Stereospecific Ring Opening Metathesis Polymerization (ROMP) with Cationic Molybdenum Imido Alkylidene CAAC Complexes

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Stereospecific ring opening metathesis polymerization (ROMP) of enantiomerically pure 2,3-dicarbomethoxynorborn-5-ene ((+)-DCMNBE) and 2,3-dimethoxymethylnorborn-5-ene ((+)-DMMNBE) was accomplished by the action of cationic tetra- and pentacoordinated molybdenum imido alkylidene cyclic alkyl amino carbene (CAAC) complexes[1] that are chiral at molybdenum. All complexes were moderately to highly active and biased towards *trans*-isospecificity, offering up to 97% *trans*-it repeat units. It is crucial to comprehend how the ligand sphere influences the stereospecificity of polymers since tacticity has a significant impact on their mechanical and thermal properties. Although the imido ligand's function has been studied in complexes of a similar nature, the effects of the carbene ligand (*N*-heterocyclic carbene or CAACs) and the anionic "X" ligand remain unclear. In this work the observed stereospecificity was correlated with the percentage of buried volumes of the individual ligands to obtain a structure-activity relationship. In contrast to their *N*-heterocyclic carbene analogues,[2] bulky CAAC ligands with very high values for the buried volume ($\%V_{bur}$) affect stereoselectivity by forcing the imido ligand towards the intermediary metallacyclobutane, thereby inducing increased steric hindrance and, consequently, high *trans*-isospecificity via a turnstile mechanism.

[1] K. Kundu, J. V. Musso, M. J. Benedikter, W. Frey, J. Kästner, M. R. Buchmeiser, *Chem. Eur. J.* **2023,** *29*, e202301818; doi.org/10.1002/chem.202301818; [2] a) M. J. Benedikter, R. Schowner, I. Elser, P. Werner, K. Herz, L. Stohr, D. A. Imbrich, G. M. Nagy, D. Wang, M. R. Buchmeiser, *Macromolecules* **2019**, *52*, 4059-4066;b) J. V. Musso, M. J. Benedikter, P. Gebel, V. Gramm, D. Wang, R. Schowner, M. R. Buchmeiser, *Polym. Chem.*, **2021**, *12*, 5979-5985, 10.1039/d1py01158h.