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Scalable, Solution-Phase Routes Towards Metal Carbides

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The overall goal of our AFOSR program is to establish a scalable, solution-phase routes for the synthesis of amorphous, crystalline, and nanoparticle early transition metal carbides, as well as ternary transition metal carbides. These materials occupy a unique niche in the aerospace industry, particularly for high-temperature applications due to the fact that they are incredibly refractory, chemically robust and electronically conducting ceramic materials. However, the traditional way of synthesizing carbide materials requires ultra-high temperatures (>1000 C), on account of the slow diffusion constants of carbon through most materials. The need for high temperatures are not only resource intensive and costly, but make it virtually impossible to control the morphology, lead to graphitic side products, and limit the achievable phases to those with high thermodynamic stability. Our central hypothesis is that a solution-phase route for synthesizing a broad class of metal carbide materials can be uniquely enabled via the 'transmetalation' of molecular C4- precursors that contain 4 C-B bonds with metalhalogen
(M-X) bond containing precursors to form M-C bonds.
During this last cycle we established that the nitrogen-containing C4- precursor tetrakis(1,3-propanediaminoboryl)methane i.e. C[B(pn)]4 can serve as an ideal carbon source for the low temperature sol-gel synthesis of transition metal carbides. The solvothermal reaction between this compound and TiBr4 at 210 C enabled the formation of an amorphous branched Ti-C polymer that had a mass loss and Ti:Br ratio indicative of 3 C-Ti bonds. Annealing this tri-substituted product above 300 C resulted in complete substitution and elimination of residual boryl groups and the formation of an amorphous TiC product. Annealing this product at 650-750 C, enabled the formation of crystalline TiC products with >100 nm domain sizes. Th

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"Scalable, Solution-Phase Routes Towards Metal Carbides"

The overall goal of our AFOSR program is to establish a scalable, solution-phase routes for the synthesis of amorphous, crystalline, and nanoparticle early transition metal carbides, as well as ternary transition metal carbides. These materials occupy a unique niche in the aerospace industry, particularly for high-temperature applications due to the fact that they are incredibly refractory, chemically robust and electronically conducting ceramic materials. However, the traditional way of synthesizing carbide materials requires ultra-high temperatures (>1000 $_{o}$C), on account of the slow diffusion constants of carbon through most materials. The need for high temperatures are not only resource intensive and costly, but make it virtually impossible to control the morphology, lead to graphitic side products, and limit the achievable phases to those with high thermodynamic stability. We initially hypothesized that a solution-phase route for synthesizing a broad class of metal carbide materials can be uniquely enabled via the "transmetalation" of molecular C_{4-} precursors that contain $C\text{-}B(OR)_2$ bonds with metal-halogen or metal-alkoxide (M-X/M-OR) bond containing precursors to form M-C bonds. Our original aims were; a) to determine the conditions necessary to facilitate this chemistry through the preparation of novel small molecules containing M-C bonds, b) show that amorphous, nanoparticle, and sol-gel carbides can indeed be synthesized using this chemistry, and, if successful, c) create ternary metal carbides using this approach.

We established the ~20g scale synthesis of a variety of molecular C_{4-} precursors that contain a central carbon surrounded by 4 boryl groups; $C[B(OR)_2]$ and $C[B(NR)_2]_4$ (R= $-CH_3$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$).

Through attempts to synthesize $C[Si(CH_3)_3]_4$, and $C[Ge(CH_3)_3]_4$ we then established that the oxygen containing C_{4-} precursor $C[B(OR)_2]$ R=$-CH_2CH_2CH_2-$ has significant barriers for exchanging all 4 C-B bonds to form C-Si and C-Ge bonds. After exploring a variety of substitution reactions, we found that only two C-B bonds can be readily replaced with C-Si/Ge bonds, using a low-temperature organolithium base-activated substitution. Further attempts to substitute further C-B bonds led to C-H bond formation. In addition, the reaction product of any transition metal halide (i.e. $TiCl_4$, $TiBr_4$, $HfCl_4$, $NbCl_4$, WCl_5, VCl_4) with this oxygen-containing precursor $C[B(OR)_2]$ (R= $-CH_3$, $-CH_2CH_2CH_2-$) always led to the formation of transition metal oxide and a graphitic species upon annealing. Thus, these oxygen containing C_{4-} precursors are not suitable for the synthesis of carbide materials at low temperature, due to the strong thermodynamic propensity of metal-oxygen bond formation as an undesired side reaction.

Finally, we established that the nitrogen-containing C_{4-} precursor tetrakis(1,3-propanediaminoboryl)methane i.e. $C[B(pn)]_4$ can serve as an ideal C source for the low temperature sol-gel synthesis of transition metal carbides. The solvothermal reaction between this compound and $TiBr_4$ at 210 $_{o}$C enabled the formation of an amorphous branched Ti-C polymer that had a mass loss and Ti:Br ratio indicative of 3 C-Ti bonds. Annealing this tri-substituted product above 300 $_{o}$C resulted in complete substitution and elimination of residual boryl groups and the formation of an amorphous TiC product. Annealing this product at 650-750 $_{o}$C, enabled the formation of crystalline TiC products with >100 nm domain sizes. This is the lowest reported temperature for the synthesis of crystalline TiC, and is a consequence of the Ti-C bonding in the amorphous network. Overall, this work shows that oxygen-free, tetrakis(diaminoboryl)methane molecules are ideal C_{4-} synthons for the formation of transition metal carbides, enabling future explorations of morphological control.

These efforts are documented in one publication, and three graduate student dissertations. This funding supported the training of the technical workforce leading to the graduation of two students with a PhD (Zachary Baum and Rick Morasse) and one student with a MS (Jingtao Zhang). The abstracts are below;

Publications:

1) Z. Baum, J. Zhang, R. Morasse, J.E. Goldberger, "**Stepwise trimethylsilyl and trimethylgermyl substitutions at tetraborylmethane**" J. Organometallic Chem. 873, 50-56 (2018).

Abstract: In exploring the suitability of tetraborylmethane precursors as C_{4-} synthons, we have studied the limits of stepwise trimethylsilyl and trimethylgermyl substitutions on tetrakis (1,3-propanediolatoboryl)methane. In contrast to previous reports indicating minimal silylation of tetraborylmethanes, we have shown that organolithium-mediated deborylation-metalation methodologies readily proceed for up to two substitutions. This enables the synthesis of new borylmethane derivatives including $(TMS)_2CB(pg)_2$ and $(TMG)_2CB(pg)_2$(pg = 1,3-propanediolate, TMS = trimethylsilyl, TMG = trimethylgermyl). While further base-activated deborylation attempts lead to protodeboronation, limited reactivity, or de-esterification of the boronate ester, increasing the degree of substitution imparts air- and water-stability to the boronate esters.

Dissertations:

Zachary Baum
PhD dissertation - August 2018

"Reactivity of Tetraborylmethanes and Electronic Structure Calculations of Dimensionally Reduced Materials"

http://rave.ohiolink.edu/etdc/view?acc_num=osu1531736836448112

Abstract

The combined use of organic and inorganic precursors enables the discovery of new hybrid organic inorganic materials as well as the development of improved synthetic routes to conventional solids.

Herein, we present three major directions: the application of tetraborylmethanes as organometallic single-C synthons for carbon-metal bond formation in carbides, the synthesis and theoretical study of low-dimensional early transition metal dichalcogenide derivatives, and a separate study on the development of a new layered exfoliatable Zintl phase. In Chapter 2, we present the stepwise deborylation-homologation of $C(Bpg)_4$ (pg = 1,3-propanediolate) with trimethylsilyl and trimethylgermyl groups as organometallic models for the initial carbon-metal bond formation in SiC and GeC. We demonstrate that 2 substitutions with these tertiary substituents proceed readily, and that the disubstituted derivatives are recalcitrant towards further homologation. In Chapter 3, we explore various strategies to utilize tetraborylmethanes as a carbido source with the intent to form solid state metal carbide materials at low temperatures. We present the thermal co-decomposition of $C(Bpg)_4$ with Si(IV) and Nb(V) sources, which ultimately formed intimate SiO_2:B_2O_3/C and Nb_2O_5/C mixtures. We also discuss the synthesis of a single-source Si-C precursor molecule, $SiCl_3C(Bpg)_3$, and its chemistry with activating bases and hydride sources. In Chapter 4, we present the rational synthesis, characterization, and electronic structure of 1D- TiS_2 derivatives TiS_2(en) (en = ethylenediamine) and TiS_2(pn) (pn = 1,3-propylenediamine), which feature direct band gaps attractive for near-IR optoelectronics. Additionally, we discuss the synthesis of $[V_7S_8Cl_2(en)_8]Cl_4$ (en = ethylenediamine), the first early transition metal chalcogenide dicubane, and DFT calculations explaining its observed magnetic behavior. In Chapter 5, we present the synthesis, electronic structure calculations, and exfoliation studies of the layered Zintl phase $EuSn_2As_2$. This anisotropic pseudo-2D material features anti-ferromagnetic coupling out-of-plane and ferromagnetic coupling in-plane. Overall, the work presented herein builds on our understanding of polyborylmethane chemistry as well as the rational synthesis and properties of low-dimensional metal-organic solids, and motivates further exploration of 2D Sn-containing lattices for the discovery of novel magnetic phenomena.

Rick Morasse
PhD Dissertation – November 2017

"Low-Temperature, Solution-Phase Synthesis of Chalcogenide and Carbide Materials"

http://rave.ohiolink.edu/etdc/view?acc_num=osu1513253677021066

Abstract

Despite the fact that new dimensionally reduced hybrid organic-inorganic compounds have attracted considerable interest due to their unique optical and electronic properties, the rational synthesis of these new materials remains elusive. Here we studied the influence of the major synthetic parameters including temperature, ligand structure and ligand-to-metal stoichiometry on the preparation of dimensionally reduced TiS_2. One-dimensional TiS_2 phases tend to form at high ligand to metal ratios and relatively lower temperatures, while the parent two-dimensional lattices are preferred at higher temperature. The organic ligand structure dictates the temperature window at which a dimensionally reduced phase can be accessed. Although a small change in ligand structure, such as from ethylenediamine, *en*, to propylenediamine, *pn*, will significantly influence the stability of these phases, it will only subtly change the electronic structure. By developing a systematic understanding of the effects of various factors during the synthesis we provide a pathway to rationally create new dimensionally reduced materials.

A second project in this dissertation focuses on the development of a solution-phase route towards carbide materials. We hypothesized that a broad class of metal carbide materials can be created via the transmetallation of precursors that contain four $C\text{-}B(OR)_2$ bonds with metal-halogen (M-X) bond containing precursors to form networks containing M-C bonds. While this chemistry is an essential step in many well-known organic reaction pathways, it has not been explored for the synthesis of carbide materials in part due to the lack of commercially availability and complicated synthesis of the $C[B(OR)_2]_4$ precursors. To these ends we established the synthesis of the tetrasubstituted cyclic boronic ester, tetrakis(1,3 propanediolatoboronate) methane, which we denote as $C(B\mathit{pg})_4$. We have adapted and improved upon the previously reported route, which utilizes precursors that are not commercially available, and have been able to synthesize this material on the 20 g scale with an overall ~50% yield.

Upon establishing the large scale synthesis of $C(B\mathit{pg})_4$ precursors we explored whether GeC can be created. Due to the commercial impact of SiC in a broad range of applications such as optoelectronics and ceramic materials, GeC has attracted considerable theoretical interest, yet no such phase currently exists. In these experiments we describe the reactions between $C(B\mathit{pg})_4$ with many different germanium precursors across multiple different solvent and temperature conditions. These reactions and subsequent characterizations reveal that an analogous precursor, $HC(B\mathit{pg})_3$, generates an amorphous GeCH phase while the $C(B\mathit{pg})_4$ precursor does not immediately react and rather forms an oxidized Ge phase. The X-ray diffraction (XRD) of these materials display show no long-range crystallinity, and synchrotron X-ray Pair-distribution function (PDF) identified the presence of Ge-C bonds at 1.86 Å in the amorphous GeCH phase in addition to Ge-O bonds at 1.74 Å in the GeO_2 phase. The Raman analysis shows no crystalline modes in the GeCH phase until annealing above 500 $_o$C, at which point graphite and crystalline

germanium modes appear. The lack of direct reactivity between $C(B\textit{pg})_4$ with tetrasubstituted Ge precursors merits the future exploration of base-activation procedures.

In summary, the low-temperature, solution-phase syntheses of $TiS_2(\textit{en})$ and $C(B\textit{pg})_4$, and the progress towards carbides and small-molecule carbide analogues represent progress towards the wider use of solution-phase synthetic methods in order to generate advanced materials.

Jingtao Zhang
MS thesis – July 2019

“Solution Phase Route towards Titanium Carbide”

http://rave.ohiolink.edu/etdc/view?acc_num=osu1563391108014095

Abstract

Carbide materials have broad applications in industry because they are refractory, chemically robust, and electronically conducting ceramic materials. Additionally, some carbide materials, such as WC, have unique catalytic potentials in hydrogen evolution reactions, oxygen evolution reactions and fuel cell reactions. However, the traditional way of synthesizing carbide materials requires ultra-high temperatures (>1000 $_o$C) on account of the slow diffusion constants of carbon through most materials. The need high temperatures are not only resource intensive and costly; they make it virtually impossible to control the morphology. Furthermore, in many carbide materials, such as SiC, these high temperatures often result in the formation graphitic side products either on the surface, or as inclusions, due to the evaporation of the metals. Thus, establishing lower-temperature scalable, solution-phase routes for solid-state carbide materials would enable the creation of carbide materials in a variety of highly controlled morphological form factors, as well as potential reduce the formation of graphitic carbon.

Our overall strategy is to explore the solution-phase synthesis of carbide materials through the transmetalation reaction between the electron rich carbon center in tetraborylmethanes and metal halides. In exploring the possibility of this kind of reaction, we first explored the feasibility of forming metal-carbon bonds via this transmetalation pathway via molecular reactivity studies. First, tetrakis (1,3-propanediolatoboryl)methane (compound 1) was chosen as our carbanion precursor for its stability, solubility and reactivity as our carbide synthon. We studied the conditions and limits of trimethylgermyl substitution. We established that organolithium-mediated deborylation-metalation methodologies could substitute up to two trimethyl groups on the central methane. $(TMG)CB(pg)_3$ and $(TMG)_2CB(pg)_2$ (pg= 1,3-propanediolate, TMG = trimethylgermyl) were successfully synthesized and characterized. However, we found that additional attempts to replace additional boryl groups on the central carbon center always resulted in protodeboronation over a broad range of temperatures. While these proof of concept studies do indicate that we can readily form two C-Ge bonds from these precursors, these studies indicate higher temperatures are likely necessary for complete substitutional reactivity to the carbide.

After confirming the desired molecular reactivity, we subsequently established a sol-gel process for creating crystalline titanium carbide using tetraborylmethane precursors. First, the reaction of compound 1 with TiBr4 always resulted in the formation of TiO_2 at high temperature. Thus, an oxygen-free derivative, tetrakis (1,3-propanediaminoboryl)methane (compound 5) was synthesized and characterized. We established that the solvothermal reaction of compound 5 and $TiBr_4$ at 210 $_o$C followed by a 300 $_o$C annealing process produced an amorphous titanium carbide framework. Then, crystalline titanium carbide with >100 nm domain sizes is obtained after annealing at 650-750 $_o$C. Overall, these initial results are a pivotal first step of a solution-phase route towards transition metal carbides, enabling future explorations on the creation of different metal carbide materials and morphological control.