Synthesis, Characterization, and Ethylene Oligomerization Action of $[(C_6H_5)_2PC_6H_4C(O\text{-}B(C_6F_5)_3)O\text{-}\kappa^2P,O]Ni(\eta^3\text{-}CH_2C_6H_5)$

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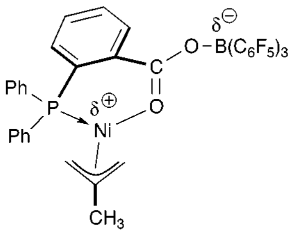
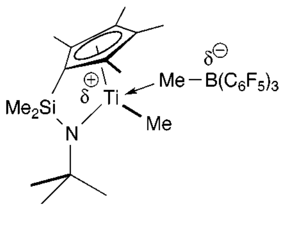
We recently reported that $[(C_6H_5)_2PC_6H_4C(O\text{-}B(C_6F_5)_3)O\text{-}\kappa^2P,O]\text{-}Ni(\eta^3\text{-}CH_2CMeCH_2)$ (**1**) and $\{[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)]TiMe\}\text{-}\{MeB(C_6F_5)_3\}$[1] (**2**) form a well-matched pair of homogeneous initiators for the preparation of branched polyethylene using only ethylene.[2] This tandem process can be tuned such that the 1-butene produced by the nickel species is inserted into the growing polyethylene chain at the titanium site. It is possible to obtain a linear correlation between the Ni/Ti ratio and the branching content of the polymer chain. Compound **1** is obtained by addition of $B(C_6F_5)_3$ to $[(C_6H_5)_2PC_6H_4C(O)O\text{-}\kappa^2P,O]Ni(\eta^3\text{-}CH_2CMeCH_2)$, which forms part of the family of Ni compounds used in the SHOP process[3,4] and which was originally reported by Keim.[5] Carbonyl coordination to the borane[6] is important to raise the affinity of Ni for ethylene so that it matches the consumption rate at Ti.



1



2

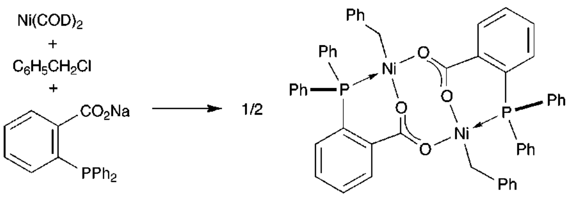
One drawback of **1** is that the methallyl functionality is less reactive than the propagating species, resulting in only a small fraction of the Ni centers participating in the polymerization process.[7] It seemed logical that substitution of methallyl for the isoelectronic η^3-benzyl fragment[8] would result in a complex that would initiate more efficiently and would therefore offer more control in tandem polymerizations.

We report here on the synthesis and characterization of the benzyl analogue of **1**. We show that a faster initiation is indeed observed; however, the oligomerization sequence shows unexpected features. Specifically, the K factor, defined by

$$K = (\text{moles } C_{n+2} \text{ olefin})/(\text{moles } C_n \text{ olefin}) = R_P/(R_P + R_{CT})$$

where R_P and R_{CT} are the rates of propagation and chain termination, respectively, is independent of monomer pressure and the distribution of alkene products shifts to higher molecular weights with *increasing* reaction temperature. In view of the rising importance of late metal catalysts in olefin polymerization[9] and oligomerization[10,11] reactions, we also examine this molecular weight dependence.

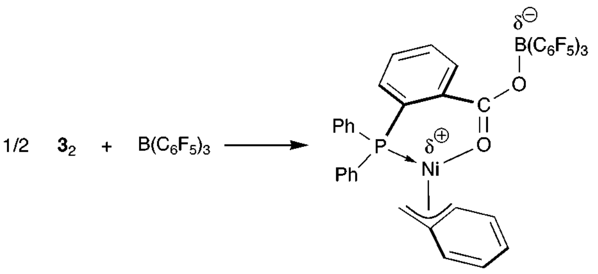
Addition of bis(cyclooctadiene)nickel to a mixture containing benzyl chloride and sodium 2-(diphenylphosphino)benzoate in THF gives $\{[(C_6H_5)_2PC_6H_4(\mu\text{-}CO_2)\text{-}\kappa^3P,O,O']Ni(\eta^1\text{-}CH_2C_6H_5)\}_2$ ($\mathbf{3}_2$ in eq 1) in 89% yield. The dimeric nature of $\mathbf{3}_2$ and coordination mode of the carboxylate functionalities were confirmed by a single-crystal X-ray diffraction study (Supporting Information).



$\mathbf{3}_2$

(1)

Treatment of $^1/_2\mathbf{3}_2$ with $B(C_6F_5)_3$ gives $[(C_6H_5)_2PC_6H_4C(O\text{-}B(C_6F_5)_3)O\text{-}\kappa^2P,O]Ni(\eta^3\text{-}CH_2C_6H_5)$ (**4** in eq 2). The nuclearity of **4** and the hapticity of the benzyl ligand were confirmed by structural characterization (Figure 1).



4

(2)

More ethylene is consumed in the first hour when starting with **4**, relative to the reaction with **1** (Table 1, entries 3 vs 4 and 7 vs 8). The ratio of 1-butene to 1-hexene is not affected, consistent with **1** and **4** giving rise to the same catalytic species. Therefore, initiation is faster with the benzyl ligand. The larger quantity of 1-alkene produced by $\mathbf{4}/C_2H_4$ per unit time increases the probability of secondary reactions, resulting in a higher fraction of 2-alkyl-1-alkenes and internal olefins (entries 3 and 4). Selectivity for α-olefins improves under more dilute reaction conditions (entries 4 and 5). Tandem polymerization of ethylene ($P(C_2H_4) = 3$ atm, $T = 20$ °C, [Ni]:[Ti] = 1:100) carried out with **2** and **4** produces a polymer with 9.2% branching. No branching could be detected by ^{13}C NMR spectroscopy[12] under the same conditions by using $\mathbf{1}/\mathbf{2}/C_2H_4$.

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Table 1. Oligomerization of C_2H_4 by **1** and **4**[a]

					α-olefin distribution[b]		olefin distribution[b]		
entry	pre-cat.	*P* (atm)	[Ni] (*μ*M)	activity[c]	% 1-butene	% 1-hexene	% α-olefin	% 2-alkyl-1-alkene	% internal
1	**1**	1	125	56	92	8	97	3	
2	**4**	1	12.5	1070	92	8	95	5	
3	**1**	3	125	430	90	10	79	17	4
4	**4**	3	125	2110	90	10	31	55	14
5	**4**	3	12.5	2540	91	9	89	9	2
6	**1**	3	12.5	630	92	8	97	3	
7	**1**	7	12.5	1840	90	10	97	3	
8[d]	**4**	7	12.5	14500	91	9	97	3	

[a] Reaction conditions: toluene, 1 h, 20 °C. [b] Mole percent determined by ^1H NMR spectroscopy. [c] Kilograms of ethylene consumed per mole of *pre*catalyst per hour. [d] Reaction time was limited to 10 min to control temperature changes from reaction exothermicity.

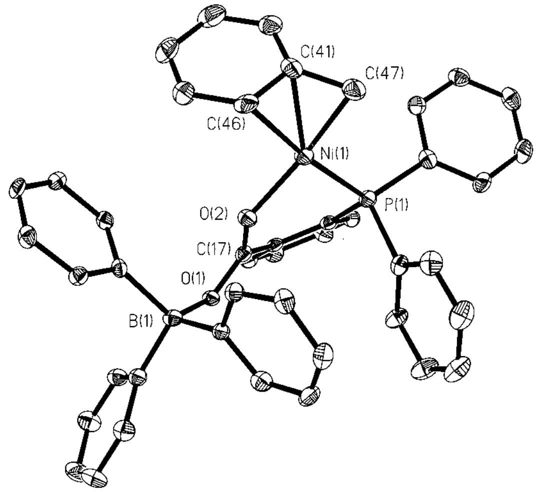

Figure 1. ORTEP view of **4**, showing atom-numbering scheme. Thermal ellipsoids at 30% probability level. Hydrogen and fluorine atoms omitted.

Table 2. Oligomerization of C_2H_4 by **4**[a]

temp (°C)	% 1-butene[b]	% higher α-olefins[b]	k_{CT}/k_P	*K*-factor
1	97	3	32	0.030
21	93	7	13	0.071
47	89	11	8.1	0.11
60	87	13	6.7	0.13
70	80	20	4.0	0.20

[a] Solvent is toluene. Reaction time is 10 min. $P(C_2H_4) = 5$ atm. $[Ni] = 25.0$ *μ*M. [b] Determined by ^1H NMR spectroscopy, average of multiple runs.

Entries 2, 5, and 8 in Table 1 show that increasing the ethylene pressure at a constant temperature increases the rate of monomer consumption but does not alter the 1-butene to 1-hexene ratio. Higher concentrations do not affect the chain length distribution (entries 4 and 5). Thus, the propagation and chain transfer steps are first order in monomer and catalyst. A similar order is observed with the iron catalyst derived from $\{[(2\text{-ArN}{=}C(Me))_2\text{-}C_5H_3N]FeCl_2\}$ (Ar = 2-C_6H_4Et) and methylaluminoxane.[11b]

Table 2 shows that, at a constant pressure, the ratio of 1-butene to higher 1-alkenes *decreases* with *increasing* temperature.[13] The *K* factor, determined by integrating the ^1H NMR signals of 1-butene, 1-hexene, and 1-octene, and by GC for 1-decene, 1-dodecene, and 1-tetradecene, is constant as a function of chain length. These observations, together with the pressure independence of *K*, indicate that the ratio of 1-butene to the sum of *all* the higher 1-alkenes corresponds to the ratio of the rate constant for chain transfer (k_{CT}) to the rate constant for propagation (k_P) for the nickel−butyl species. Since a Shulz−Flory distribution[14] is observed, this k_{CT}/k_P ratio is maintained for longer chain species.

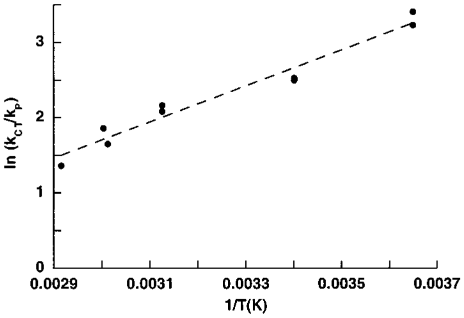

Figure 2. Graph of $\ln(k_{CT}/k_P)$ vs T^{-1} for **4**/C_2H_4.

From the Eyring equation one obtains:

$$\ln\left(\frac{k_{CT}}{k_P}\right)=\ln\left(\frac{[C_4H_8]}{\sum\limits_{n\geq 3}[C_{2n}H_{4n}]}\right)=\left(\frac{1}{T}\right)\left(\frac{\Delta H_P^{\ddagger}-\Delta H_{CT}^{\ddagger}}{R}\right)+\left(\frac{\Delta S_{CT}^{\ddagger}-\Delta S_P^{\ddagger}}{R}\right)$$

A plot of ln[ratio of 1-butene to all higher α-olefins] against $1/T$ should therefore yield the difference in activation enthalpy for propagation and chain transfer ($\Delta H^{\ddagger}_P - \Delta H^{\ddagger}_{CT}$) and the difference in activation entropies ($\Delta S^{\ddagger}_{CT}$-$\Delta S^{\ddagger}_P$).[15] Indeed, as shown in Figure 2, a linear correlation is observed over a 69 °C range from which we obtain $\Delta H^{\ddagger}_P - \Delta H^{\ddagger}_{CT} = 4.8(2)$ kcal/mol and $\Delta S^{\ddagger}_{CT} - \Delta S^{\ddagger}_P = -11(1)$ eu.[16] The enthalpy factor thus favors chain transfer; however, since $\Delta S^{\ddagger}_P > \Delta S^{\ddagger}_{CT}$, the rate of propagation increases more quickly with increasing temperature.

In summary, the initiation rate for nickel complexes such as **1** can be increased by substitution of the η^3-methallyl fragment for the isoelectronic η^3-benzyl ligand. Tandem catalysis by **4**/**2**/C_2H_4 produces polymers with significantly more branching than the **1**/**2**/C_2H_4 combination. Interestingly, the oligomerization reaction using **4** exhibits a *K* factor that is pressure independent and increases with increasing temperature. This trend is due to a larger (less negative) entropy of activation for propagation. In other words, while propagation and chain transfer are second-order processes, the transition state for chain transfer is more organized.

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Supporting Information Available: Complete details for experimental procedures and the crystallographic studies of **3** and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Data in Table 2 obtained under short reaction times. Under these conditions there is negligible formation of 1-alkene dimers and 2-alkenes (<5%).

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