

Functionalization and metallization of diamondoids: hybrid nanomaterials for energy, catalysis and biological applications

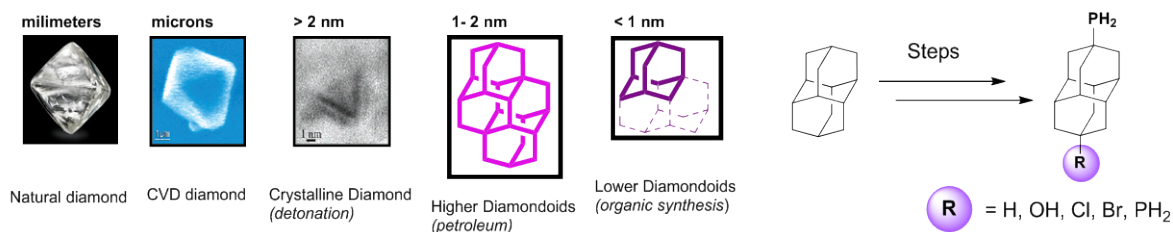
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Summary

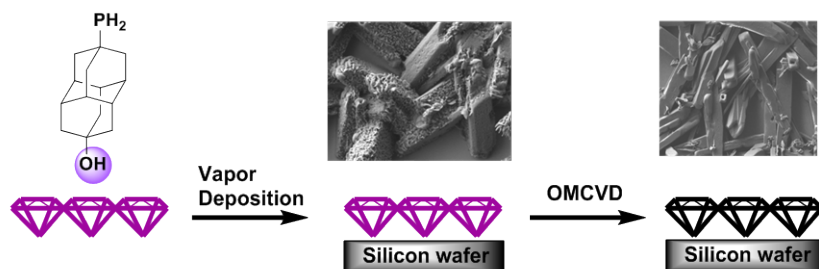
Widespread application of primary alkyl phosphines is limited due to their high sensitivity towards oxidation, often resulting in pyrophoricity. Introduction of bulky substituents that can kinetically stabilize primary phosphines is one method for decreasing their oxygen sensitivity. Bulky cage hydrocarbons like diamondoids, which are naturally occurring molecules, can therefore be ideal substituents for stabilizing primary phosphines.

The work described herein deals with the synthesis and applications of primary diamondoid phosphines. Firstly, they are used as building blocks for the construction of organo-hybrid materials by mild vapor deposition, and secondly, as ligands in metal catalyzed arylation reactions of *N*-heterocycles.

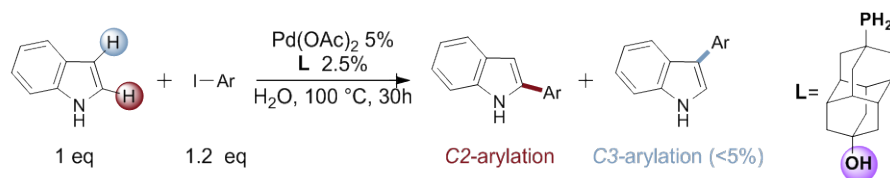
Chapter 1: Synthesis of diamondoid phosphines



Chapter 2: Elaboration of Metal@Diamondoid Nanohybrid materials by mild vapor deposition



Chapter 3: Diamondoid phosphines for biphasic metal catalyzed C2 arylation of indoles



An important advance in the chemistry of diamondoids was made possible after their discovery and isolation in large quantities from natural sources like petroleum. Functionalization of diamondoids composed of higher number of cages than adamantane was first explored in the mid-1960s. Various functionalities have been introduced onto diamondoids resulting in new derivatives with outstanding properties. In order to fully explore the potential of these molecules, desymmetrization of the cages was investigated as a means for obtaining well-defined structural building blocks with two different functionalities suitable for thin film growth. This process had been achieved previously only by protection/deprotection sequences.

Our first aim was to develop a new synthetic approach governed by the kinetically controlled reaction in strong acidic media, which enables direct access to unequally functionalized diamondoids. This type of reaction was successful for phosphorylated diamondoids which upon reduction gave diamondoid primary phosphines, a new class of pure alkyl primary phosphines that were found to be relatively air stable. Further post-functionalization of these molecules was also achieved.

Revolutionary progress was made during the last decade in the area of novel carbon nanomaterials, such as sp^2 -C based fullerenes, nanotubes, and graphenes. In comparison, sp^3 -C materials based on a diamondoid scaffold that combines the unique features of both diamond and carbon nanostructures are unknown to date. Unlike metal nanocomposites based on sp^2 -carbon skeletons, which benefit from a rich surface chemistry due to many functional groups, metal/ sp^3 -carbon based nanostructures are much less developed and many challenging functionalization issues remain. The synthesis of novel organohybrid material with core-shell like structure will be discussed. The core of the hybrid is made of organic molecules, namely diamondoids, and the shell is made of a thin transition metal layer, such as palladium or platinum.

Indole is a nitrogen-containing heterocycle widely used in medicinal chemistry as a structural subunit of drug candidates for the treatment of type 2 diabetes, cancer and HIV. This scaffold is also present in a variety of natural products, therefore constituting a target in organic synthetic chemistry. The C–H activation of unprotected indole moiety in position 2 of the heterocycle will be described. The reaction was done in aqueous media under aerobic conditions and diamondoid primary phosphines were used as ligands in this biphasic synthesis. Aryl iodides were tested as coupling partners and the reaction was selective for the C2 position affording excellent yields of the desired arylated indoles. With aryl bromides, a loss in selectivity was observed; yet the reaction proceeded with a surprising P/Pd ratio of 0.5/1.