

**The Effect of Ligand Array on Stereocontrol and Molecular
Weight in Metallocene-Catalyzed α -Olefin Polymerization
And
(PNP)CrPh₃ Complexes as Well-Defined Ethylene Trimerization
Catalysts**

Thesis by

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Abstract

A series of neutral and cationic group 4 and neutral group 3 model complexes of the $\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-3-(CMe}_3\text{)-C}_5\text{H}_3)$ (tBuSp) ligand have been prepared: tBuSpZrCl₂ (**1**), tBuSpZr(CH₂SiMe₃)₂ (**8**), tBuSpZrMe₂ (**9**), [tBuSpZrH₂]₂ (**10**), tBuSpZrMeCl (**11**), tBuSpZrMe(CH₂CMe₃) (**12**), tBuSpZrMe(CH₂SiMe₃) (**13**), tBuSpScCl(THF) (**14**), tBuSpScCH(SiMe₃)₂ (**17**), [tBuSpScH] (**18**), and tBuSpTiCl₂ (**19**). The kinetically preferred isomers of **12** and **13** have been identified, and in both cases the *syn* isomer is preferred. We have obtained solid state structures of [tBuSpZrH₂]₂ (**10**), tBuSpZrMeCl (**11**), tBuSpZrMe(CH₂CMe₃) (**12**), and tBuSpScCl(THF) (**14**). Complexes **12** and **13** isomerize to form predominantly the thermodynamically preferred *anti* isomers. The ratio of isomers observed for [tBuSpZrMe]⁺[MeB(C₆F₅)₃]⁻ (**21**) and [tBuSpZrCH₂SiMe₃]⁺[Me B(C₆F₅)₃]⁻ (**22**) suggests that the tBuSp ligand does not distinguish very well between different groups in the metallocene wedge ($\Delta G^\circ = 0.27\text{-}0.89$ kcal/mol). The tBu group is not an effective stereodirector in the ground state structures and the remarkable stereodirecting capability of this ligand in propylene polymerizations must be reconciled by its effect on transition state energies.

A series of scandocene tetramethylaluminate have been prepared, including Ind₂Sc(μ-Me)₂AlMe₂ (**1**), Cp₂Sc(μ-Me)₂AlMe₂ (**2**), Cp^{*}CpSc(μ-Me)₂AlMe₂ (**3**), and *meso*-DpSc(μ-Me)₂AlMe₂ (**4**). These complexes display characteristic terminal and bridging methyl resonances in solution at room temperature, indicating static structures. Complexes **1-4** oligomerize 1-pentene to form a range of oligomers. The tetramethylaluminate complexes initiate oligomerization from a scandium-methyl species after dissociation of AlMe₃, and the primary mechanism of chain transfer is β-hydrogen elimination. Complexes **1-4** react with L donors (L = DMAP, THF, PMe₃) to form (R_nCp)₂ScMe(L) compounds (**5-9**).

To study the chromium-based ethylene trimerization catalyst involving the diphosphine ligand (*o*-MeO-C₆H₄)₂PN(Me)P(*o*-MeO-C₆H₄)₂ (PNP^{OMe} (**1**)), we have synthesized (PNP^{OMe}-*d*₁₂)CrPh₃ (**11**), (PNP^{SMe}-*d*₁₂)CrPh₃, (**12**), and (PNP^{OMe}-*d*₁₂)CrPh₂Cl (**14**) containing deuterated PNP ligands. Activation of **11** by protonation with H⁺(OEt)₂B[C₆H₃(CF₃)₂]₄⁻ in the presence of ethylene provides an active trimerization catalyst that gives similar selectivity and activity to 1-hexene as the originally reported system and represents the first examples of an active, well-defined trimerization catalyst based on chromium. The trimerization of a 1:1 mixture of C₂H₄ and C₂D₄ gives only C₆D₁₂, C₆D₈H₄, C₆D₄H₈, and C₆H₁₂, the 1-hexene isotopomers without H/D scrambling, which is consistent with a trimerization mechanism involving metallacyclic intermediates.

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