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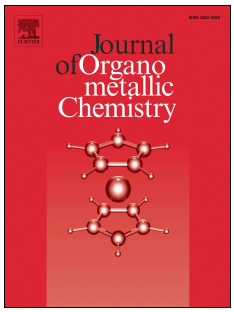

Steric factors on unsymmetrical *O*-hydroxyaryl *N*-Heterocyclic carbene ligands prevailing the stabilization of single stereoisomer of bis-ligated titanium complexes

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Steric Factors on Unsymmetrical *O*-hydroxyaryl *N*-Heterocyclic Carbene Ligands Prevailing the Stabilization of Single Stereoisomer of Bis-Ligated Titanium Complexes

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Abstract

Bis-ligated titanium(IV) metal complexes supported by bidentate unsymmetrical *o*-hydroxyaryl-substituted *N*-heterocyclic carbene ligands were synthesized and structurally identified. While the direct addition of the doubly deprotonated bulky imidazolidinium chloride salts [$^{Dipp,4\text{-}R}$NHC-H]Cl (with Dipp = 2,6-diisopropylphenyl, R = H (2-hydroxyphenyl), and R = Me (2-hydroxy-4-methyl-phenyl)) with chloro-titanium precursor favors the formation of single stereoisomer corresponding to the bis-ligated titanium complexes *trans*-([κ^2-C,O]-$^{Dipp,4\text{-}R}$NHC)$_2$TiCl$_2$ (R = H (2-hydroxyphenyl) for **4a^{H}**, and R = Me (2-hydroxy-4-methyl-phenyl) for **4a^{Me}**), the reactivity with sterically less hindered imidazolidinium chloride salts [^{Mes,H}NHC-H]Cl and [^{Dep,H}NHC-H]Cl as protio-ligands (with Mes = 2,4,6-trimethylphenyl and Dep = 2,6-diethylphenyl) did not lead to single stereoisomer, but rearranged into a tetradentate salophen-like complexes *cis*-([κ^4-O,N,N,O]-bis(imidazolidinylidene)TiCl$_2$ as major isomer via presumably the NHCs dimerization from bis-ligated intermediates. These results combined with topographic steric maps as well as the buried volume descriptor (%V_{bur}) indicate that bidentate bulky *N*-Dipp-substituted NHC ligands offer some level of steric protection preventing the formation of other possible bis-ligated (C,O)-NHC-titanium stereoisomers and constitutional isomers.

Keywords

Titanium; Bidentate ligand; Unsymmetrical N-heterocyclic carbene; Bis-ligated titanium complex; Ethylene polymerization.