

a trialkylboronate with an aryllithium or a Grignard reagent, but these strongly nucleophilic species limit the functional-group tolerance of this method. Although milder reactions that use transition metals to catalyse the borylation of aryl halides and aromatic C–H bonds improve the substrate scope of these reactions, they are unattractive to the pharmaceutical industry because of the risk of heavy-metal contamination and high costs associated with such processes. Some examples of transition-metal-free borylation reactions have been reported, but they are not without their limitations.

Now, Hajime Ito and co-workers at Hokkaido University in Japan have demonstrated that a silylborane — $\text{PhMe}_2\text{Si-B}(\text{pin})$, where pin = pinacol — can react with aryl, alkenyl and alkyl halides in the presence of an alkoxy base to give the boryl-substituted product. The formation of the B- rather than the Si-substituted product is a surprising result because the general reactivity observed for silylboranes would suggest that a silyl nucleophile (rather than a boron-based one) should be formed on treatment with a strong base. Several experiments were conducted to optimize the reaction conditions and test its compatibility with a variety of substrates. Good yields of the desired borylation product were obtained with electron-rich and electron-poor aryl bromides; ester groups were also found to be well tolerated. Moreover, boryl substitution of a very sterically hindered substrate — one that has proved difficult to react using other borylation processes — was achieved in >90% yield.

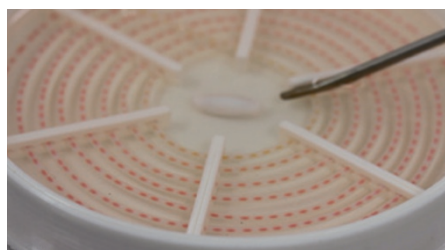
The mechanism of the reaction is currently under investigation, but preliminary experimental evidence suggests that it does not involve intermediate radical species or any form of transition-metal catalysis caused by trace metals present in the starting materials. It is speculated that the process might begin with a silyl nucleophile attacking the bromine atom on the substrate, followed by the formation of a C–B bond. HM

SEMICONDUCTING POLYMERS

Drop by drop

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With many different applications — ranging from solar cells to display technologies — there is continued interest in the development of semiconducting polymers. The compatibility of these polymers with cheap and rapid solution-phase processing is attractive, but improvements in the



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efficiencies of devices made from these materials are required for them to compete with established technologies. The polymer forms a significant fraction of the total cost of a device, and although efficient syntheses have been designed, the transition from a research route to production scale remains a problem. Now, John de Mello, Martin Heeney and co-workers from Imperial College London have developed a droplet-based flow synthesis suitable for the synthesis of poly-3-hexylthiophene (P3HT).

The electrical properties of semiconducting polymers such as P3HT are critically dependent on the regioregularity of the polymer. The standard route for making this polymer starts with an unsymmetrical dibromothiophene, in which one bromine site is selectively converted to the corresponding Grignard reagent. This AB-type monomer can be polymerized in a nickel-catalysed cross-coupling reaction to give the desired polymer. On a small scale this synthetic route is well developed, but as reaction volumes are increased, mixing of reagents and setting the temperature for a successful outcome become difficult to control. In the method developed by de Mello and co-workers, thiophene-based Grignard reagents dissolved in tetrahydrofuran (THF) are co-injected into narrow-diameter tubing along with a dispersion of the nickel catalyst in a perfluorinated polymer fluid.

These two fluids are immiscible and the THF solution forms small droplets in the polymer carrier fluid. The reaction tubing is heated by immersing it in a temperature-controlled oil bath, and reaction time can be carefully controlled by the flow rate of the droplets through the tube. Each droplet is essentially a small-scale reaction in its own right, and scale-up of polymer production can be achieved simply by increasing the total amount of reagent introduced to the system. The method produces polymers with consistent properties on anything from a sub-gram scale to multiple tens of grams. SD

Written by Stephen Davey, Russell Johnson, Hannah Moody and Anne Pichon.

blogroll

Numerous nitrogens

Kevlar-suit-wearing synthetic chemists and the art of nomenclature.

Some interesting nitrogen-based chemistry featured in the chemical blogosphere in 2012. Several bloggers commented on a peculiar (and perhaps somewhat terrifying) compound containing 10 nitrogens in a row, reported in *Inorganic Chemistry*. David Perrey at Chemical Space wrote, “The graphical abstract tells the story eloquently: the structure with a back-drop of broken lab equipment,” and muses “inadvertent explosions is a lovely expression” (<http://go.nature.com/JM4IHc>).

A picture of a Klapötke group member working with these materials was posted on the blog *Reactions from Last Night* (<http://go.nature.com/Du1TBI>) — “notice the full Kevlar suit he’s wearing” notes the caption! There are strict rules about who can do what in the group; undergraduates don’t handle explosives, masters students only work with known compounds, and PhD students are the ones who “make and characterize anything novel”.

At the other extreme, in a post on ‘Handheld chemistry’ (<http://go.nature.com/SG8zdq>) over at *The Culture of Chemistry*, Michelle Franci-Donnay advises the reader to “wash those hands” if you are going to repeat an experiment described in a 1937 chemistry-kit manual for “making ammonia in your hand,” by mixing calcium oxide and ammonium chloride with your fingers. Franci-Donnay further admits to “using Hess’ law for fun,” but follows with a serious calculation on the heat of formation for the reaction: “–635 kJ [...] for about a tablespoon of material,” to be precise.

And finally, at *The Heterocyclist* blog, dipolar-cycloaddition veteran Will Pearson ponders over an apparent mix-up between nitrogen imines and ylides (<http://go.nature.com/Kzrruf>) in the title of a paper in *Angewandte Chemie International Edition* and throws out a “What am I missing here?” Judging by the lack of objectors so far — nothing.

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