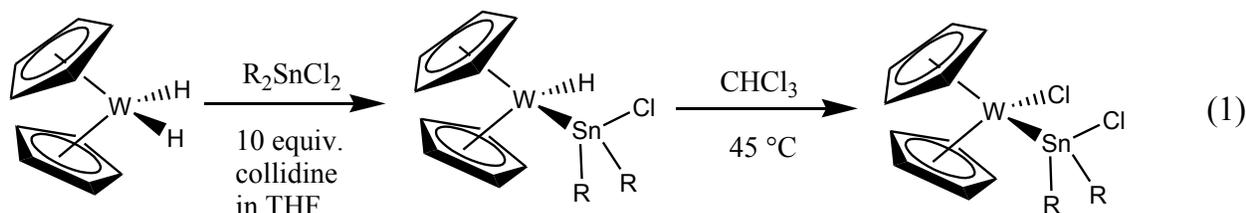


Mobley Group: Synthesis and Reactivity of Transition Metal Stannyl Complexes

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.

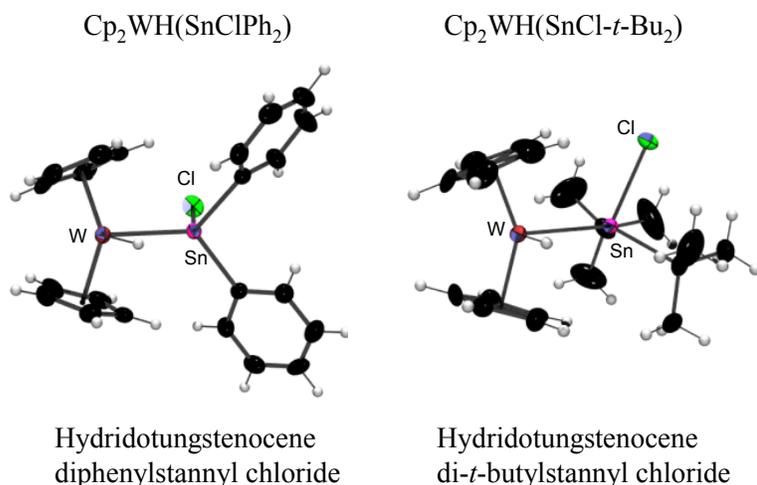


Figure 1. Comparison of structures of phenyl and *t*-butyl derivatives.

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 ($^1J_{\text{W}\text{Sn}}$) 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 exploring these structures further by systematically varying the electronics at the tin center by modifying the aryl ligands that are attached to it. This work will involve the synthesis of substituted diaryltindichlorides using the Grignard reaction followed by the synthesis of the tungstenocene stannyl complexes as described in equation 1 above. We will then study those complexes in the solution state by multinuclear NMR spectroscopy (^{183}W and ^{119}Sn as well as ^1H and ^{13}C) and in the solid state by X-ray crystallography utilizing the department's new diffractometer. For those interested, we could also undertake theoretical calculations using density functional theory (DFT).