Overview of catalytic properties of several novel Umicore homogeneous catalysts for metathesis reactions and cross-coupling reactions

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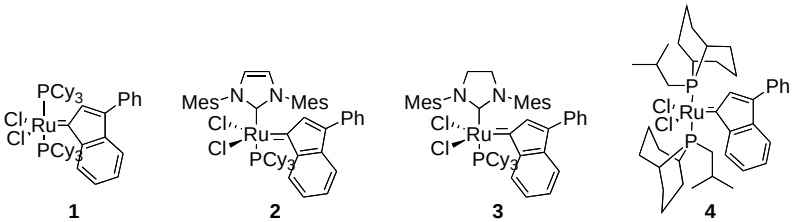
Introduction

Among the large number of organic and organometallic reactions allowing the formation of carbon-carbon bonds, the olefin metathesis and palladium-catalyzed cross coupling are two of the most powerful. These are becoming more widely employed in synthetic schemes. This success is intimately associated with to the development and commercialization of efficient catalysts.

Results and Discussion

As an alternative to Ru-benzylidene pre-catalysts [1], Ru-3-phenylindenylidene complexes [2] such as **1** [3] and its IMes analogue **2** [4] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) have been developed recently and **1**-**3** are now commercially available. These pre-catalysts were found more resistant to harsher reaction conditions (temperature and functional group tolerance) [5] than their benzylidene counterparts. Nevertheless, their catalytic activities have been scarcely examined, especially the SIMes-containing complex **3** (SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) and phobane-containing pre-catalyst **4**.



1 **2** **3** **4**

Figure 1. Indenylidene-based pre-catalysts.

Activities of complexes **1**-**3** have been investigated using kinetics studies and show moderate to excellent efficiency depending to the steric hindrance of the substrate. The scope of the two most interesting pre-catalysts, i.e. **1** and **3** has been investigated in ring-closing and enyne metathesis for a large range of olefins and a fascinating complementary of these catalysts has been observed. Moreover the activity of **1** was found equivalent to the one exhibited by the Grubbs first generation catalyst. On the other hand, **4** displayed a unique reaction profile, this will be discussed in more detail.

On the cross-coupling side, Umicore now offers a number of NHC-Pd complexes that display high activity in various cross coupling reactions. These include the Suzuki-Miyaura [6], Buchwald-Hartwig [6], Sonogashira, Kumada-Tamao-Corriu and Ketone-Arylation reactions. These Pd-NHC complexes are air stable compounds having indefinite shelflife in air. The available catalysts are capable of performing cross coupling reactions at RT sometimes in the ppm loading levels [7]. The complexes are thermally stable and workups are simple and isolated products do not contain any NHC-Pd residue after simple filtration through a small pad of silica. Reaction profiles of these pre-catalysts will be discussed.

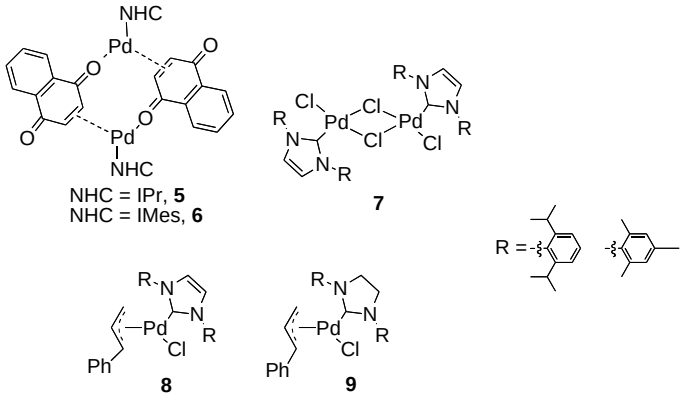


Figure 2. Selected Pd-NHC pre-catalysts for cross-coupling reactions.

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