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### Polyisobutylene (PIB)-NHC Supported Catalysts for Cross-Coupling Reactions: A Green and Sustainable Protocol

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N-Heterocyclic Carbenes (NHCs): Over the last two decades N-Heterocyclic carbenes (NHCs) have immensely attracted chemists in nearly all fields of chemistry. N-Heterocyclic carbenes are commonly encountered in coordination chemistry, they are extensively used as ligands for organometallic complexes. Perhaps the biggest hit of NHCs ligands was their use in Grubbs II catalyst for olefin metathesis chemistry. It is noteworthy that the success of NHCs ligands in catalysis is due to several factors favoring their high activity, selectivity and stability when compared to the phosphine counterparts in Grubbs I catalyst [1]. Supported Catalysts: Increased environmental and health awareness requires that designing new metal-catalysts should focus not only on increasing activity and selectivity but also on finding new strategies that help chemists recycle and separate the metal-catalyst from the reaction mixture. In general, homogenous catalysis is preferred over heterogeneous catalysis. This is due to the higher turnover number, better selectivity and usually lower operating temperatures required. On the other hand, heterogeneous catalysis has the advantage of the ease of separation of the catalyst from the final products and is generally less expensive. One important strategy is to use catalysts attached to a heterogeneous support and separate them from the products by simple filtration. Alternatively, homogeneous catalysts that can self-separate from the products by selective solvent extraction would be of great interest. The frequency of their reuse would be environmentally beneficial and to a higher extent this should overcome the lower activity of conventional heterogeneous catalysts. Metal catalysts that can self-separate from the reaction mixture are of great importance due to the reduced metal

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leaching into the product mixture. In addition, their reuse and recovery make this overall process much greener compared to the conventional homogeneous/heterogeneous catalysis systems. Ever since Herrmann et al. [2] reported the polystyrene supported NHC-palladium catalyst, studies have largely been focused on the use of polymeric supports for NHC-palladium catalysts. While polyethylene-glycol-supported catalyst can be extracted with a polar solvent, Bergbreiter et al. [3] and others have showed that polyisobutylene (PIB) is a useful support for ligands and their metal catalysts (Pd, Ru...) having preferable solubility towards solvents with low polarities such as hexanes, heptanes and decanes. In all of these biphasic systems for cross-coupling/olefin metathesis, the design is mainly focused on the recovery and the reuse of the supported catalysts. Biphasic catalysis having thermomorphic behavior have witnessed great developments due to their temperature-dependent miscibility [4]. While reactions in these biphasic mixtures can be conducted under homogeneous conditions at high-temperatures, the supported catalysts and the products/by-products can be efficiently separated by restoring the biphasic conditions at a low-temperature (Scheme 1). Herein we report the synthesis of new PIB-supported N-heterocyclic carbenes ligands having two different frameworks and their Pd-complexes, 1 and 2. The use, recovery and effectiveness of catalysts are detailed in both Heck and Suzuki cross-coupling reactions (Scheme 2). Metal leaching to the polar phase will be discussed too. Scheme 2: Heck cross-coupling and Suzuki cross-coupling using catalysts 1 and 2.

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