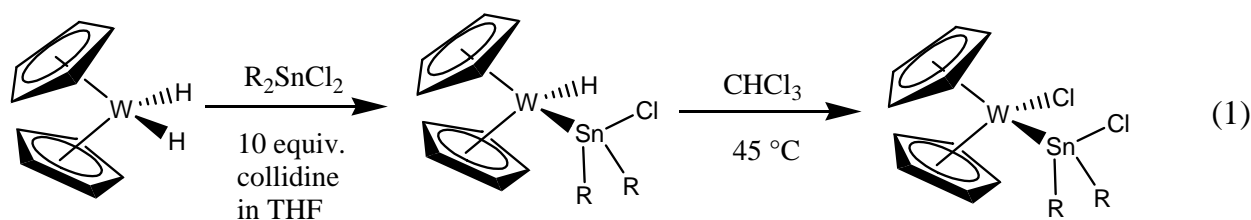


Mobley Group: Synthesis and Reactivity of Transition Metal Stannyl Complexes

Synthesis

We have found a reliable synthesis of transition metal stannyl complexes by first generating a nucleophilic transition metal complex and then allowing it to react with an organotin halide. Angel Vargas initiated investigation of this route in my laboratory, and the initial results looked promising. In 2000, Kwame Nti-Addae continued working on this route and made considerable process. He successfully generated a tungsten-tin hydrido halide complex using the reaction



shown in eq 1. Further work in the group has shown that these two classes of stannyl complexes can be made with a variety of different organic substituents on the tin (*e.g.* R = Ph, *t*-Bu). We have been studying these complexes structurally, paying particular attention to the conformational behavior of the tungsten tin bond and how the identity of the organic substituents affects the length of the tungsten tin bond. Two crystal structures of these complexes, obtained at the University of Iowa X-ray Crystallography Facility, surprised us.

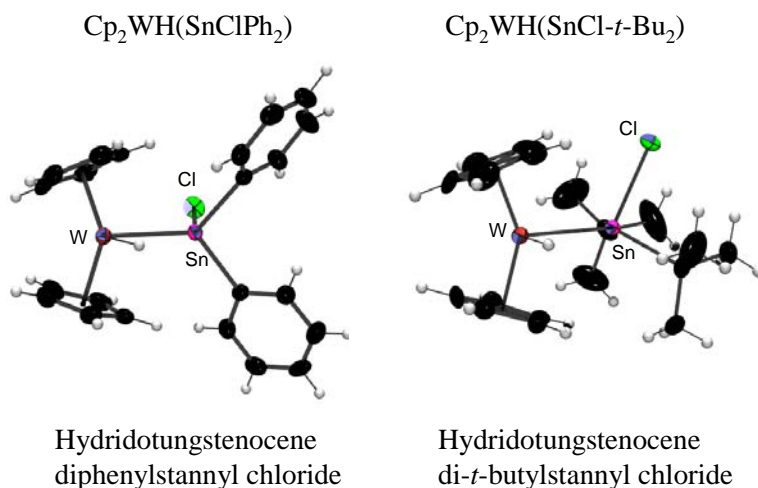


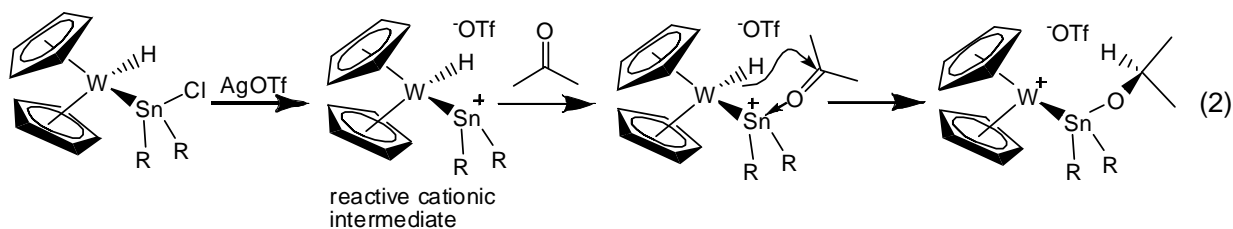
Figure 1. Comparison of structures of phenyl and *t*-butyl derivatives.

While we expected the crystal structures of the *t*-butyl derivative and the phenyl derivative to be very similar, as can be seen in Figure 1, the crystal structures indicate that these complexes adopt different conformations. In addition to this conformational difference, the tungsten tin bond length of the sterically crowded di-*t*-butyl derivative is longer than that of the diphenyl derivative. Furthermore, using variable temperature ^{119}Sn NMR spectroscopy we have found that the one bond tungsten tin coupling constant ($^1J_{\text{W-Sn}}$) varies inversely with the tungsten tin

bond length. This allows us to predict from the solution NMR spectra the tungsten tin bond length in these compounds. This work has been recently published as a full paper in the journal *Organometallics*. You can obtain a free reprint of this paper at the following URL.

<http://pubs.acs.org/doi/pdf/10.1021/om049006d>

We are interested in examining the reactivity of these complexes to determine if the two metals can react in a cooperative manner. For instance, can we make the tin act as an electrophilic Lewis acid while a tungsten ligand acts as a nucleophile? Tin reagents are often used as Lewis acids by making them electron deficient; in our case, we intend to pull off a chloride from the tin center using a Ag(I) salt (see eq 2). Metal bound hydrogens are often quite



nucleophilic, and so we hope an organic compound (such as acetone) coordinated to the tin center might be activated towards nucleophilic attack by the tungsten hydride. This summer we will begin investigations of this reactivity by first (re)generating the putative cationic species at low temperature in the NMR spectrometer (repeating an experiment that Gamaliel Dominguez did in our laboratory several years ago). We will then begin treating the new cation with several different reagents (alcohols, alkenes, alkynes, ketones, aldehydes, amines, etc.) to see what reactivity the cation has. Eventually, we are particularly interested in examining the stereoelectronic role of the substituents on the tin center in controlling this chemistry.

A second project involves the development of 1D, 2D, and 3D-NMR spectroscopy experiments for the detection of the ^{183}W nucleus in the stannyl (and hopefully eventually the stannylene) compounds by relaying magnetization through a ^{119}Sn center. We will be using the triple resonance probehead for the 400 MHz NMR spectrometer. Work on this project was begun last several summers ago and we already have a manuscript in preparation based upon the initial 1D and 2D experiments. This summer we will extend these experiments to examine nuclear Overhauser effects between the ^1H , ^{119}Sn and ^{183}W .

