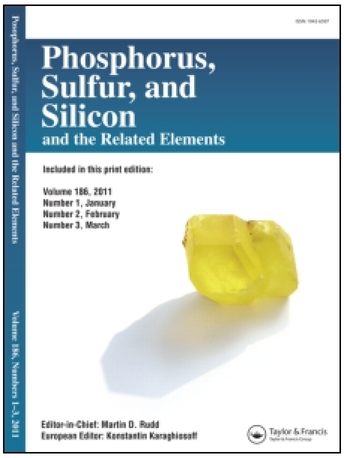

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UNUSUAL CHEMISTRY OF HYBRID BORAZINE-PHOSPHAZENE RINGS AND STRAINED [1]FERROCENOPHANES

DEREK P. GATES[a], PAUL NGUYEN[a], ARNOLD L. RHEINGOLD[b], AND IAN MANNERS[a]*
a) Department of Chemistry, University of Toronto, 80 St. George St., Toronto M5S 1A1, Ontario, Canada.
b) Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA.

Abstract Very few examples of rings constructed of boron, phosphorus and nitrogen are known. In this paper some unusual chemistry of these species and recent studies of [1]ferrocenophanes will be described.

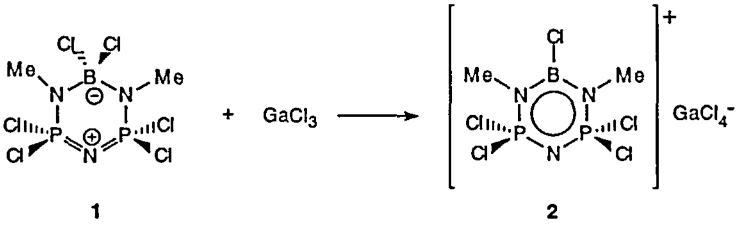
INTRODUCTION

The boratophosphazene **1** (a zwitterionic species) represents one of the best characterized boron-nitrogen-phosphorus rings and has been prepared by several routes.[1,2] Electrical conductivity measurements have provided evidence for the formation of an ion pair via chloride loss from boron in polar solvents such as nitrobenzene.[2] In order to clarify the nature of **1**, a single crystal X-ray diffraction study of this species was undertaken. The BP_2N_3

ring shows a significant deviation from planarity with the boron atom deviating from the best plane by 0.39(1) Å, and the axial B-Cl bond is highly elongated.[3]

BORAZINE-PHOSPHAZENE HYBRIDS

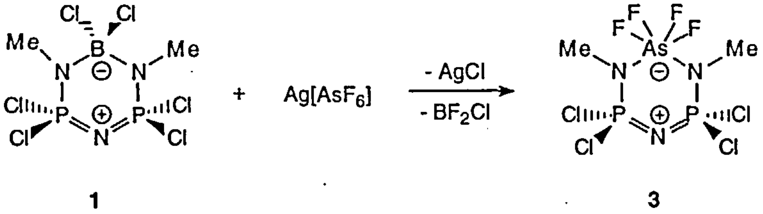
Compound **2** was prepared via Lewis acid halide abstraction from **1.** The crystal structure of **2**, shows a planar ring, in which the B-N bond lengths (1.43(1) Å) are typical of borazines indicating some π-bonding from donation of the lone pair on N(Me) into the empty 2p orbital on boron. This represents the first crystallographically characterized example of a borazine-phosphazene hybrid.[3]



SKELETAL SUBSTITUTION REACTIONS

In our recent studies of the reactivity of the cation we have found that **2** reacts with tertiary amines such as NEt_3 to reform boratophosphazene **1** together with $Et_3N{\cdot}GaCl_3$, rather than the expected adduct with boron. This observed reactivity pattern prompted us to explore the possibility of preparing analogues of **2** with alternative, less reactive fluorinated counterions such as $[AsF_6]^-$ or $[SbF_6]^-$.

When a solution of the **1** was added to a suspension of Ag[AsF_6] in CH_2Cl_2, the immediate formation of a fine white precipitate of AgCl and was observed. The reaction mixture was stirred overnight after which a large build up of pressure had taken place inside the vessel. The solution was decanted, and the solvent was removed yielding a white crystalline solid. This solid material was analyzed by ^{31}P NMR in $CDCl_3$, which showed the presence of a dominant singlet at 30.6 ppm together with a very minor byproduct at 16.7 ppm. Neither of these resonances were consistent with the formation of the analogue of borazine-phosphazene hybrid, **2** with AsF_6^- as counterion (for **2** $\delta(^{31}P, CDCl_3) = 35.0$ ppm). Remarkably, no non-volatile boron containing species were detected by ^{11}B NMR. The dominant product could be separated from the byproduct by extraction of the solid into a mixture of dichloromethane/hexanes (ca. 1:10). ^1H NMR analysis of the purified product revealed a second order multiplet at 3.16 ppm which is similar to that of **1**. Colourless crystals were obtained by slow evaporation of solvent from a solution of the product in dichloromethane/hexanes (1:1). A crystal was analyzed by X-ray diffraction, and surprisingly showed the product of the reaction to be the arsenic(V) heterophosphazene **3** (Figure 1).[4]

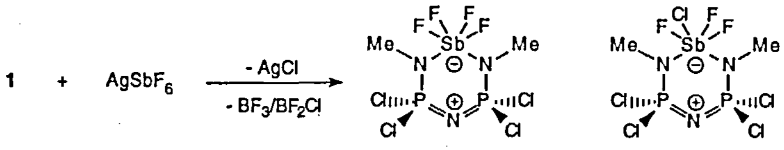


Mass spectrometric analysis of **3** supports the result of the X-ray structure analysis with the identification of a molecular ion M^+ with the expected isotope pattern.

Skeletal substitution reactions of an atom in an inorganic ring are rare and are, to our knowledge, unknown for boron-containing rings.[5] It is also noteworthy that, AsF_6^- is often used as a "non-coordinating" anion to isolate very reactive cations. Remarkably this anion appears to react readily with the borazine-phosphazene cation, which we assume is formed initially in the reaction mixture containing **1** and $Ag[AsF_6]$. We believe that the thermodynamic driving force for the observed reaction is the formation of B-F bonds from As-F bonds (B-F, 613 ± 53 kJ/mol; As-F, ca. 406 kJ/mol) and the subsequent elimination of volatile BF_xCl_{3-x}.

In order to explore the generality of this new synthetic procedure, we have also studied the reaction of **1** with $Ag[SbF_6]$ in Ch_2Cl_2. Again, an immediate white precipitate of AgCl formed and a pressure buildup was detected. After workup, a crystalline solid was obtained and analysis by ^{31}P NMR in $CDCl_3$ revealed two dominant resonances at 28.9 and 27.5 ppm and a very small resonance at 17.1 ppm. This is consistent with skeletal replacement of boron however, suggests that more than one product is obtained from this reaction. Mass spectral analysis indicated that both **4a** and **4b** were formed. Conclusive proof of the formation of **4a** and **4b** was provided by X-ray crystallographic analysis.[4]

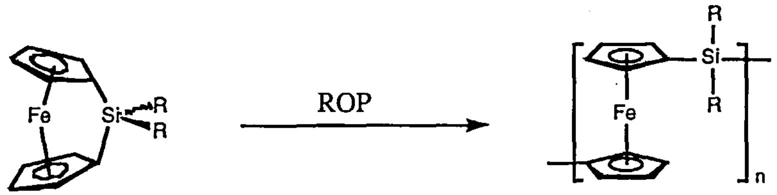
Further work is underway aimed at studying the mechanism and exploring the generality of this new class of reaction with emphasis on the incorporation of both metals and non-metals into the ring structure. The reactivity of the new heterocycles (including their ring-opening polymerization behavior) is also currently being explored.



4a 4b

RING-OPENING POLYMERIZATION (ROP) OF STRAINED METALLOCENOPHANES

Since the first report in 1992,[6] thermal ROP of strained metallocenophanes (e.g. **5**) has been developed as versatile route to a variety of high molecular weight transition metal-based polymers (such as **6**). We are now attempting to extend the ROP route still further to both related and unrelated systems whilst concentrating on detailed studies of the properties of the polymers and mechanisms of the polymerization reactions.[7,8]



5 6

Recent results include the synthesis of the first poly(ferrocenylsilanes) with OR and NR_2 substituents via halogen substitution reactions with the readily accessible $SiCl_2$-bridged

[1]ferrocenophane derivative **5** (R = Cl). Reaction of the latter with alcohols, phenols, or amines in the presence of NEt_3 as HCl acceptor affords excellent yields of the new ferrocenophanes **5** (R = OR or NR_2) which undergo either thermal or transition metal catalyzed ROP to yield the new high polymers **6** (R = OR or NR_2) (Table 1).[9]

Table 1: Characterization Data for Selected New Poly(ferrocenylsilanes) 6

R	$\delta\,^{29}Si$	M_w[a]	M_n[a]	PDI	T_g(°C)
OMe	-17.2	2.9×10^5	1.5×10^5	2.1	19
OEt	-20.9	8.1×10^5	3.8×10^5	2.1	0
OC_6H_5	-24.2	4.5×10^5	2.3×10^5	2.0	54
NMe_2[b]	-	5.7×10^5	1.5×10^5	3.8	-

[a] Determined by GPC in THF using polystyrene standards.
[b] For the soluble polymer fraction extracted with hot THF.

Amorphous films of poly(ferrocenylsilanes) are insulators but on exposure to iodine weak semiconducting materials ($\sigma = 10^{-7}$-10^{-8} Scm^{-1}) are formed.[7] Recent work has shown that oriented films of polymers **6** (R = Me or n-Bu) give I_2-doped conductivities of up to c.a. 2×10^{-4} Scm^{-1}, a dramatic increase of 10^{10} over their pristine precursors. Hole mobilities for poly(ferrocenylsilanes) are also promising (e.g. for **6** (R = Me/Ph) mobility = c.a. 10^{-5} cm^2/Vs).[10] Future work will involve the evaluation of devices utilizing these materials.

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