

PRF# (56027-ND3)

Highly Active Organometallic Complexes Obtained through Mechanochemical Synthesis  
Dr. Timothy P. Hanusa, Department of Chemistry, Vanderbilt University

## NARRATIVE REPORT

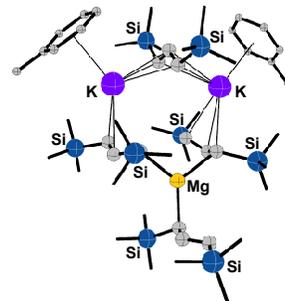
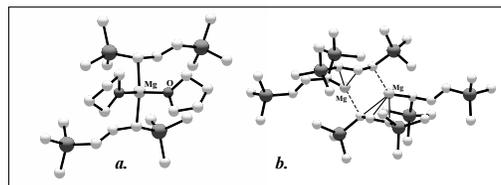
**General Goals and Impact:** The general aim of the grant is to explore the use of mechanochemical methods of synthesis (e.g., with grinding and milling) in the preparation of new organometallic compounds that may display high reactivity and/or catalytic activity. Such solid-state reactions provide the opportunity to investigate compounds not attainable when a solvent is present, either because useable solvents interfere with the interaction of the reagents, or because solvent molecules could bind strongly to the product and change its structure and reactivity. It is also a type of “green” chemistry, which complements the use of earth-abundant metals in synthesis. The general lack of information about organometallic mechanochemistry ensures that there will be important discoveries to be had with a variety of ligands and with metals from across the periodic table.

The results achieved to date have had a major, continuing impact on the direction of my research and with the students involved with the project. Mechanochemical synthesis has attracted the interest of both potential graduate students and undergraduate researchers. Two of the graduate students gave presentations at the Southeast Regional Meeting of the ACS in Nov. 2017, and at the ACS National Meeting in Aug. 2018, both times in conjunction with symposiums on mechanochemistry. Another student has worked with the Vanderbilt Institute for Digital Learning (VIDL) to prepare YouTube videos that provide insight into STEM research for those without the opportunity to visit university research labs, or who have not had mentorship in STEM education. The mechanochemistry conducted in my lab features prominently in the second video (Ep002, “Phuture Doctors” channel, [Mechanical Energy in Chemistry Research](#)). In conjunction with Prof. James Mack (Univ. of Cincinnati) and Tomislav Friščić (McGill Univ.), the PI organized a symposium at the ACS National Meeting in Boston (Aug. 2018). Entitled “M-CHEM: A Whole Lot of Shaking Going On”, it highlighted the recent work of researchers in mechanochemistry in both the US and several foreign countries (France, Germany, Ireland, Mexico, Singapore, and Canada). The symposium was notable for being one of 10 symposia given a special mention in the “ACS Meeting Insider” guide. An NSF proposal was submitted that incorporated early results from the ACS-PRF grant, and it was subsequently approved for funding in 2017. The stimulus provided by the New Directions grant has been substantial and far-reaching. It is probably the most transformative financial support I have received from the ACS-PRF during my career.

## Research Results

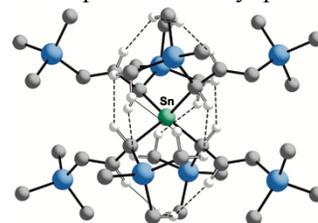
### 1. Magnesium allyl complexes: new reactivity with mixed-metal assistance

One of the goals of this project is the use of mechanochemical synthesis to facilitate the production of metal complexes with low coordination numbers that would be more active than ether-solvated analogues. The solvated magnesium complex  $[\text{MgA}'_2(\text{THF})_2]$  ( $[\text{A}'] = [1,3\text{-(SiMe}_3)_2\text{-C}_3\text{H}_3]^-$ ) (*a* at right), for example, is inactive as a catalyst, but studies had shown that the unsolvated version (which forms a dimer,  $[\{\text{MgA}'_2\}_2]$ , *b* at right)) displayed modest activity ( $\text{TOF} = 3,000 \text{ hr}^{-1}$ ) in methyl methacrylate polymerization. Preparation of the unsolvated compound is tedious, however, and an attempt was made to streamline the process by milling  $\text{K}[\text{A}']$  and  $\text{MgBr}_2$  in a 2:1 ratio. The hexane-soluble product was revealed to be the heterobimetallic species  $[\text{K}_2\text{MgA}'_4]$ , which is the (evidently kinetic) product of a 4:1 reaction of the allyl anion (i.e.,  $4 \text{ K}[\text{A}'] + \text{MgBr}_2 \rightarrow [\text{K}_2\text{MgA}'_4] + 2 \text{ KBr}$ ), and not the 2:1 ratio of starting materials (see figure at right). In collaborative work with the Brian Long group (Univ. TN, Knoxville), we have found that  $[\text{K}_2\text{MgA}'_4]$ , like  $[\{\text{MgA}'_2\}_2]$ , is also active in methyl methacrylate polymerization, but that it provides a lower polydispersity index ( $\text{PDI} = 1.48$ ) than either  $\text{K}[\text{A}']$  ( $\text{PDI} = 2.72$ ) or  $[\{\text{MgA}'_2\}_2]$  ( $\text{PDI} = 3.83$ ). The reasons for such control over chain length compared to the homometallic counterparts are not yet clear, but it indicates that the two metals in  $[\text{K}_2\text{MgA}'_4]$  are synergistically involved in the catalysis. These results broaden our understanding of the complex metal-ligand relationships that emerge from the interaction of multiple dissimilar metals and the allyl anion. Exploration of heterometallic (main group/lanthanide) allyl chemistry is also underway.



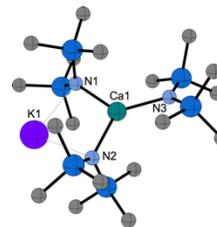
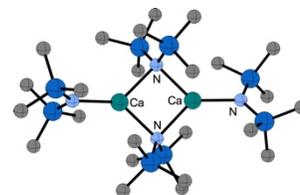
## 2. Mechanochemical formation of dispersion-stabilized organotin complexes

Main group compounds have a long history of use in synthetic organic chemistry, and allyltin compounds, in particular, are employed as a non-basic source of a weakly basic nucleophilic allyl group. A simple bis(allyl)tin(II) complex could be a potentially useful reagent, but no examples of such a compound are known. An attempt to form such a compound through ball milling a mixture of the bulky allyl  $K[A']$  ( $[A'] = [1,3-(SiMe_3)_2C_3H_3]^-$ ) and  $SnCl_2$  in a 2:1 ratio led instead to the tri(allyl) stannate  $[SnA'_3K]_n$ , which forms a coordination polymer in the solid state. An attempt to improve the yield of the reaction by employing a 3:1 ratio of reagents instead initiated a disproportionation reaction, and the neutral tetra(allyl)tin(IV) species  $[SnA'_4]$  was produced. The latter is sterically crowded, and decomposes relatively quickly ( $< 1$  hr) in hydrocarbon solvents. In the solid state, it is much more persistent (several months), and likely owes its stability to internal London dispersion interactions, as evidenced by multiple close  $H \cdots H'$  interligand contacts (at right). Dispersion-corrected DFT calculations were used to confirm the critical contribution of dispersion interactions to the stability of the tetra(allyl)tin species. Neither of these highly reactive products is available in their isolated forms from solution-based reactions, demonstrating the ability of mechanochemical synthesis to unlock otherwise unobserved organotin chemistry.



## 3. Metal bis(trimethylsilylamides)

The bis(trimethylsilylamides) of the alkaline-earth metal calcium, strontium, and barium (calcium compound at right) have found expanding use as reagents in synthetic and materials chemistry, and have been employed in the synthesis of a wide variety of organometallic and inorganic compounds. They have also been used in the study of enolization reactions of ketones. Multiple preparative routes have been developed for these silylamides, including the reaction of  $K[N(SiMe_3)_2]$  with  $AeI_2$  ( $Ae =$  alkaline-earth metal) in diethyl ether or toluene. Further study of these routes has demonstrated that despite its wide use, the halide metathesis route in solution is not reliable. The products are invariably contaminated with ‘-ate’ species,  $K_xAe[N(SiMe_3)_2]_{x+2}$  (a portion of the crystal structure of  $[K\{Ca[N(SiMe_3)_3]\}_n]$  is at lower right). (Rather than being solely a disadvantage, however, calcium-alkali metal ( $M = Li, K$ ) complexes display synergistic advantages in their properties, and also assist in the generation of mixed-metal enolates from ketones. Heterometallic “-ate” complexes as a rule display higher reactivity than their neutral counterparts, and this is true for  $\{Ae[N(SiMe_3)_3]\}^-$ .) Nevertheless, the neutral alkali metal free species are those most used, and we have found that ball milling  $CaI_2$  and  $K[N(SiMe_3)_3]$  in a 1:1 ratio for 10 min produces the neutral  $[Ca[N(SiMe_3)_3]_2]$  by itself. The use of mechanochemical preparation avoids the use of solvent, and the reaction can be scaled to gram amounts. Although the outcome seems counterintuitive (e.g., the reaction as written leaves a considerable amount of  $CaI_2$  unreacted ( $2 CaI_2 + 2 K[N(SiMe_3)_3] \rightarrow Ca[N(SiMe_3)_3]_2 + 2 KI + CaI_2$ ), raising the  $CaI_2 : K[N(SiMe_3)_3]$  ratio to 1:2 produces a mixture of  $K\{Ca[N(SiMe_3)_3]\}$  and  $Ca[N(SiMe_3)_3]_2$ ). This underscores the need to conduct mechanochemical reactions with electropositive elements in a range of stoichiometries. The magnesium analogue  $[Mg[N(SiMe_3)_3]_2]$  can also be made through grinding by starting with  $MgBr_2$ . We plan to extend these studies to the mechanochemical generation of the lanthanide analogues (Yb, Sm).



## 4. Cyclopentadienyl complexes of titanium formed through mechanochemical synthesis

This part of the research explored the shift in product distribution that often occurs in reactions when conducted mechanochemically compared to solution routes. This is believed to be a consequence of the trapping of kinetic products, as mechanochemically driven reactions are often far from equilibrium. For example, the reaction of  $Cp_2TiCl_2$  with potassium *tert*-butoxide produces *four* different products when conducted by ball milling ( $[Cp_2Ti(OtBu)_2]$ ,  $[CpTi(OtBu)_3]$ ,  $[Cp_3Ti(OtBu)]$ , and  $[Ti(OtBu)_4]$ ). Counterintuitively, the major product is  $[CpTi(OtBu)_3]$  (47%), despite the less than optimum stoichiometric ratios of reagents. (When the same reaction is conducted in THF, the majority product is the expected  $[Cp_2Ti(OtBu)_2]$  (70%).) Mechanochemical activation completes the reaction in a far shorter time than is the case in solution (15 min vs. 8 hours, respectively). An equally important finding was that reagents that are unsuitable for solution-based reactions (e.g.,  $TiBr_4$ , which reacts with ethers) can be used successfully with mechanochemical approaches. Thus, grinding a mixture of  $LiCp$ ,  $TiBr_4$ , and  $K[OtBu]$  yields the new complex  $CpTiBr_2(OtBu)$  (see figure at right). The use of such reagents opens up new routes to previously inaccessible complexes.

