



ALMA MATER STUDIORUM  
UNIVERSITÀ DI BOLOGNA



CENTER FOR  
CHEMICAL CATALYSIS

*The Center for Chemical Catalysis presents:*

# **C<sup>3</sup> DAY 2024**

**4<sup>th</sup> June 2024**

**AULA O "CIAMICIAN" - POLO NAVILE U.E. 4  
VIA PIERO GOBETTI, 85 – BOLOGNA**

**BOOK OF  
ABSTRACTS**

## LOOKING FOR DEACTIVATION PATHWAYS IN PALLADIUM-CATALYZED POLYMERIZATION REACTIONS

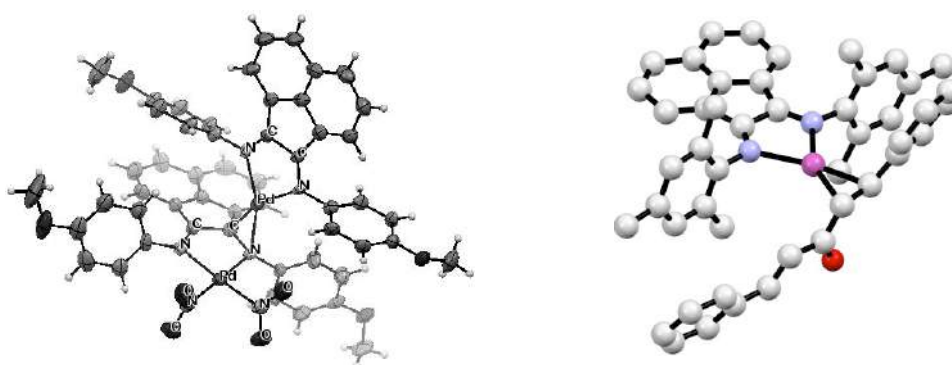
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Palladium complexes with Ar-BIAN ligands (Ar-BIAN = bis(arylimino)acenaphthene) are employed as catalysts in numerous reactions, among which ethylene polymerization and styrene/CO copolymerization have been widely investigated. Some years ago, a work in our group based on the analysis of kinetic data showed that the likely deactivation pathway for the catalyst in the CO/styrene copolymerization reaction involves the formation of a Pd(0) complex, followed by reaction of the latter with a Pd(II) complex to form a Pd(I) dimer [1]. While trying to identify both the putative Pd(0) and the Pd(I) dimer or their analogues, we found that the known instability of (Ar-BIAN)Pd(0)(olefin) complexes when the olefin lack electronwithdrawing groups is due to the tendency of palladium to coordinate to the C=N double bond of another (Ar-BIAN)Pd complex. Among others, we have isolated and crystallographically characterized the complex in Figure 1, left, which features a formally mixed valence Pd(0)-Pd(II) complex, which may mimic the real structure of the putative Pd(I) dimer. Coordination of the Ar-BIAN C=N double bond can be inhibited by steric hindrance and when the MeOC<sub>6</sub>H<sub>4</sub>- group in the ligand is substituted by a mesityl one, the complex (Mes-BIAN)Pd(0)(dba) (dba = dibenzylideneacetone) could be isolated and crystallographically characterized, Figure 1, right. The stability of the latter complex may constitute one of the reasons for which steric hindrance is essential to provide stability to (bis-imine)Pd catalysts for ethylene polymerization.



**Figure 1.** Palladium complexes modelling those involved in catalyst deactivation.

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[1] F. Amoroso, E. Zangrando, C. Carfagna, C. Muller, D. Vogt, M. Hagar, F. Ragaini, B. Milani, *Dalton Trans.*, **2013**, 42, 14583-14602.