KEES ELSEVIER'S BIAN LIGANDS: A MILESTONE IN HOMOGENEOUS CATALYSIS

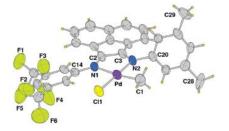
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The capability of tailoring the chemical environment around the catalytic centre is one of the strength points of homogeneous catalysis. Most of the times this is performed by the fine tuning of steric and electronic properties of spectator ligands coordinated to the metal center.¹ In this contest, during the last three decades, in the class of bidentate nitrogen-donor ligands a pivotal role has been played by α -diimine molecules featuring an acenaphthene or a 1,4-diaza-1,3-butadiene skeleton, the so called BIAN and DAB derivatives, respectively. As for the BIAN molecules the starting point of this development is brought back to Kees Elsevier's seminal work,² followed by Brookhart's discovery of the capability of the relevant Pd(II)-complexes to act as excellent catalysts for both ethylene homopolymerization and ethylene/acrylic esters copolymerization.³

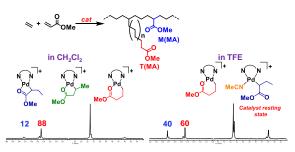
In this lecture an initial overview of the research work performed in collaboration with Kees



Elsevier in the field of homogeneous catalysts for the polyketone synthesis will be presented. The evolution of symmetrical BIANs to their corresponding nonsymmetrical counterparts (Figure to the left) led to better performing catalysts as the result of a proper balance between catalyst stability and activity.⁴

In the second part of the lecture I will present our recent results in the field of Pd-catalysts based on DAB-ligands for the synthesis of functionalized polyethylene. We discovered that

the way of incorporation of the polar vinyl monomer, methyl acrylate in this case, into the polyolefin skeleton is remarkably affected by both the reaction medium of the catalytic process and the labile ligand bound on the fourth coordination site of palladium.⁵ A detailed mechanistic investigation, carried out by NMR



spectroscopy, allowed us to identify a novel catalyst resting state (Figure above).

References

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