# Dinuclear Group 4 Metallocene Catalysts of the Type $[(Cp_2M)_2(\mu\text{-}Me)(\mu\text{-}C_2R)]$: Structure-Activity Relationships in Ethylene Polymerisation

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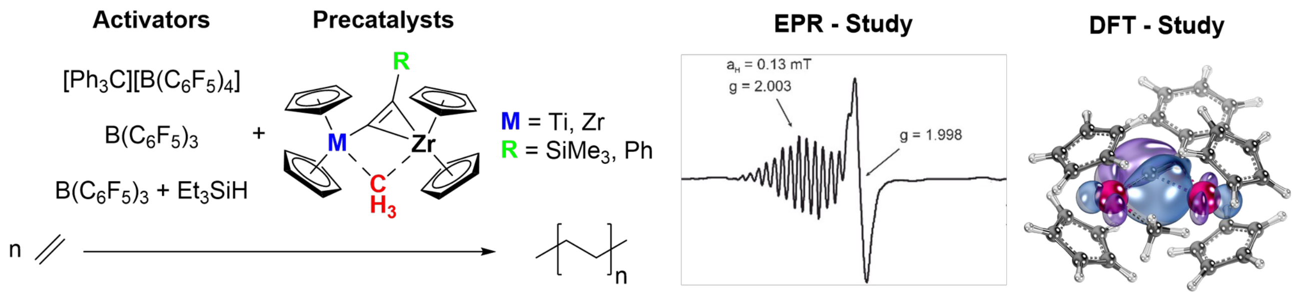
The modular synthesis of the alkynyl methyl bridged dinuclear group 4 complexes was first reported by Erker in 1998.[1] Recently, some of us found that these species serve as precatalysts in the dehydrocoupling of amine boranes[2] and can be used for the activation of small molecules.[3]
In this contribution, we systematically investigate four representatives of this class of complexes $[(Cp_2M)_2(\mu\text{-}Me)(\mu\text{-}C_2R)]$ (M = Ti, Zr; R = $SiMe_3$, Ph) with regard to their catalytic activity in the polymerisation of ethylene (Figure, left). The modular structure of the bridged complexes facilitates the preparation of homodinuclear (Zr, Zr) and heterodinuclear (Ti, Zr) complexes, as well as the variation of the substituents at the alkynyl unit. The study evaluates the influence of three different activation sequences on the catalytic activity of the precatalysts (Figure, left). In particular, the phenylalkynyl-bridged precatalysts show high activity similar to that of the reference complex $Cp_2ZrMe_2$,[4] while the $SiMe_3$-substituted derivatives are significantly less active. With the help of EPR, NMR and DFT studies, a structure-activity relationship is revealed that can contribute to the further development of analogous precatalysts.



**Figures: Investigated dinuclear group 4 precatalyst's and activators (left), representative EPR signals after activation with $[Ph_3C]^+$ (middle), and alkynyl assisted intermetallic intrinsic binding orbital (right).**

**Keywords:** Dinuclear Catalysts, Polyethylene, Structure-Activity-Relationship

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