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FINAL REPORT

INVESTIGATION OF OPTICAL NONLINEARITES, CONDUCTIVITY, AND MAGNETISM IN ORGANOMETALLIC MATERIALS

Substantial progress was made in several key areas of the proposed research. With regard to the production of new materials via the organometallic "doping" of polydiacetylenes with diorganostannylenes, we have elucidated the steric and electronic factors which govern the reactivity of stannylenes towards alkynes (Technical Report No. 1). New classes of cyclic organostannane compounds were produced which include the first examples of stannacyclopropenes and 1,2-distannacyclobut-3-enes. Derivatives of the latter ring system were found to be both air and moisture stable which allows them to be used as important synthetic precursors to new cyclic stystems containing tin. Oxidation of a 1,2-distannacyclobutene (with iodine was achieved to produce an air and moisture stable tin-centered cationic species. Future work is being performed to produce monomers for ring-open polymerization via olefin metathesis which contain the 1,2-distannacyclobutene) moiety. Upon oxidative doping, new ionic polymers maybe formed. Finally ab initio molecular orbital calculations were performed on the metallacyclopropenes of silicon, germanium, and tin and this information supports the model of reactivity and stability that was formulated for alkynes and stannylenes. [illegible] New compounds, → [illegible]

With regard to polystannanes, important progress was made with the synthesis and characterization of the first examples of polycyclic polystannanes (Technical Report Nos. 2 and 3). The unique optical properties displayed by these molecular frameworks can be correlated with a "σ-delocalization" effect which is identical to that proposed to explain the optical properties of linear polysilanes. The polycyclic polystannanes also display unique thermal properties and these compounds may prove to be important models for the design of new solid state materials. Synthetic methodology is still being developed which can be used to produce any desired polycyclic polystannane structure thorugh a rational approach. A very important polycyclic structure that we have characterized is a pentastanna[1.1.1]propellane derivative. The tin-bonded framework of this structure can be viewed as being "nonclassical" with bridgehead tin atoms that are of inverted tetrahedral geometry. A controversy exists concerning the nature of bonding between the bridgehead atoms of compounds of this class, however, we have obtained results which support our conclusion that there is no formal bond between the bridgehead tin atoms in our compound. We have generated and fully characterized the extremely stable radical anion of our pentastanna[1.1.1]propellane which includes ESR data that shows the unpaired electron to be delocalized over the five tin atoms of the system. We have also prepared the first example of a bicyclo[1.1.1]pentastannane and can now use the propellane to prepare a variety of these new compounds. As with the carbon propellane analogue, which can be polymerized to produce rigid-rod polymers, we believe that future exploration of the chemical reactivity of the readily available pentastanna[1.1.1]propellane will lead to new and exciting materials which possess unique solid state properties.

Finally, synthetic methodology was developed to produce new cyclic alkenyl disilanes which might be useful as monomers for ring-open polymerization via olefin metathesis, such as 1,1,2,2-tetramethyl-1,2-disilacyclopent-3-ene (Technical Report No. 4).

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Publications Emanating from Grant

1. Sita, L.R., Kinoshita, I., Lee, S.P. "Reactions of Stannylenes with Alkynes: The Synthesis and Chemical Reactivity of a Stable 1,2-Distannacyclobut-3-ene," *Organometallics*, in press.

2. Sita, L.R.; Bickerstaff, R.D. "2,2,4,4,5,5-Hexakis(2,6-diethylphenyl)-pentastanna[1.1.1]propellane: Characterization and Molecular Structure," *J. Am. Chem. Soc.* **1989**, *111*, 6454.

4. Sita, L.R.; Bickerstaff, R.D. "Isolation and Molecular Structure of the First Bicyclo[2.2.0]hexastannane" *J. Am. Chem. Soc.* **1989**, *111*, 3769.

5. Sita, L.R.; Bickerstaff, R.D. "Investigation of the Factors Influencing the Structure and Stability of Stannacyclopropenes: The Synthesis and Molecular Structure of Two Derivatives," *Phosphorus and Sulfur*, **1989**, *41*, 31.

6. Sita, L.R.; Kinoshita, I. "Chemical Reduction of a Pentastanna[1.1.1]-propellane Derivative and the Synthesis and Molecular Structure of a Bicyclo[1.1.1]pentastannane," *J. Am. Chem. Soc.*, submitted 2/90.

7. Sita, L.R. "Polycyclic Polystannanes," *Polyhedron*, invited manuscript to a Symposium-in-Print issue, 8/90.

Lists of Technical Reports

Technical Report No. 1 - Sita, L.R.; Bickerstaff, R.D. "Ivestigation of the Factors Influencing the Structure and Stability of Stannacyclopropenes: The Synthesis and Molecular Structure of Two Derivatives." 5/24/89.

Technical Report No. 2 - Sita, L.R.; Bickerstaff, R.D. "Isolation and Molecular Structure of the First Bicyclo[2.2.0]hexastannane." 5/24/89.

Technical Report No. 3 - Sita, L.R.; Bickerstaff, R.D. "2,2,4,4,5,5,-Hexakis(2,6-diethylphenyl)pentastanna[1.1.1]propellane: Characterization and Molecular Structure." 5/24/89.

Technical Report No. 4 - Sita, L.R.; Lyon, S.R. "A New Strategy for the Construction of Carbocyclic Alkenyl Silanes: The Synthesis of 1,1,2,2-tetramethyl-1,2-disilacyclopent-3-ene." 5/24/89.

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