
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.

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\begin{array}{ccc}
\text{Hydridotungstenocene} & \text{Hydridotungstenocene} \\
\text{diphenylstannyl chloride} & \text{di-}t\text{-butylstannyl chloride}
\end{array}
\]

Figure 1. Comparison of structures of phenyl and \(t\)-butyl derivatives.
While we expected the crystals structures of the i-butyl derivative and the phenyl derivative to be very similar, as can be see 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 (1JWSn) 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 submitted as a full paper to the journal Organometallics.

**Future Projects**

Projects this summer could include the synthesis of novel examples of these compounds where we vary the size of the groups on the tungsten by using cyclopentadienyl groups fully substituted with methyls (eq 2). In addition, students will be furthering our knowledge of the reactivity of these complexes. As these compounds should be electrophilic at the tin center but nucleophilic at the tungsten center, they may be useful as catalysts in organic reactions. We will be screening these compounds as potential Lewis acid catalysts for formation of enolates in aldol type reactions (eq 3).