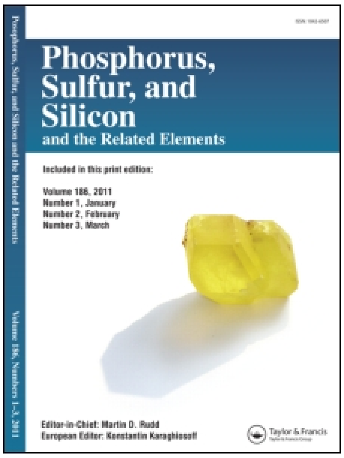

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Synthesis and Ring-Opening Polymerization (ROP) of Strained Phosphorus-Containing Rings

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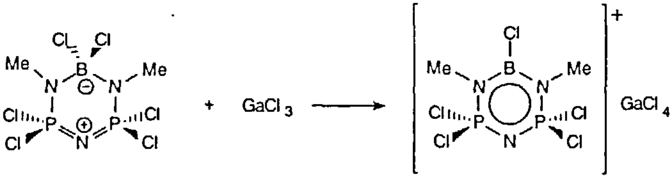
Studies of inorganic and organometallic rings containing phosphorus are described. Novel skeletal substitution reactions are reported for B-N-P heterocycles and cyclic thionylphosphazenes are found to undergo ambient temperature ROP in the presence of $GaCl_3$. The phosphorus-bridged [1]ferrocenophane $Fe(\eta\text{-}C_5H_4)_2PPh$ undergoes living anionic polymerization. This provides access to block copolymers such as poly(ferrocenylphosphine)-poly(dimethylsiloxane) which dissolve in hexanes to yield interesting micellar aggregates with organometallic cores.

STUDIES OF INORGANIC RINGS CONTAINING PHOSPHORUS

The borazine-phosphazene hybrid **2** was prepared via Lewis acid halide abstraction from the known species **1**.[1,2] Attempts to extend the range of salts analogous to **2** to other counterions such as $[AsF_6]^-$ or $[SbF_6]^-$ led to unexpected skeletal substitution reactions to afford e.g. $N(Cl_2PNMe)_2AsF_4$ (3) and the Sb analog.[2]

Cyclic thionylphosphazenes such as $[NSOCl(NPCl_2)_2]$ (4) undergo thermal ROP at 165°C. Generation of a cation derived from 4 via loss of chloride from the sulfur(VI) center represents the initiation step in the proposed cationic chain growth mechanism. Recent attempts to generate the cation have led to unusual reactivity

Recent attempts to generate the cation have led to unusual reactivity and the discovery of an ambient temperature ROP of **4** in solution in the presence of $GaCl_3$.[3]

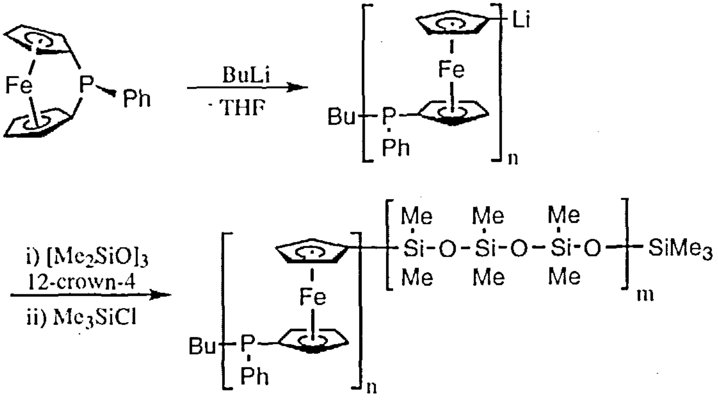


1 **2**

ORGANOMETALLIC RINGS CONTAINING PHOSPHORUS: SYNTHESIS AND PROPERTIES OF POLY(FERROCENYLPHOSPHINE) BLOCK COPOLYMERS

ROP of strained, ring-tilted metallocenophanes provides a general route to a variety of interesting new high molecular weight poly(metallocenes). We have previously reported that living anionic ROP of silicon-bridged [1]ferrocenophanes is possible and that this permits molecular weight control, end-group functionalization, and the synthesis of multiblock copolymers.[4,5] Studies of the diblock copolymers such as polystyrene-poly(ferrocenylsilane) (PS-PFS) and poly(ferrocenylsilane)-poly(dimethylsiloxane) (PFS-PDMS) by TEM and Atomic Force Microscopy (AFM) has shown that different morphologies such as spheres, cylinders, and lamellae are possible in the solid state and novel micellar aggregates are also formed in solution. The nature of these depends on the ratio of the blocks and the method of sample preparation.[5-8]

We have also shown that phosphorus-bridged [1]ferrocenophanes undergo living anionic polymerization.[9] We have prepared, for example, novel block copolymers such as the poly(ferrocenylphosphine)-b-poly(dimethylsiloxane) (PFP-PDMS). Recently, in collaboration with the group of Prof. Mitch Winnik in our Department, we have studied PFP-PDMS block copolymer materials with, e.g, a PFP:PDMS ratio of c.a. 1 : 3.[10] These form spherical micellar aggregates in hexanes (a good solvent for the PDMS block and a poor solvent for PFP). The organometallic cores are readily visualized by TEM (see Figure 1).[10]



PFP-PDMS

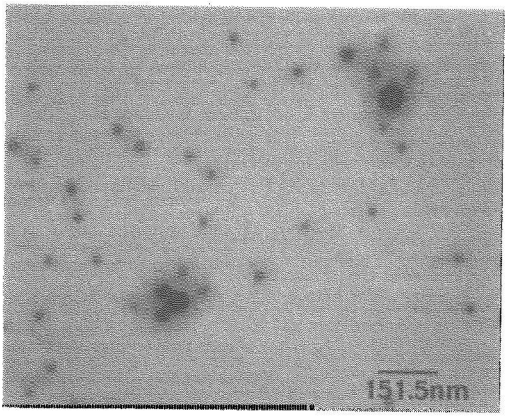


Figure 1 TEM of micelles aerosol-sprayed from a hexanes solution of PFP$_{50}$-PDMS$_{141}$ (M_n = 24,000, PDI = 1.14)

The cores are surrounded by a PDMS corona. No staining is necessary because of the intrinsic electron density contrast between the blocks.

These novel organometallic-inorganic aggregates are of considerable interest as possible precursors to magnetic materials (e.g. via pyrolysis), novel conductive materials, or as catalytic materials after coordination of transition metals to the phosphorus sites.[5-8]

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