Ruthenium Catalysts Bearing Benzimidazolylidene Ligands for the Metathetical Ring-Closure of Tetrasubstituted Cycloolefins

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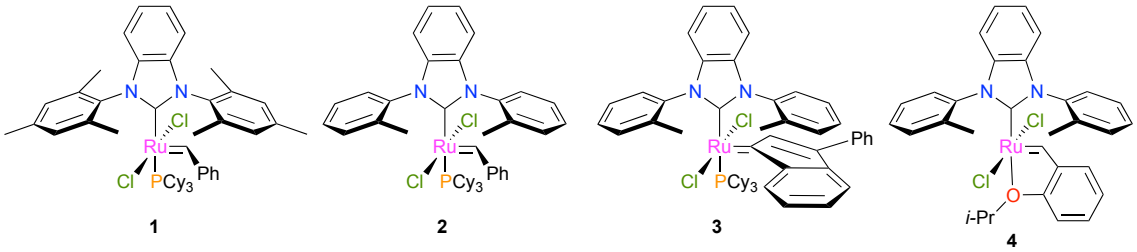
The introduction of N-heterocyclic carbene (NHC) ligands on well-defined ruthenium complexes has already afforded a wealth of highly active catalysts for various types of olefin metathesis reactions [1,2]. However, the synthesis of tetrasubstituted alkenes and cycloalkenes remains a challenging task for most of these second-generation initiators, including the benzimidazolylidene derivative **1** that we first reported in 2013 [3]. Removing one of the ortho-substituents on the N-aryl groups of the NHC ligand is an efficient way to bypass this limitation and to ease the access of sterically hindered olefins to the catalytic center. This strategy was pioneered by Grubbs [4] and further implemented by other groups [5,6]. We have successfully applied it to the benzimidazolylidene family of ligands by replacing the mesityl-based NHC in complex **1** by its 2-tolyl analogue in catalysts **2**–**4** [7].



In this communication, we shall discuss the stereochemical implications of the use of non-symmetrical aryl substituents on the NHC ligand of second-generation ruthenium-alkylidene complexes. We will also report on our latest investigations on this family of catalysts for the metathetical ring-closure of tetrasubstituted cyclo-olefins.

[1] C. Samojłowicz, M. Bieniek, K. Grela, Chem. Rev., **2009**, 109, 3708-3742.
[2] G. C. Vougioukalakis, R. H. Grubbs, Chem. Rev., **2010**, 110, 1746-1787.
[3] Y. Borguet, G. Zaragoza, A. Demonceau, L. Delaude, Dalton Trans., **2013**, 42, 7287-7296.
[4] I. C. Stewart, T. Ung, A. A. Pletnev, J. M. Berlin, R. H. Grubbs, Y. Schrodi, Org. Lett., **2007**, 9, 1589-1592.
[5] F. Grisi, A. Mariconda, C. Costabile, V. Bertolasi, P. Longo, Organometallics, **2009**, 28, 4988-4995.
[6] C. Torborg, G. Szczepaniak, A. Zieliński, M. Malińska, K. Woźniak, K. Grela, Chem. Commun., **2013**, 49, 3188-3190.
[7] Y. Borguet, G. Zaragoza, A. Demonceau, L. Delaude, Dalton Trans., **2015**, 44, 9744-9755.