[13] involve a ring-opening polymerization (ROP) reaction. With this in mind, interest in the polymerization behaviour of other inorganic rings has recently gathered momentum. Polysilanes **7**,[14] poly(carbophosphazenes) **8**,[15] and poly(thiophosphazenes) **9**[16] represent examples of well characterized polymers which have been successfully prepared by ROP in the past decade.

The use of inorganic rings to construct solid-state materials with novel properties has also been successfully developed. For example, materials with interesting electronic, magnetic and conductive properties have been prepared from sulfur–nitrogen or selenium–nitrogen heterocycles.[17,18] In addition, inorganic rings have attracted considerable attention as precursors to ceramics *via* thermolysis: examples include the use of aluminum–nitrogen or gallium–arsenic heterocycles to prepare AlN and GaAs, respectively.[19,20]

In this perspective we describe two areas of research on main group heterocycles which have been pursued in our research group. These involve, first, boron–nitrogen–phosphorus heterocycles and secondly, rings of sulfur(VI), nitrogen and phosphorus atoms. Our focus has been on the discovery of new structures and reactivity and, in particular, on the potential use of these species as precursors to new polymers *via* ROP reactions.



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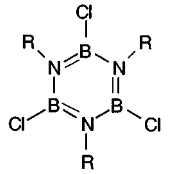

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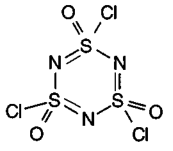

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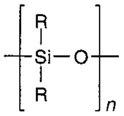

$[-\mathrm{SiR_2}-\mathrm{O}-]_n$

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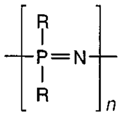

$[-\mathrm{PR_2}{=}\mathrm{N}-]_n$

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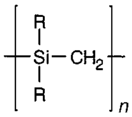
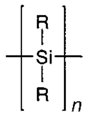


$[-\mathrm{SiR_2}-\mathrm{CH_2}-]_n$

6



$[-\mathrm{SiR_2}-]_n$

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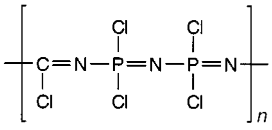

$[-\mathrm{CCl}{=}\mathrm{N}-\mathrm{PCl_2}{=}\mathrm{N}-\mathrm{PCl_2}{=}\mathrm{N}-]_n$

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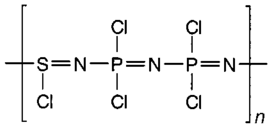

$[-\mathrm{SCl}{=}\mathrm{N}-\mathrm{PCl_2}{=}\mathrm{N}-\mathrm{PCl_2}{=}\mathrm{N}-]_n$

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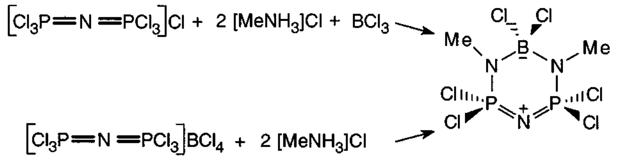

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Boron–Nitrogen–Phosphorus Rings

Early work on B–N–P heterocycles

Cyclic species containing boron, nitrogen, and phosphorus atoms were first described about 30 years ago. The first report of a BP_2N_3 ring was published by Sherif and Schmulbach[21] in 1966 and described the use of a [5 + 1] cyclocondensation reaction between $[H_2NPh_2P{=}N{=}PPh_2NH_2]Cl$ and $RBCl_2$ (R = Ph or Cl) to yield boron–nitrogen–phosphorus heterocycles. However, by present day standards, the characterization was poor.[21] Nevertheless, applications of these rings as pesticides were claimed in a patent.[22]

The perchlorinated boratophosphazene **10** was subsequently synthesized by two very similar routes. In 1968 Becke-Goehring and Müller[23] reported the reaction of $[Cl_3P{=}N{=}PCl_3]Cl$ with BCl_3 and $[MeNH_3]Cl$ in 1,2-dichloroethane and gave a 77% yield of **10**. In 1971 a slight modification of the Becke-Goehring synthesis was reported by Binder.[24] This route involved the reaction of $[Cl_3P{=}N{=}PCl_3]BCl_4$ with $[MeNH_3]Cl$ and gave improved yields of 84–90%. Convincing structural characterization of this white crystalline compound was provided by NMR spectroscopy. For example, ^{11}B NMR showed a

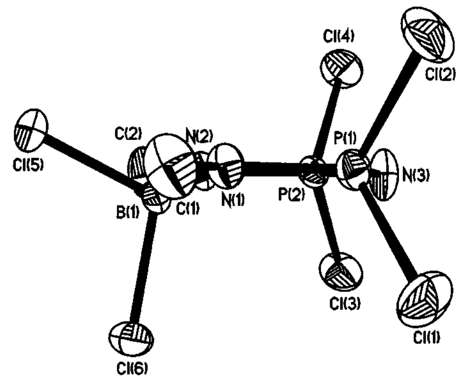
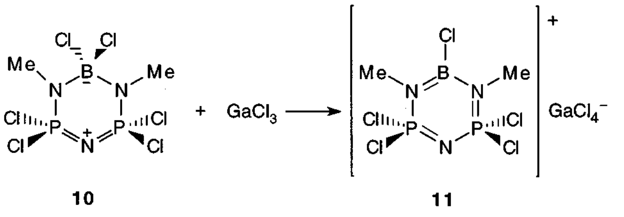


Fig. 1 Molecular structure of the boratophosphazene **10**. Reproduced from ref. 26 with permission



singlet resonance [^{11}B δ 6.2 (t) in 1,2-dichloroethane] which indicated that the boron atom was four-co-ordinate and there was no dissociation of the B–Cl bonds in solution.[25] In addition, Binder and co-workers reported studies of the halogen replacement reactions of **10** to afford a variety of well characterized products. In most cases, the reactivity of the B–Cl bonds was found to be greater than those of the P–Cl units.

Synthesis of borazine–phosphazene cations

When our group initiated research in this area in 1991 we were surprised to find that there were no reports of X-ray crystallographic studies of these boron–nitrogen–phosphorus ring systems. We therefore determined the structure of the boratophosphazene **10** (Fig. 1) which was synthesised by Binder's route.[26] The structure showed that the BP_2N_3 ring deviates significantly from planarity with the boron atom substantially removed [by 0.39(1) Å] from the best plane of the other five ring atoms. However, the most interesting features of the structure of **10** involve the environment at the boron atom. Surprisingly, one boron–chlorine bond adopts an equatorial position approximately located in the best plane of the ring, whereas the other boron–chlorine bond is in an axial position and is approximately perpendicular to the ring plane. Moreover, the axial boron–chlorine bond is much longer than the equatorial bond [1.903(4) *vs.* 1.847(5) Å] suggesting that the axial chlorine atom is fairly close to heterolytic dissociation. Significantly, as mentioned above, this structure was not predicted by ^{11}B NMR spectroscopy which indicated that boron was in a tetrahedral environment (in 1,2-dichloroethane).

In view of the distorted environment at boron in **10**, we attempted halide abstraction using the Lewis acid $GaCl_3$. This allowed us to access the borazine–phosphazene hybrid ring **11**, which was well characterized spectroscopically by ^{11}B, ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy.[26] Significantly, the ^{11}B NMR spectrum in CH_2Cl_2 of **11** clearly showed that boron was in a planar 'borazine-like' environment with a broad resonance at δ 31.7 which is similar to that of $[ClBNMe]_3$ (^{11}B δ 31.2). Conclusive evidence for the abstraction of chlorine at boron was provided by X-ray analysis of colourless crystals obtained from the reaction mixture. The structure of **11** (Fig. 2) clearly showed that there are no significant interactions between the tetrachlorogallate anion and the borazine–phosphazene hybrid cation. In addition, and in contrast to the situation in **10**, the structure of **11** showed that the B–N–P ring was virtually planar. Of particular note is that the boron–nitrogen bond length in **11** [1.429(10) Å] was significantly shorter than that in **10** [1.533(5) Å] and is typical for borazines (1.43 Å),[27] suggesting a large degree of π-bonding in **11** which is formally a 6π-electron system.

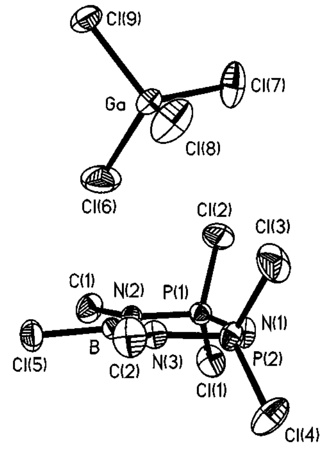
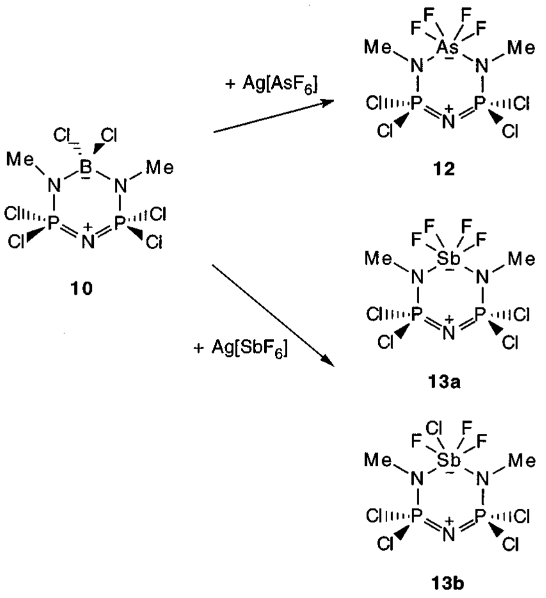


Fig. 2 Molecular structure of the borazine–phosphazene hybrid **11**. Reproduced from ref. 26 with permission



Skeletal substitution reactions

Remarkably, attempts to generate further examples of salts of the borazine–phosphazene cation in **11** with fluorinated counter anions rather than $[GaCl_4]^-$ have uncovered a new class of reaction for heterocycles containing boron.[28] Thus, treatment of the boratophosphazene **10** with the silver(I) salts $Ag[AsF_6]$ or $Ag[SbF_6]$ gave the completely unexpected arsenic(V)- and antimony(V)-containing heterophosphazenes **12** and **13a** or **13b**.

A side view of the structure of **12** (Fig. 3) shows that the six-membered ring adopts a boat conformation with both the arsenic and a nitrogen atom [N(1)] above the plane of the other four ring atoms. Although arsenic(V)–nitrogen–phosphorus rings such as $[(NAsPh_2)(NPPh_2)_2]$ are known,[29,30] to our knowledge there are no structurally characterized examples of antimony(V)-containing heterophosphazenes.† This reaction has potential to generate a wide variety of heterophosphazenes and may even be generalized to other boron-containing ring systems.

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† An Sb^V heterophosphazene was claimed,[31a] however recent unsuccessful attempts to reproduce these results[31b] raise some doubts about the validity of the original work.

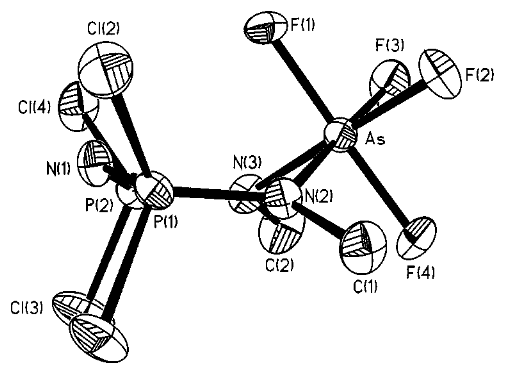
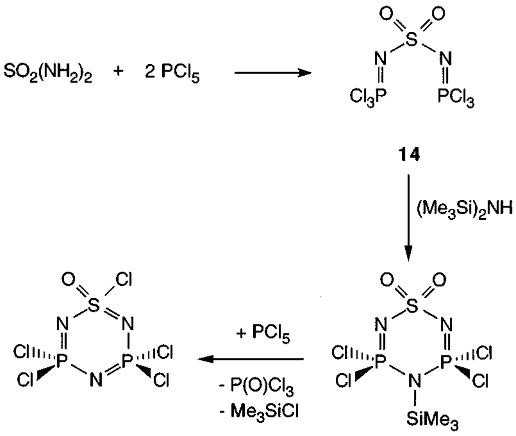


Fig. 3 Molecular structure of the arsenic(v) heterophosphazene **12**. Reproduced from ref. 28 with permission



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16

15

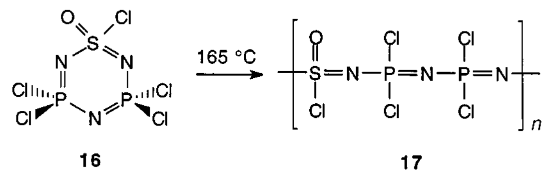
Of particular note is that, in general, reactions where an atom in a ring is replaced by another atom ('skeletal substitution') are extremely rare, and to our knowledge unprecedented for boron-containing heterocycles. Previous examples of skeletal replacement in inorganic rings include the reactions of titanocene chalcogenide heterocycles with Group 16 dihalides to form rings where titanium has been replaced by a chalcogen atom,[32] and the use of zirconocene-containing metallacycles to prepare various main-group heterocycles.[33] In addition, transmetallation reactions of SnS_2N_2 rings with Pt complexes to yield PtS_2N_2 rings have been observed.[34] The zirconocene reaction has been generalized to allow the synthesis of a number of new rings, including heterocycles containing gallium and phosphorus.[35,36]

A major interest for us concerning boron–nitrogen–phosphorus rings involves their polymerization behaviour. To date, attempts to induce the ROP of species such as **10** at elevated temperatures have been unsuccessful. Some of the products formed at 250 °C include the borazine $[ClBNMe]_3$ and oligophosphazenes $[Cl_2PN]_x$ ($x = 4$–8). However, studies of the ROP behaviour of related species are ongoing. In this article we now turn to our studies of another ring system which we found does afford ring-opened polymers on thermal treatment.

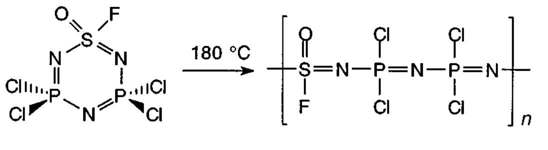
Sulfur–Nitrogen–Phosphorus Rings and Polymers

Previous work on S^{VI}–N–P rings

One of the most well studied heterophosphazenes is the thionylphosphazene **16** which was first prepared in 1972 by two different low yield routes. van de Grampel and co-workers[37] reported the synthesis of small quantities of this species *via* the vacuum thermolysis of $Cl_3P{=}N{-}PCl_2{=}N{-}SO_2Cl$. An alternative, low yield route was provided by Klingebiel and Glemser[38] using a [3 + 3] cyclocondensation route between $[Cl_3P{=}N{=}PCl_3]PCl_6$ and sulfamide $SO_2(NH_2)_2$. The best synthetic route to **16** is that described by Suzuki *et al.*[39] in 1983, which involves the reaction of sulfamide with PCl_5 followed by a [5 + 1] cyclocondensation reaction between the bis(phosphazo)sulfone **14** with hexamethyldisilazane. The chlorination of the cyclic species **15** is accomplished by reaction with PCl_5 in a mixture of EtOH–$CHCl_3$ affording **16** in yields of 40–75%. Two comprehensive reviews on the chemistry of **16** with particular emphasis on halogen side group replacement reactions have been published by van de Grampel[40,41] in 1981 and 1992.



16 **17**



18 **19**

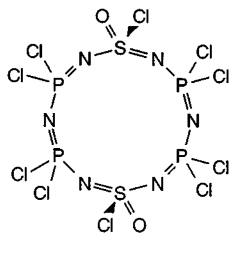
ROP of cyclic thionylphosphazenes

In 1991[42] we reported that when the cyclic thionylphosphazene **16** is heated in the melt at 165 °C, thermal ROP takes place to yield the poly(thionylphosphazene) **17** with chlorine substituents at both sulfur and phosphorus.

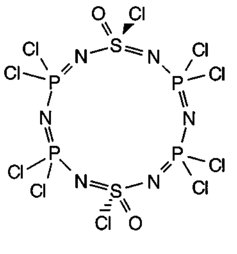
The fluorinated derivative **18**, which can be prepared by reaction of the perchlorinated thionylphosphazene with AgF_2[43] or alternatively with HgF_2–$AlCl_3$,[44] also undergoes thermal ROP when heated in the melt at 180 °C.[45]

As a consequence of the hydrolytically sensitive main-group-element–halogen bonds the gummy polymers **17** and **19** are very sensitive to moisture and must be handled under an inert atmosphere. Therefore, molecular weight measurements on these perhalogenated poly(thionylphosphazenes) have not yet been reported. Nevertheless, insight into the conformational flexibility of the main chain present in these new polymer structures was obtained from an analysis of their thermal transition behaviour by Differential Scanning Calorimetry (DSC). Glass–rubber transitions, T_gs, which reflect the onset of large-scale conformational motion of the polymer chain, were detected at −46 °C for **17** and −56 °C for **19**. These values are intermediate between those of related polyphosphazenes $[N{=}PCl_2]_n$ ($T_g = -63$ °C)[46] and poly(oxothiazenes) such as $[NS(O)Me]_n$ ($T_g = 55$–65 °C)[47] reflecting the hybrid nature of the polymer structure. This increase in T_g for **17** and **19** relative to $[N{=}PCl_2]_n$ suggests that there is a decrease in conformational flexibility of the perhalogenated polymers when S(O)Cl or S(O)F groups replace a PCl_2 unit in the backbone. This is probably a consequence of: (*i*) the smaller size of sulfur relative to phosphorus and (*ii*) increased intermolecular interactions when a highly polar S=O moiety is present. The lower T_g (−56 °C) of polymer **19** which has fluorine at sulfur, compared with that of **17** (−46 °C) which has a chlorine substituent can be attributed to the smaller size and lower polarizability of a fluorine side group compared with chlorine. This trend is also observed with polyphosphazenes and organic polymers. For example, the T_g of $[N{=}PF_2]_n$ (−96 °C) is significantly lower than that of $[N{=}PCl_2]_n$ (−66 °C) and the T_g of poly(vinylidene fluoride) $[CH_2CF_2]_n$ (−39 °C) is lower than that of poly(vinylidene chloride) $[CH_2CCl_2]_n$ (−19 °C).

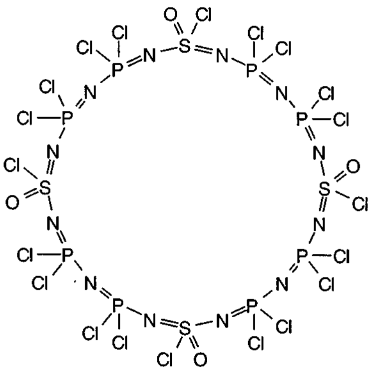
Ab initio molecular orbital calculations on short-chain model compounds of poly(thionylphosphazenes) **17** and **19** have also been carried out to study the conformations and bonding present, and to provide insight into the factors that influence chain flexibility.[48] Geometry optimizations show that the model compounds adopt a non-planar *trans-cis* structure which has been



20a



20b



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attributed to the presence of two different substituents on sulfur. The calculations suggest that the isotactic polymer [*i.e.* one in which the sulfur(VI) stereocentres have the same configuration] would form a 12/5 helix in an extended conformation and that highly polar S–N and P–N bonds are present where sulfur and phosphorus are electron deficient and nitrogen is electron rich. The torsional flexibility was also studied, and revealed that the torsional barriers for rotation of the S–N–P and P–N–P bond angles decrease when changing from chlorine on sulfur in **17** to fluorine on sulfur in **19**. This calculated increase in flexibility in **19** is consistent with the observed lowering of the T_g when fluorine replaces chlorine as a substituent on sulfur.

Isolation of macrocycles

The dominant compounds present in the crude reaction mixture after heating **16** for 4 h at 165 °C are unreacted cyclic thionylphosphazene **16** and polymer **17** (*ca.* 80%). In addition to these species several other minor products can be detected by ^{31}P NMR spectroscopy.[49] Furthermore, Fast Atom Bombardment mass spectrometry indicated that 12-, 18-, 24-, 30- and 36-membered rings, $[(NSOCl)(NPCl_2)_2]_n$ ($n = 2–6$), are also formed. From this mixture the *cis* and *trans* isomers of the 12-membered ring **20a** and **20b** have been successfully isolated and characterized by X-ray diffraction. The two rings were found to be significantly non-planar which was not unexpected as the rings formally have 12π-electrons and are anti-aromatic. The P–N–P bond angles are highly expanded [134(1)–163(1)°] relative to **16** [122°], whereas the S–N–P angles are only slightly expanded. Interestingly, the angles at sulfur are much smaller in **20a** and **20b** than in **16**, whereas the angles at phosphorus are similar. The bond lengths in the heterocycles are typical for P–N and S–N double bonds.

Fractional recrystallization also yielded the remarkable 24-membered macrocycle **21** which was characterized *via* crystallographic analysis. Compound **21** is among the largest inorganic heterocycles to be structurally characterized to date.‡

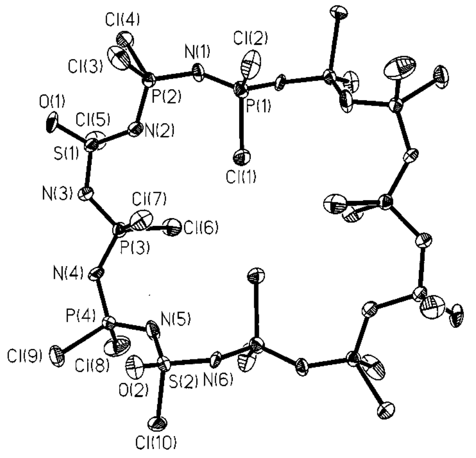
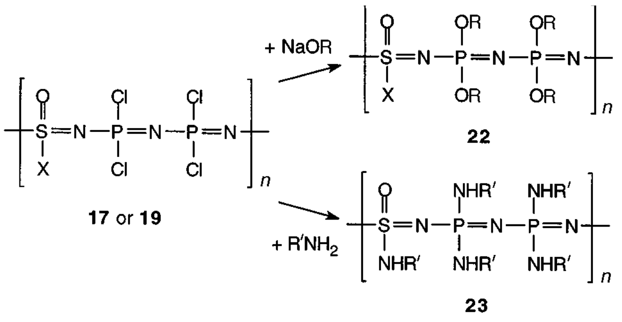


Fig. 4 Molecular structure of the 24-membered thionylphosphazene **21**. Reproduced from ref. 49 with permission



The molecular structure of **21** is shown in Fig. 4, and the structural features of **21** are similar to those of **20a** and **20b**, however in this case the crystal contained only the *cis/trans/cis/trans* isomer in which the PCl_2 fragments alternate between being exo- and endo-cyclic. Studies of this type may provide insight into the mechanism(s) of polymerization/oligomerization and also may also provide access to novel complexes with metal ions.

Synthesis and properties of moisture-stable poly(thionylphosphazenes)

In order to prepare hydrolytically stable poly(thionylphosphazenes) the perchlorinated polymers were treated with nucleophiles to substitute the hydrolytically sensitive main-group-element–halogen bonds.[42,45] This type of post-polymerization structural modification is well-established in polyphosphazene chemistry.[46,51] Thus, aryloxide nucleophiles or primary amines were used to substitute the polymers leading to poly[(aryloxy)thionylphosphazenes] **22** and poly[(amino)thionylphosphazenes] **23** respectively.[52,53]

In the case of the reaction with aryloxides, only substitution of the P–Cl bonds can be achieved even after prolonged reaction times. Interestingly, the sulfur–chlorine (in **17**) or sulfur–fluorine (in **19**) bonds remain intact. This regioselective substitution pattern is exactly the opposite to that observed with poly(thiophosphazenes) **9** which contain sulfur(IV) centres where perhalogenated derivatives substitute with aryloxides preferentially at sulfur.[54] In contrast to aryloxides, amines readily substitute **17** or **19** at both the phosphorus and sulfur sites at ambient temperature. The resulting moisture-stable poly(thionylphosphazenes) range from elastomeric materials (see Fig. 5) to glassy polymers (Table 1).

The poly[(aryloxy)thionylphosphazenes] **22** and poly[(amino)thionylphosphazenes] **23** show no noticeable change after storage in air for several years. However, in solution, polymer **22** rapidly decomposes in the presence of strong bases such as NaOH or excess sodium aryloxide at elevated temperatures.

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‡ To our knowledge, only two other examples of 24-membered inorganic heterocycles have been structurally characterized: the 24-membered phosphazene $[N{=}PPh_2]_{12}$;[50a] and a 24-membered imidoantimony(III) metallacycle which was recently reported.[50b]

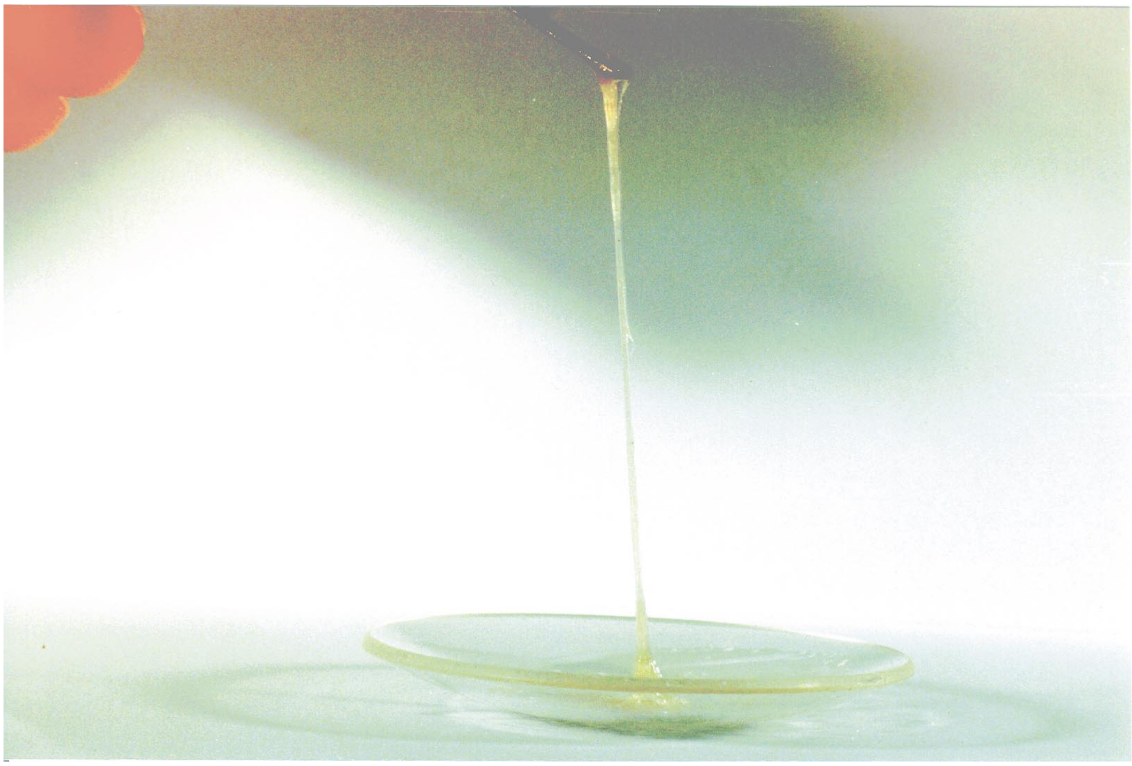

Fig. 5 A typical poly(thionylphosphazene) elastomer

Table 1 Characterization data for selected poly(thionylphosphazenes)

			Molecular weight			
	R	R′	M_w	PDI[a]	T_g/°C	Type of material
17	Cl	Cl	—	—	−46	Gum
19	F	Cl	—	—	−56	Gum
22a	Cl	OPh	58 000	1.4	10	Gum
22b	Cl	OC_6H_4Ph-*p*	140 000	2.7	55	Glass
22c	F	OPh	38 000	1.5	−15	Gum
22d	F	OC_6H_4Ph–*p*	90 000	1.6	48	Glass
23a	NHMe	NHMe	5 000[b]	1.5	22	Glass
23b	NHEt	NHEt	37 000	2.3	4	Gum
23c	NHPr	NHPr	49 000	1.9	6	Gum
23d	NHBu	NHBu	49 000	2.0	−16	Gum
23e	$NH(C_6H_{13})$	$NH(C_6H_{13})$	71 000	1.9	−18	Gum
23f	NHPh	NHPh	130 000	1.8	82	Glass
23g	OCH_2CF_3–NHBu		39 000[c]	1.4	−30	Gum

[a] Polydispersity index (PDI) is the measure of the distribution of molecular weights in a polymer sample and is defined as the ratio of the weight average molecular weight (M_w) and the number average molecular weight (M_n). [b] The molecular weight of this water soluble polymer is likely a dramatic underestimate because of its anticipated small hydrodynamic size in thf solution. [c] *ca.* 80% OCH_2CF_3 and 20% NHBu.

These reactions are presumably initiated by nucleophilic attack at the sulfur(VI) centre. The molecular weights of the polymers **22** and **23** have been estimated by Gel Permeation Chromatography (GPC) relative to polystyrene standards (Table 1). In addition, an absolute value of the weight average molecular weight (M_w) for polymer **22b** was determined by low-angle laser light scattering (LALLS) studies in thf solution and gave a value of $M_w = 64\,000$ compared to the value determined by GPC (140 000). This result showed that GPC, a relative technique, overestimates the molecular weight of aryloxy-substituted poly(thionylphosphazenes) by a factor of 2. In contrast, LALLS for **23d** gave $M_w = 105\,000$ which is substantially greater than that determined by GPC ($M_w = 49\,000$). Thus, poly[(amino)thionylphosphazenes] appear to be poorly solvated in thf and therefore the effective hydrodynamic size of the polymer coils is compact with respect to polystyrene, whereas for poly[(aryloxy)thionylphosphazenes] the exact opposite is true. Thus, polymer molecular weights of **22** are overestimated and underestimated for **23**, since GPC separation of polymers is based on effective hydrodynamic size.

The thermal transition behaviour of the aryloxy polymers was studied by DSC and, as expected, bulkier aryloxy side-groups, such as *para*-phenylphenoxide led to an increase in T_g over less bulky side groups such as phenoxide. For poly[(amino)thionylphosphazenes], the T_g values can be easily modified by varying the type and length of side-chain used. The use of bulky amines, such as aniline to substitute the polymer leads to a high T_g of 82 °C for **23f**. The T_g values show a general decrease as the length of the alkyl chain is extended from methyl (**23a**) ($T_g = 22$ °C) to hexyl (**23e**) ($T_g = -18$ °C). This effect arises from the free volume increase as the longer alkyl side groups push the polymer chains further apart. Interestingly, in contrast to the situation for perhalogenated poly(thionylphosphazenes), the aryloxy- and amino-substituted materials generally possess lower T_gs than the analogous classical polyphosphazenes. For example, the butylamino polymer **23d**

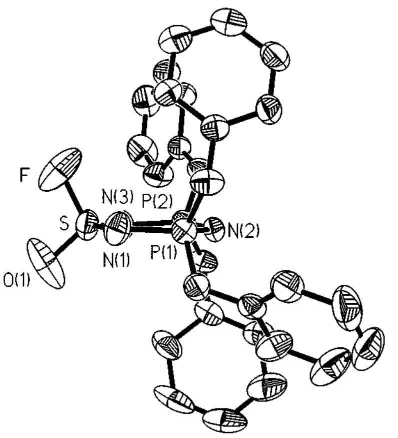

Fig. 6 Molecular structure of a regioselectively phenoxide-substituted thionylphosphazene. Reproduced from ref. 56 with permission

has a significantly lower T_g (−16 °C) than $[N{=}P(NHBu^n)_2]_n$ (T_g = 8 °C).[55] This is a consequence of the presence of the small S=O group which leads to only five substitutents of significant size per six skeletal atom repeat unit in poly(thionylphosphazenes) compared to six substituents for polyphosphazenes. Providing that the substituents are not small this effect overrides the lower flexibility introduced by the replacement of a phosphorus atom by a sulfur(VI) moiety discussed above. Another interesting difference from polyphosphazenes is that all of the poly(thionylphosphazenes) prepared so far are amorphous and, to date, none shows melting transitions by DSC. Their amorphous nature has been confirmed by wide-angle X-ray scattering studies which give featureless diffractograms.

Attempts completely to substitute the polymers **17** and **19** with alkoxide nucleophiles have led only to degradation of the polymer backbone. The unexpected regioselectivity of substitution of the poly(thionylphosphazenes) with aryloxide nucleophiles and the rapid degradation of the polymer backbone with alkoxide nucleophiles prompted us to model this behaviour by studying the reactions of the cyclic thionylphosphazenes **16** and **18** towards representative aryloxide and alkoxide reagents.[56] The substitution reactions with NaOPh were found to conform to the following general order of reactivity, PCl_2 > PCl(OPh) > S(O)X (X = Cl or F). As in the case of the polymer, the substitution of the S−Cl bonds did not take place under normal reaction conditions, but it was found that upon the addition of an excess of NaOPh and reaction for several days at 25 °C or reflux for 4 h, the fully substituted cyclic thionylphosphazene could be formed. In the case of the fluorinated cyclic thionylphosphazene, even after prolonged reflux with excess NaOPh, no substitution of the S−Cl bond was detected and only the regioselectively tetrasubstituted thionylphosphazene could be isolated (see Fig. 6).

Two alkoxide nucleophiles, trifluoroethoxide and butoxide, were chosen to model the substitution pattern of **16** and **18**. The reaction of cyclic thionylphosphazene with NaOBu was found to follow the same order of reactivity as NaOPh, however unlike NaOPh the substitution of the S−Cl bond was facile at room temperature and the substitution of the S−F bond required an excess of nucleophile. Although following the same general order of reactivity as NaOPh or NaOBu, the reaction of the cyclic thionylphosphazenes with $NaOCH_2CF_3$ was found to differ in that a significant enhancement in reaction rate was detected with each equivalent of trifluoroethoxide added. Although the reason for the backbone degradation in the reaction of **17** and **19** with alkoxides is still not clear, these results have encouraged the recent synthesis of poly[(alkoxy)thionylphosphazenes] such as **23g** with high loadings (*ca*. 80%) of trifluoroethoxide and low T_gs (−30 °C).[57] Further developments in this area are expected to furnish polymers with even lower glass transitions.

Applications of poly(thionylphosphazenes) as matrices for oxygen sensors

Poly(thionylphosphazenes) represent an interesting class of new polymers and we have begun to explore the possible applications of these materials. One area where significant potential has already been established involves their use as phosphorescent oxygen sensor matrices.[58] Phosphorescent sensors based on composites comprising transition-metal-based dyes {*e.g.* $[Ru(L)_3]^{2+}$ (L = 4,7-diphenyl-1,10-phenanthroline)} with oxygen quenchable excited states dispersed in polymer matrices of high gas permeability (*e.g.* crosslinked polysiloxanes) have attracted attention as oxygen sensors for biomedical applications.[59] In addition, much interest exists in the use of such sensors for barometric applications such as the determination of the air pressure distribution over aircraft models in a wind tunnel. Information of this type plays a vital role in aircraft design and testing. Current techniques involve the use of solid-state pressure taps which are monitored individually. However, this technology is very expensive, gives pressure information only at points where the taps are located, and is limited to stationary objects. The use of pressure sensing composites has the potential to overcome all of these problems. For example, simply spray-coating a film of the composite onto a surface of interest allows the pressure distribution over the whole surface to be readily monitored *via* illumination of the excitation wavelength of the dye and data acquisition in the region of phosphorescent emission, the intensity of which depends on the air (*i.e.* oxygen) pressure at that point.

As part of a broad collaborative effort we have shown that poly[(amino)thionylphosphazenes], **23**, offer significant advantages over existing materials for pressure-sensing composite technology (see Fig. 7) and it has even been found that rotating objects such as propellers can be imaged. The key advantages of poly[(amino)thionylphosphazenes] for this type of application involve the high solubility and high diffusion coefficient for oxygen in these materials,[60] the good compatibility with the dye due to the polar polymer structure, and the ability to access high quality films without the need for crosslinking. In addition, the relatively low T_gs for **23** are important as large-scale conformational motions are usually vital for effective gas diffusion in a material. Glass transition values of less than −10 °C, which represents a typical low-temperature limit in a wind tunnel, are therefore critical.

Conclusion

Exploration of the chemistry of boron–nitrogen–phosphorus and sulfur(VI)–nitrogen–phosphorus ring systems has led to the discovery of interesting new inorganic heterocycles, unusual reactivity, and new inorganic polymer systems. For example, an investigation of boratophosphazene chemistry has shown that pseudo-aromatic borazine–phosphazene hybrid rings can be synthesised and has led to the discovery of unusual skeletal substitution reactions involving normally unreactive non-coordinating anions. Our study of the chemistry of cyclic thionylphosphazenes has uncovered interesting reactivity patterns and novel, stable sulfur–nitrogen–phosphorus macrocycles and polymers. The polymers have also been found to have interesting properties which have led to their use as matrices for phosphorescent sensing composites with potential applications in the aerospace industry.

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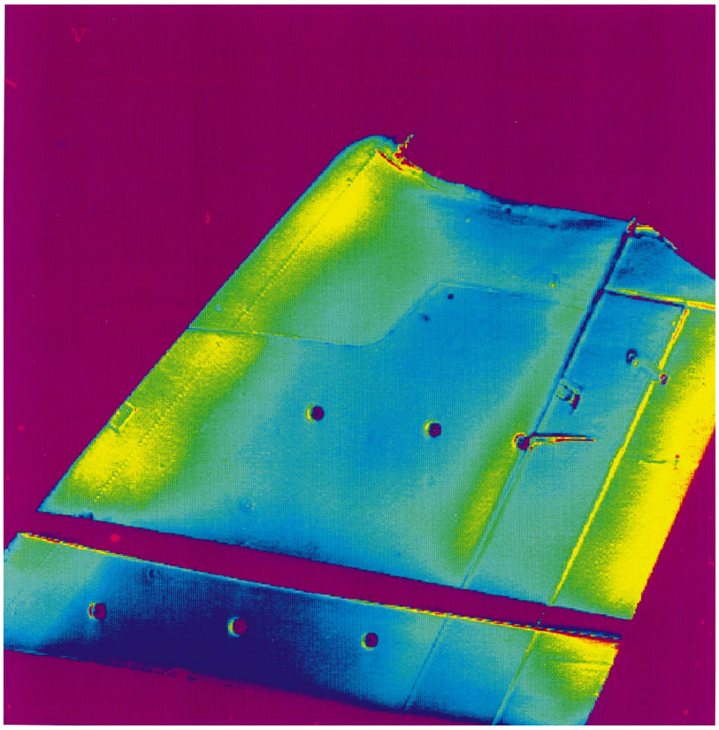

Fig. 7 Phosphorescent image of a section of a model aircraft wing showing the surface pressure distribution during a wind tunnel experiment. The colours, whilst artificial, reflect the pressure at different points on the surface. The upper section shows a polysiloxane matrix whereas the lower portion involves a poly[(amino)thionylphosphazene] as the matrix. The dye in each case was $[Ru(L)_3]Cl_2$ (L = 4,7-diphenyl-1,10-phenanthroline). The image is courtesy of Dr. X. Gu of the Ontario Laser and Lightwave Center and was obtained from a series of tests run at the National Research Council Wind Tunnel in Ottawa

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