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ORGANIC/ORGANOMETALLIC CHEMISTRY. Synthetic and reactive studies of novel organometallic complexes. Applications of nuclear magnetic resonance to structural and mechanistic problems in organometallic chemistry.

My group is interested in synthesizing novel organometallic complexes and then studying their reactive behavior. Specifically we are interested in the possibility of making transition metal complexes of stannylene ligands which exhibit multiple bond character between the transition metal and the tin atom.

**Metal Stannylene Complexes**

A “free” stannylene is a tin compound in which the tin center has a formal oxidation state of two, Sn (II), and two groups bound to it, SnR₂. We want to synthesize metal complexes in which these “free” stannyles act as ligands to a transition metal center. Metal stannyles are inherently interesting due to the unusual nature of bonding between two “heavy metal” atoms. Unlike bonding between “light” atoms such as carbon, understanding the bonding characteristics of “heavy” atoms such as tin and tungsten is complicated by d-orbital participation, ease of electron cloud polarization, and even sometimes relativistic effects. The nature of multiple bonds between “heavy” atoms is particularly poorly understood, and the existence of a tin-transition metal double bond has yet to be proven.

**Synthesis**

We are attempting the synthesis of these stannyles by first generating a metal based anion (or dianion) and then allowing it to react with a metal halide. In the case where we make a tin dianion, the starting materials are diorganotin dihalides. There are reports in the literature that diorganotin dihalides can be reduced with either sodium or lithium to form the metal salt of a diorganotin dianion.

\[
R_2SnCl_2 + Na \rightarrow Na_2SnR_2 + Cl^{-}
\]

In our proposed synthesis these dianions would react with a metal dihalide to form the stannylene species.

\[
CP_3WX_2 + Na_2SnR_2 \rightarrow CP_3WSnR_2 + 2NaX
\]

In the summer of 1999, Kerstin Wolf and Angel Vargas started down the synthetic pathway for the synthesis of Bz₂SnLi₂, ṬBu₂SnLi₂, Ph₂SnLi₂, and Bu₂SnLi₂. They were quite successful in the
preparation of the diorganotin dihalides; however, the generation of the dianion species did not proceed as easily as indicated in the literature. Through careful work it was found that varying the reaction conditions resulted in different physical and spectroscopic observations. Unfortunately, we do not believe that we have observed the tin dianion species as of yet.

It is also possible to allow a transition metal based anion to react with the diorganotin dihalide. This route has recently been explored by Angel Vargas in my laboratory, and initial results look promising. Specifically, Angel has attempted to generate the lithiotungstenocene hydride shown below and treat it with \( \text{Ph}_2\text{SnCl}_2 \). This reaction generated a new compound which we are now trying to identify.

The starting point for my group's research for the summer of 2000 will be these anionic synthetic routes. Our initial work will be based upon the work of Wolf and Vargas from last summer and this year. The success of their reactions should provide a good launching point to move further along the pathway to synthesizing transition metal stannylenes. Using their notebook descriptions as well as literature descriptions for the preparation of the organotin dihalides, disodium salts and transition metal anions, we will prepare these compounds. Assuming that all goes well, we then move on to our own chemistry of making novel metal stannylenes.

References


(2) Lappert, M. F.; Rowe, R. S. *Coord. Chem. Rev.* **1990**, *100*, 267.
