

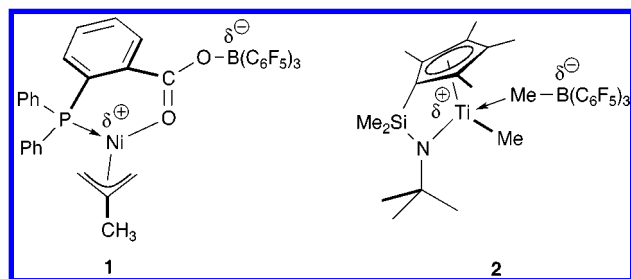
Synthesis, Characterization, and Ethylene Oligomerization Action of $[(C_6H_5)_2PC_6H_4C(O-B(C_6F_5)_3)O-\kappa^2P,O]Ni(\eta^3-CH_2C_6H_5)$

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We recently reported that $[(C_6H_5)_2PC_6H_4C(O-B(C_6F_5)_3)O-\kappa^2P,O]Ni(\eta^3-CH_2CMeCH_2)$ (**1**) and $\{[(\eta^5-C_5Me_4)SiMe_2(\eta^1-NCMe_3)]TiMe\}-\{MeB(C_6F_5)_3\}$ (**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 $[(C_6H_5)_2PC_6H_4C(O)O-\kappa^2P,O]Ni(\eta^3-CH_2CMeCH_2)$, 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 borane⁶ is important to raise the affinity of Ni for ethylene so that it matches the consumption rate at Ti.



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 fragment⁸ would result in a complex that would initiate more efficiently and would therefore offer more control in tandem polymerizations.

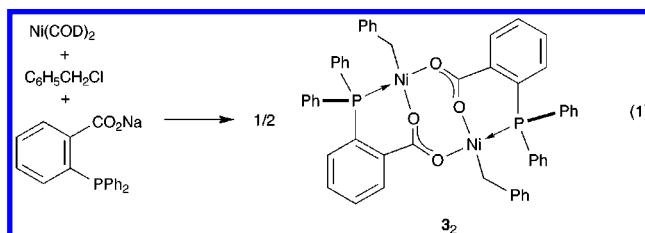
We report here on the synthesis and characterization of the benzyl analogue of **1**. We show that a faster initiation is indeed observed; however, the oligomerization sequence shows unexpected features. Specifically, the *K* factor, defined by

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

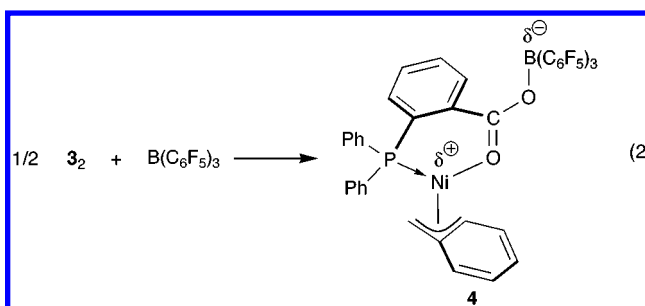
where R_p and R_{CT} are the rates of propagation and chain termination, respectively, is independent of monomer pressure

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 polymerization⁹ 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 $\{[(C_6H_5)_2PC_6H_4(\mu-CO_2)-\kappa^3P,O,O']Ni(\eta^1-CH_2C_6H_5)\}_2$ (**3** in eq 1) in 89% yield. The dimeric nature of **3** and coordination mode of the carboxylate functionalities were confirmed by a single-crystal X-ray diffraction study (Supporting Information).



Treatment of $1/2$ **3** with $B(C_6F_5)_3$ gives $[(C_6H_5)_2PC_6H_4C(O-B(C_6F_5)_3)O-\kappa^2P,O]Ni(\eta^3-CH_2C_6H_5)$ (**4** in eq 2). The nuclearity



of **4** and the hapticity of the benzyl ligand were confirmed by structural characterization (Figure 1).

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 **4**/C₂H₄ 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 ¹³C NMR spectroscopy¹² under the same conditions by using $1/2$ C₂H₄.

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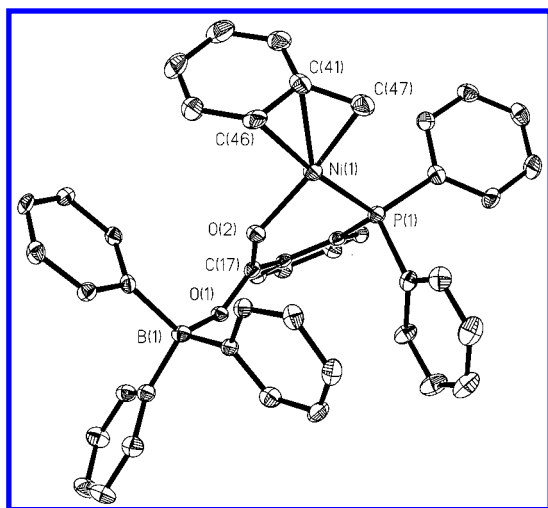
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Table 1. Oligomerization of C₂H₄ by **1** and **4**^a

entry	pre-cat.	P (atm)	[Ni] (μM)	activity ^c	α-olefin distribution ^b		olefin distribution ^b		
					% 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 precatalyst 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 C₂H₄ by **4**^a

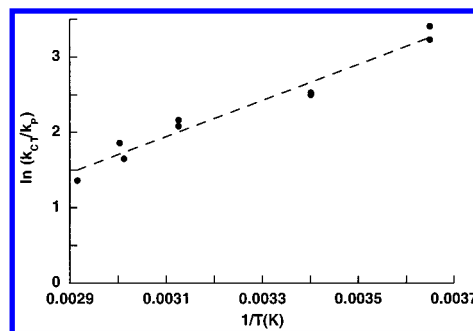
temp (°C)	% 1-butene ^b	% higher α-olefins ^b	k _{CT} /k _P	K-factor
1	97	3	32	0.030
21	93	7	13	0.071
47	89	11	8.1	0.11
60	87	13	6.7	0.13
70	80	20	4.0	0.20

^a Solvent is toluene. Reaction time is 10 min. P(C₂H₄) = 5 atm. [Ni] = 25.0 μM. ^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-ArN=C(Me))₂-C₅H₃N]FeCl₂} (Ar = 2-C₆H₄Et) 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 Schulz–Flory distribution¹⁴ is observed, this k_{CT}/k_P ratio is maintained for longer chain species.

(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%).

**Figure 2.** Graph of ln(k_{CT}/k_P) vs T⁻¹ for **4**/C₂H₄.

From the Eyring equation one obtains:

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

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 (ΔH_P[‡] – ΔH_{CT}[‡]) and the difference in activation entropies (ΔS_{CT}[‡] – ΔS_P[‡]).¹⁵ Indeed, as shown in Figure 2, a linear correlation is observed over a 69 °C range from which we obtain ΔH_P[‡] – ΔH_{CT}[‡] = 4.8(2) kcal/mol and ΔS_{CT}[‡] – ΔS_P[‡] = –11(1) eu.¹⁶ The enthalpy factor thus favors chain transfer; however, since ΔS_P[‡] > ΔS_{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 η³-methylallyl fragment for the isoelectronic η³-benzyl ligand. Tandem catalysis by **4**/C₂H₄ produces polymers with significantly more branching than the 1/2/C₂H₄ 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>. JA002042T

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