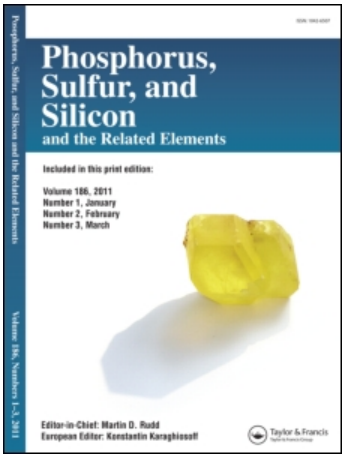

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Synthesis and Characterization of the First Hybrid Borazine-Phosphazene Ring

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SYNTHESIS AND CHARACTERIZATION OF THE FIRST HYBRID BORAZINE-PHOSPHAZENE RING

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Abstract Whereas borazines and phosphazenes represent two of the most well studied classes of inorganic heterocycles, very few examples of rings constructed of boron, phosphorus and nitrogen are known. This work presents our investigation of these interesting heterocycles.

INTRODUCTION

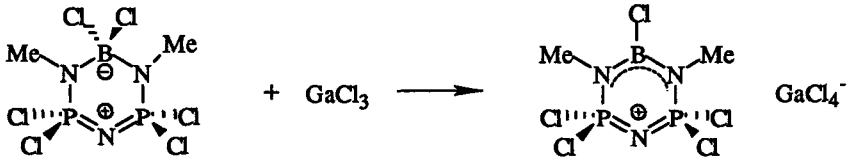
Cyclic heterophosphazenes have attracted considerable attention because of their intrinsically interesting structural features and as potential precursors to new polymer systems via ring-opening polymerization. In particular, species containing transition metals (molybdenum and tungsten) or main group elements (carbon, sulfur(IV) or sulfur(VI)) thermally polymerize to yield novel classes of inorganic polymers.

BORATOPHOSPHAZENES

The boratophosphazene **1** (a zwitterionic species) represents one of the best characterized boron-nitrogen-phosphorus rings and has been prepared by several routes.[1] 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.

Preliminary studies of the thermal ring-opening polymerization behaviour of **1** at 260°C have shown that the classical polyphosphazene $[NPCl_2]_n$ is formed along with the borazine $[MeBNCl]_3$, $N_4P_4Cl_8$, and MeCl together with other products.

BORAZINE-PHOSPHAZENE HYBRIDS



1 **2**

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] Compound **2** has also exhibited some interesting chemistry, reacting at the boron center with tertiary amines.

ACKNOWLEDGMENTS

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