HORIZON 2020

Main group chemistry, inorganic polymers, catalysis, silicon- and phosphorus-based polymers

Reporting

Project Information

LWIMT

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Project closed

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Periodic Reporting for period 1 - LWIMT (Main group chemistry, inorganic polymers, catalysis, silicon- and phosphorus-based polymers)

Reporting period: 2016-03-01 to 2018-02-28

Summary of the context and overall objectives of the project

This project tackles the problem of activation of main group substrates and their transformation into useful products. This field is virtually unexplored and the work to date has focused on expensive transition metal catalysts which can lead to toxic residues. Main group molecules and materials are of widespread interest as a result of their useful combination of physical and chemical properties, which offer exciting opportunities for their use as synthetic reagents and advanced materials for many different applications. For example, they have societal uses as fire retardants, elastomers, LEDs, ceramic precursors, and as reagents in organic synthesis. As silicon is the earth’s second most abundant element, compounds containing silicon have much potential because of their lower price. Traditionally, silylphosphanes have been prepared by the reaction of chlorosilanes with alkali metal phosphanides, a process that generates at least one equivalent of salt waste and has limited functional group tolerance. The production of salt waste will cause the erosion of reactors and thus limit its bulk production and also not economic. As part of the Marie Curie project we have developed a new catalytic dehydrocoupling method to prepare E-E' bonds using a metal-free borane as the catalyst. This process only produces H2 as a side product, the hydrogen gas is easy to separate from the reaction product and it can also be used as energy source. The work has been published in the top high-impact journal J. Am. Chem. Soc. and creates a new and convenient method for making silylphosphines which are highly deserable organic substrates.

The project is important for society because with the new catalytic route there are no wasteful byproducts and the process also does not involve the use of toxic and expensive transition metals like most current catalytic processes. The new route to silylphosphines provides a prototype example of how main group substrates can be converted into useful products.

The overall long term objective is to harness main group substrates based on abundant elements such as silicon and phosphorus as precursors to a wide variety of useful products, both molecular and polymeric.

Furthermore, the skills learned during the project enabled Dr. Wu to return to his homeland, China, with a faculty position in Lanzhou institute of Chemical Physics and to obtain a prestigious “1000 talents” award.

Work performed from the beginning of the project to the end of the period covered by the report and main results achieved so far

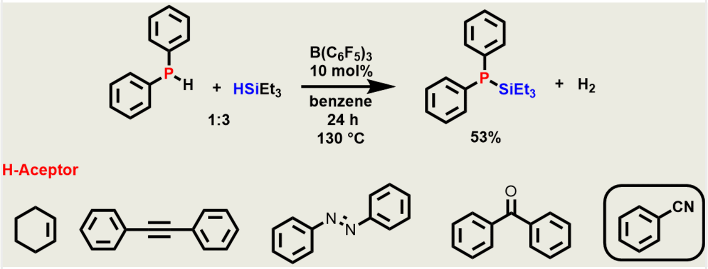
Initially we started the reaction by using of organic and organometallic compounds like DCA, Eosin Y (organic dyes has red or yellow color) and Ru, Ir complexes as photo-initiator (which absorb the energy of light and transfer to the reactant), we found that by using DCA there was around 27% yield of silylphosphane produced. So then compounds with –CN functional group were applied to find the suitable photoinitator. We found that even without light the reaction could also take place so then the role of compounds with –CN were studied. We found that the presence of PhCN can largely promote the dehydrocoupling of secondary phosphine with hydrosilane at room temperature.

Remarkably, we found that by using PhCN as the H2-acceptor (absorb the H2 release during the reaction) we could obtain silylphosphane in 99% yield within 20 min at 25°C. This is a dramatic acceleration effect and allowed the reaction to be performed with only 1 mol% catalyst loading and still gave 99% yield at 25°C, further-more, with even 0.5 mol% catalyst loading at 50 °C the re-action was essentially complete in 3 h with 99% yield.

We also explore the possibility of using PhCN free system for the heterodehyrodcoupling of phosphines (R1R2PH) with hydrosilanes (R1'R2'R3'SiH). We first examined the reaction between PhPH2 and Et3SiH in the presence of catalytic amounts of various Lewis acids ([Ph3C][B(C6F5)4], AgNO3, Zn(OAc)2), carbene (IMes) or combinations of B(C6F5)3 with different bulky Lewis bases. We found that B(C6F5)3 alone gave superior results and produced mono-silylation product and bis-silylation product. It is worth noting that no reaction took place with-out the addition of B(C6F5)3 even at 130 °C. Further experiments showed that this reaction was sensitive to temperature: at 80 °C after 16 h only 50% of PhPH2 was consumed albeit with 100% selectivity to mono-silyphosphanes. The reaction conditions were optimized with 10 mol% B(C6F5)3, at 100 °C for 16 h in benzene to give 95% conversion of PhPH2 and 98% selectivity for mono-silyphosphanes.

Progress beyond the state of the art and expected potential impact (including the socio-economic impact and the wider societal implications of the project so far)

As mentioned above there was no non-metal catalyzed dehydrocoupling reaction of phosphine with hydrosilanes in the literature, we expected that at the end of the project we should be able to find a suitable catalytic system of using non-metal catalyst to realized reactions with general substrates scope.



initial results of using HA for dehydrocoupling reactions

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