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Steric Control of the Chromium-Catalyzed Oligomerization of Ethylene[1)]

Arno Döhring, Vidar R. Jensen, Peter W. Jolly,* Walter Thiel, Jan C. Weber

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

SUMMARY: Catalysts for the oligomerization and polymerization of ethylene have been obtained by activating phosphinoalkyl-substituted cyclopentadienyl chromium complexes, e.g. $(\eta^1,\eta^5\text{-}R_2PC_2H_4C_5H_4)CrCl_2$, with methylalumoxane (MAO). DFT-calculations indicate that the observed dependence of the degree of oligomerization upon the size of the substituents (R) on the P-donor atom is a result of a steric influence on the stability of the transition state for the chain termination step.

Introduction

Although a number of single component, homogeneous chromium catalysts have been reported which polymerize ethylene, e.g. $(\eta^3\text{-}C_3H_5)_3Cr$, $Cp^*Cr(CH_2SiMe_3)_2$, $[Cp^*Cr(THF)_2Me]^+$, as well as two component systems containing N,O- or N,N-chelating ligands and a Lewis acid, the activity of none is particularly impressive.[2)] Recently, however, we reported that highly active catalysts for the polymerization of ethylene may be generated by treating amino-substituted cyclopentadienyl chromium compounds, e.g. $(\eta^1,\eta^5\text{-}Me_2NC_2H_4C_5Me_4)CrCl_2$, with methylalumoxane (MAO).[2,3)] We have now investigated the related phosphinoalkyl-substituted derivatives, e.g. $(\eta^1,\eta^5\text{-}R_2PC_2H_4C_5H_4)CrCl_2$, and have observed a remarkable dependence of the product composition of the reaction with ethylene upon the steric properties of the substituent (R) on the P-atom.

Results and Discussion

The chromium complexes have been prepared by treating spiro [2.4] hepta-4,6-diene with the appropriate alkalimetal-phosphide followed by reaction with $Cr(THF)_3Cl_3$ (Figure 1). The molecular structure, with a metal-bonded P-atom, has been confirmed by X-ray crystallography for the compounds where R is phenyl (Ph) and cyclohexyl (Cy) as well as for $(\eta^1,\eta^5\text{-}Cy_2PC_2H_4C_5H_4)CrMe_2$ (prepared by reacting the corresponding dichloride with MeLi). Treatment of these complexes with MAO leads to the generation of highly active catalysts for

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the oligomerization and polymerization of ethylene whereby the degree of oligomerization and catalytic activity are dependent upon the nature of the substituent (R) on the P-atom (see Table 1). That this effect is largely steric in origin is apparent from a comparison with the cone angle (θ) of the related triorganophosphine (PR_3) compounds as defined by Tolman[4)] and is underlined by the results for the phenyl- and o-tolyl-substituted derivatives shown in the Table.

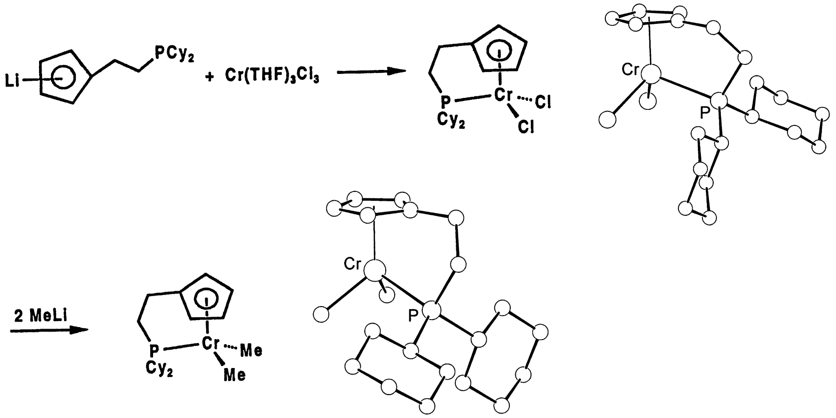


Fig. 1: Preparation of catalyst precursors for R=Cy with accompanying X-ray structures.

Table 1. The $(R_2PC_2H_4C_5H_4)CrCl_2$–MAO Catalyzed Oligomerization and Polymerization of Ethylene.[a]

R	Product (%)	Activity[c]	θ (PR_3)[d]
CH_3	C_4(83.6), C_6(13.0), C_{8+}(3.5)	4620	118
CH_2CH_3	C_4(21.3), C_6(26.5), C_8-C_{14}(49.5), C_{16+}(2.7)	4450	132
$CH_2C(CH_3)_2H$	C_4(10.6), C_6(12.5), C_8-C_{10}(25.1), C_{12+}(51.8)	4230	143
$CH(CH_3)_2$	C_4-C_{10}(3.1), PE (96.9, M_W 6.3•10^4)	3590	160
C_6H_{11}-cyclo	C_6-C_{10}(3.1), PE (96.9, M_W 1.8•10^5)	1450	170
$C(CH_3)_3$	C_6-C_8(15.7), PE (84.4, M_W 1.3•10^5)	590	182
C_6H_5	C_4-C_8(9.5), C_{10}-C_{14}(7.0), C_{16+}(81.0) PE (2.2)	4950	145
$C_6H_4CH_3$-o	C_6-C_{10}(4.1), PE (95.9)	2330	194

[a] Cr:MAO = 1:100; t = 4min; solvent = toluene; $P(C_2H_4)$ = 2 bar; T = 21°C, ΔT = 4°C
[b] C_4 = 1-butene; C_6 = 1-hexene etc. [c] kg Product / mol Cr·h. [d] Tolman cone angle.[4)]

An effect as dramatic as that shown here has not been reported previously for a chromium catalyst. Of particular industrial interest is presumably the formation of a 1-butene/1-hexene mixture where R is Me, the mixture of long chain olefins where R is Ph or i-Bu and polyethylene where R is i-Pr or Cy: the butene/hexene mixture could be copolymerized with ethylene directly to LLDPE while the long chain olefin mixture could form the basis of a Cr-catalyzed SHOP-type long chain alcohol synthesis.

The mechanistic origin of this steric effect has been explored by means of density functional theory (DFT).5) The active center is assumed to be a cationic chromium-alkyl species and the further reaction has been shown to proceed through 4-membered (propagation involving Cossee-Arlman-type direct insertion) or 6-membered (termination through β-hydrogen transfer) transition states as depicted in Figure 2.

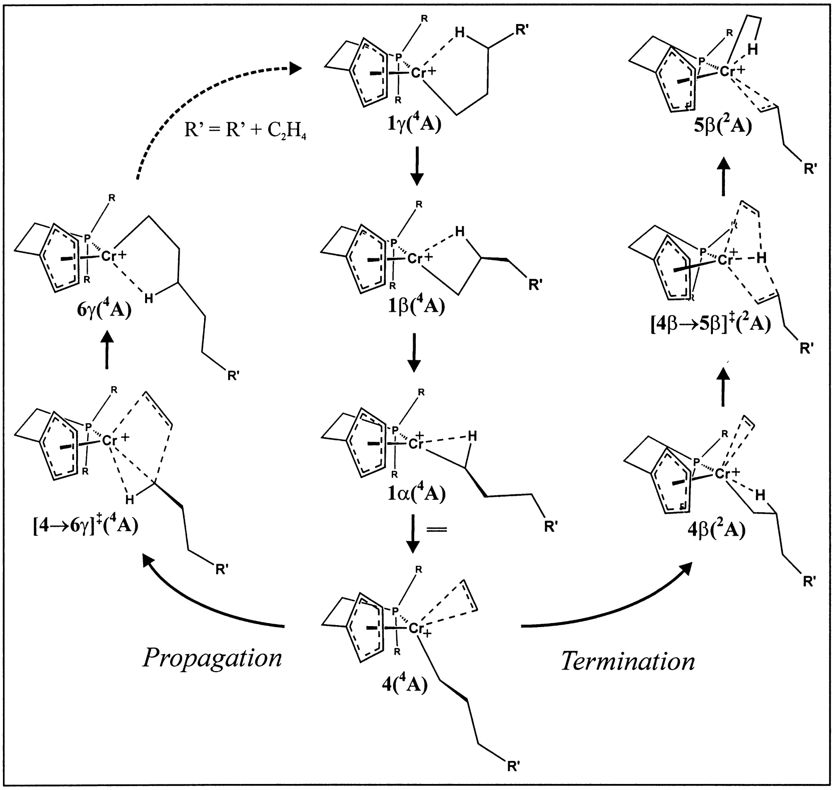
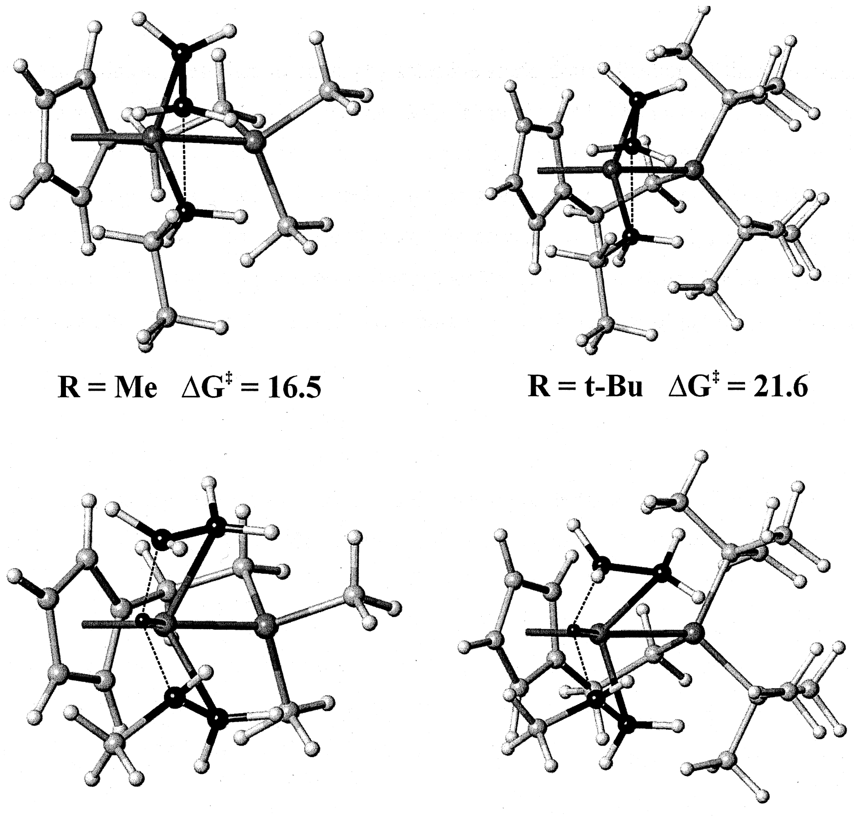


Fig. 2: The catalytic cycle as obtained from DFT calculations. **1β(⁴A)** is the resting state.

The calculations suggest that an unusually selective steric destabilization of the 6-membered transition state (TS) is responsible for the chain-length control. The activation free energies for insertion and termination are practically equal when the substituent on the P-atom is sterically undemanding (Me) and therefore the propagation cycle will terminate after a few insertion steps and short chain products result. In contrast, in the presence of the sterically demanding t-butyl group propagation is favored by 10–15 kcal/mol over termination through β-hydrogen transfer and multiple insertion occurs with the formation of polyethylene (Figure 3).



R = Me $\Delta G^{\ddagger} = 16.5$ **R = t-Bu $\Delta G^{\ddagger} = 21.6$**

R = Me $\Delta G^{\ddagger} = 16.8$ **R = t-Bu $\Delta G^{\ddagger} = 34.6$**

Fig. 3: DFT-optimized TS structures for ethylene insertion (above, $[\mathbf{4}\rightarrow\mathbf{6}\gamma]^{\ddagger}(^{4}\mathbf{A})$ in Figure 2) and β-H transfer to monomer (below, $[\mathbf{4}\beta\rightarrow\mathbf{5}\beta]^{\ddagger}(^{2}\mathbf{A})$ in Figure 2). Energies (kcal/mol) relative to $\mathbf{1}\beta(^{4}\mathbf{A})$.

Propagation is found to occur on a high-spin (^4A) surface and, since coordination of the migrating H-atom is energetically unfavorable in the electronically saturated high-spin state, termination proceeds on the low spin (^2A) surface. This concept of two-state-reactivity6) may well play a crucial role in Cr-catalysis.

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