The Effect of Ligand Array on Stereocontrol and Molecular Weight in Metallocene-Catalyzed α-Olefin Polymerization
And
(PNP)CrPh$_3$ Complexes as Well-Defined Ethylene Trimerization Catalysts

Thesis by

Susan J. Schofer

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Abstract

A series of neutral and cationic group 4 and neutral group 3 model complexes of the $Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}3\text{-}(CMe_3)\text{-}C_5H_3)$ (tBuSp) ligand have been prepared: $tBuSpZrCl_2$(**1**), $tBuSpZr(CH_2SiMe_3)_2$ (**8**), $tBuSpZrMe_2$ (**9**), $[tBuSpZrH_2]_2$ (**10**), tBuSpZrMeCl (**11**), $tBuSpZrMe(CH_2CMe_3)$ (**12**), $tBuSpZrMe(CH_2SiMe_3)$ (**13**), tBuSpScCl(THF) (**14**), $tBuSpScCH(SiMe_3)_2$ (**17**), [tBuSpScH] (**18**), and $tBuSpTiCl_2$ (**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 $[tBuSpZrH_2]_2$ (**10**), tBuSpZrMeCl (**11**), $tBuSpZrMe(CH_2CMe_3)$ (**12**), and tBuSpScCl(THF) (**14**). Complexes **12** and **13** isomerize to form predominantly the thermodynamically preferred *anti* isomers. The ratio of isomers observed for $[tBuSpZrMe]^+[MeB(C_6F_5)_3]^-$ (**21**) and $[tBuSpZrCH_2SiMe_3]^+[Me\ B(C_6F_5)_3]^-$ (**22**) suggests that the tBuSp ligand does not distinguish very well between different groups in the metallocene wedge (ΔG° = 0.27-0.89 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 $Ind_2Sc(\mu\text{-}Me)_2AlMe_2$ (**1**), $Cp_2Sc(\mu\text{-}Me)_2AlMe_2$ (**2**), $Cp^*CpSc(\mu\text{-}Me)_2AlMe_2$ (**3**), and *meso*-$DpSc(\mu\text{-}Me)_2AlMe_2$ (**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 $AlMe_3$, and the primary mechanism of chain transfer is β-hydrogen elimination. Complexes **1**-**4** react with L donors (L = DMAP, THF, PMe_3) to form $(R_nCp)_2ScMe(L)$ compounds (**5**-**9**).

To study the chromium-based ethylene trimerization catalyst involving the diphosphine ligand (o-MeO-C_6H_4)$_2$PN(Me)P(o-MeO-C_6H_4)$_2$ (PNP^{OMe} (**1**)), we have synthesized (PNP^{OMe}-d_{12})CrPh$_3$ (**11**), (PNP^{SMe}-d_{12})CrPh$_3$, (**12**), and (PNP^{OMe}-d_{12})CrPh$_2$Cl (**14**) containing deuterated PNP ligands. Activation of **11** by protonation with $H^+(OEt_2)_2B[C_6H_3(CF_3)_2]_4^-$ 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 C_2H_4 and C_2D_4 gives only C_6D_{12}, $C_6D_8H_4$, $C_6D_4H_8$, and C_6H_{12}, the 1-hexene isotopomers without H/D scrambling, which is consistent with a trimerization mechanism involving metallacyclic intermediates.

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