

Ethylene Polymerization and Ethylene/Methyl 10-Undecenoate Copolymerization Using Nickel(II) and Palladium(II) Complexes Derived from a Bulky P,O Chelating Ligand

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Received February 21, 2002

Summary: Cationic Ni(II) and Pd(II) complexes based on the bulky P,O ligand phenacyldi-*tert*-butylphosphine have been shown to be active for the polymerization of ethylene and copolymerization of ethylene and methyl 10-undecenoate, a functionalized monomer.

The discovery in 1995 that Ni(II) and Pd(II) diimine complexes of the general type $[(\text{ArN}=\text{C}(\text{R})\text{C}(\text{R})=\text{NAr})\text{M}(\text{CH}_3)(\text{OEt}_2)]^+\text{BAR}'_4^-$ (Ar = 2,6-(Me)₂C₆H₃, 2,6-(*i*-Pr)₂-C₆H₃; Ar' = 3,5-(CF₃)₂C₆H₃) are highly active catalysts for polymerization of ethylene and α -olefins has led to renewed interest in late-metal catalysts for olefin polymerizations.^{1–6} An attractive aspect of late-metal catalysts is their reduced oxophilicity and potential functional group compatibility. The key structural feature of these d⁸ metal catalysts is incorporation of bulky substituents on the ligand which serve to retard chain transfer and lead to high-molecular-weight polymers. In addition to the aryl-substituted diimine ligands, other bulky chelating ligands employed on Ni(II) and Pd(II) centers for ethylene polymerization include N,O, P,P, and P,O systems.^{7–9} We report here use of the readily prepared¹⁰ P,O chelate phenacyldi-*tert*-butyl-

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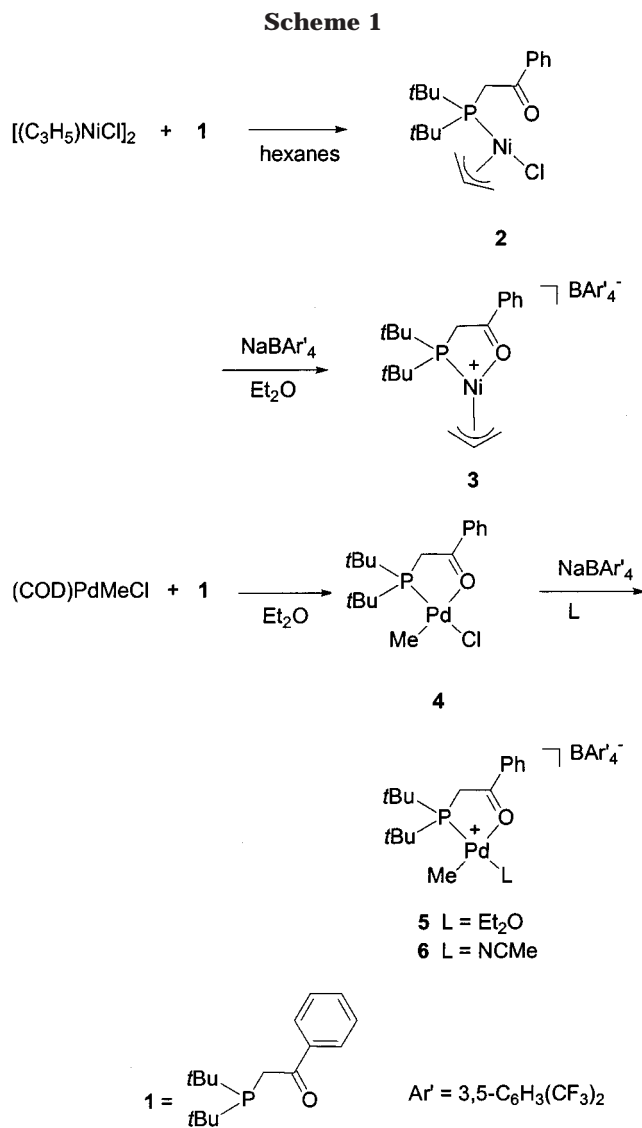
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phosphine (**1**) as a supporting ligand on Ni(II) and Pd(II) centers for ethylene polymerization and copolymerization of ethylene and methyl 10-undecenoate, a functionalized monomer.

The catalysts employed for polymerization studies are the cationic nickel allyl complex **3** and the palladium methyl complexes **5** and **6**. Synthetic routes to these compounds are depicted in Scheme 1. Treatment of $[(\text{C}_3\text{H}_5)\text{NiCl}]_2$ with **1** yields the neutral π -allyl complex

Table 1. Ethylene Polymerization Data^a

entry	cat.	amt of cat. (10 ⁶ mol)	ethylene pressure (atm)	temp (°C)	reacn time (h)	yield (g)	TOF (10 ⁻³ h ⁻¹)	<i>M_w</i> ^b	PDI
1	3	8.2	1.0	60	3	0.131	0.570	5500	2.1
2	3	4.1	6.8	26 (42) ^c	1	14.8	128	6100	2.5
3	3	4.1	13.6	26 (46) ^c	1	27.6	239	10000	2.7
4	3	4.1	27.2	26 (88) ^c	1	77.9	677	14000	2.5
5 ^d	3	16.4	27.2	50	2.5	23.9	20.8	1900	5.0
6	5	10	1.0	25	3	0.204	0.242	300 ^e	
7	5	10	1.0	60	3	0.612	0.727	300	
8	6	10	1.0	25	3	0.009	0.011	350	
9	6	10	1.0	60	3	0.352	0.418	330	
10	5	3.88	13.6	25	3	0.135	0.413	380	
11	5	3.88	13.6	80	3	6.582	20.2	280	
12	6	3.88	13.6	25	3	0.052	0.159	400	
13	6	3.88	13.6	80	3	6.526	20.0	340	

^a All polymerizations run in toluene, except entry 5. ^b Determined by GPC. ^c Highest temperature recorded during polymerization (result of reaction exotherm). ^d Polymerization run in 95 mL of CH₂Cl₂ + 5 mL of EtOAc. ^e *M_n* value determined by ¹H NMR spectroscopic analysis of the oligomer.

2, in which the ligand carbonyl group remains uncomplexed. Abstraction of chloride from **2** with NaBAR₄ yields the cationic bidentate complex **3**. The palladium complex **4** is generated by displacement of COD (1,5-cyclooctadiene) from (COD)PdMeCl with **1** followed by chloride abstraction with NaBAR₄ in the presence of either Et₂O or CH₃CN to yield **5** or **6**.

Results of ethylene polymerization studies using **3**, **5**, and **6** are summarized in Table 1. Exposure of **3** to 1 atm of ethylene results in rather low yields of PE (entry 1). However, polymerizations run at 6.8–27.2 atm exhibit very high activities that are comparable to highly active early-metal catalysts.^{11–15} At catalyst loadings of 2 × 10⁻⁵ M, the reaction exotherm cannot be completely controlled by the internal cooling manifold inside the autoclave reactor (entries 2–4). Increasing the ethylene pressure results in an increase in the reaction exotherm, polymerization activity, and polymer molecular weight. In all cases the polymer produced by **3** is a white powdery solid with *T_m* values between 127 and 131 °C. ¹H NMR analysis indicates linear polymer chains with 6–8 methyl branches per 1000 carbons. Catalyst **3** remains active toward ethylene polymerization in the presence of 5% ethyl acetate (entry 5), although the polymer molecular weight is reduced and a broadened molecular weight distribution is observed.

Pd catalysts **5** and **6** show modest activity at 25 and 60 °C under 1 atm of ethylene pressure. The more labile ether complex is typically more reactive than the acetonitrile adduct, particularly at low temperatures. Much higher activities are exhibited by **5** and **6** at 13.6 atm and increase with increasing temperatures. At high temperature and pressure the activities of **5** and **6** are approximately equal. The Pd catalysts generate low-molecular-weight PE oligomers with *M_n* ≈ 350 as determined by ¹H NMR analysis. The physical properties of the PE generated by **5** and **6** change considerably with ethylene pressure. At 1 atm of ethylene pressure, the oligomeric product is a viscous oil (*T_m* = 5 °C, 42 branches per 1000 carbons), while at higher ethylene

Table 2. Polymerization Data Demonstrating Slow Initiation^a

entry	temp (°C)	time (min)	yield (g)	TOF (10 ⁻⁴ h ⁻¹)	<i>M_w</i> ^b	PDI
1	30	15	0.5	8.6	15 400	2.4
2	30	20	2.5	33.5	14 900	2.3
3	30	25	4.4	47.4	13 700	2.1
4	30	30	15.3	136	9 800	2.4
5	30	40	33.4	224	8 400	2.3

^a Conditions: 0.8 μmol of **3**; 200 mL of toluene; 27.2 atm of ethylene. ^b Determined by GPC.

pressures the product is an amorphous solid (*T_m* = 22 °C, 16 branches/1000 carbons).

An NMR investigation of the reaction of **3** with ethylene has been carried out. Exposure of **3** to 10 equiv of ethylene in CD₂Cl₂ at 25 °C results in consumption of ethylene and formation of polyethylene with a -(CH₂)_{*n*}- resonance appearing at 1.28 ppm but no decrease in the intensity of the Ni-allyl resonances. These observations suggest that only a small fraction of **3** is initiated, followed by very rapid propagation and chain growth. Slow initiation of **3** was verified by polymerization experiments summarized in Table 2. Using a very low catalyst loading (0.8 μmol in 200 mL of toluene) and 400 psig of ethylene, the reaction exotherm could be better controlled. As seen by examining entries 1–5, TOF's (calculated from polymer yields) dramatically increase with time. Only 0.5 g of PE forms after 15 min, yet after 40 min 33.4 g of PE is produced, corresponding to a TOF of 2.24 × 10⁶ h⁻¹. Recognizing that little polymer is formed in the first 20 min and that at 40 min all catalyst may still not be activated, the intrinsic TOF of this catalyst under these conditions must exceed 3 × 10⁶ h⁻¹ (8.4 × 10⁴ kg of PE (mol of Ni)⁻¹ h⁻¹).^{16,17}

Exposure of **5** to 5 equiv of ethylene in CD₂Cl₂ at -78 °C generates the methyl ethylene complex **7**, which was

(16) In comparison, certain Ni(II) α-diimine catalysts exhibit ethylene polymerization activities of up to 1.0 × 10⁵ kg of PE (mol of Ni)⁻¹ h⁻¹.⁶

(17) Shell higher olefin process (SHOP) systems based on the neutral nickel P,O catalysts of the type [Ph₂PC(R)=C(R)O]Ni(Ph)L generate low-molecular-weight oligomers to high-molecular-weight PE (*M_n* up to 10⁶ g mol⁻¹) with activities of up to 1.4 × 10³ kg of PE (mol of Ni)⁻¹ h⁻¹ depending on reaction conditions: (a) Keim, W.; Kowalt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466. (b) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123. (c) Starzewski, K. A. O.; Witte, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 63.

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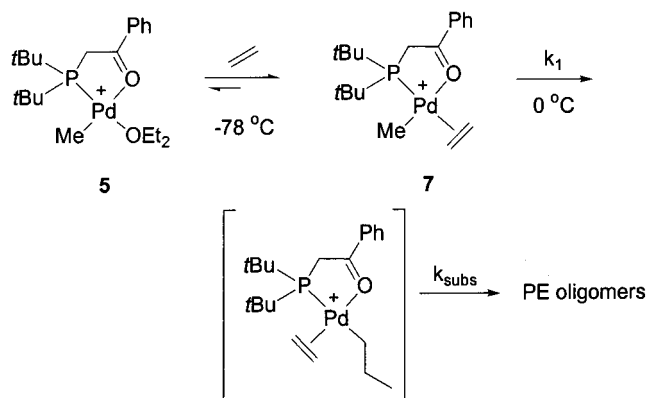
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Table 3. Copolymerization of Ethylene/Methyl 10-Undecenoate^a

entry	comon concn (M)	pressure (psig)	temp (°C)	yield (g)	TON (C ₂ H ₄)	comon incorp (mol %)	M _w ^b	PDI
1	0.90	100	60	0.31	900	4.8	3400	1.7
2	0.45	100	60	2.1	8 000	1.6	4000	1.8
3	0.22	100	60	3.2	12 800	1.0	4500	1.8
4	0.22	100	80	3.1	12 000	1.2	3300	1.8
5	0.22	200	60	3.9	15 700	0.63	4300	1.8

^a All polymerizations run in toluene. ^b Determined by GPC.

Scheme 2

characterized by NMR spectroscopy (Scheme 2). Warming to 0 °C results in migratory insertion and chain growth. The first-order rate constant for migratory insertion of the methyl ethylene complex at 0 °C was measured by monitoring decrease of the methyl resonance and found to be $k_1 = 4.3 \times 10^{-5} \text{ s}^{-1}$, with $\Delta G^\ddagger = 21.4 \text{ kcal/mol}$. The average rate of subsequent insertions was estimated from both the decrease in the bound ethylene signal and the increase of the oligomer $-(\text{CH}_2)_n-$ signal and found to be $k_{\text{subs}} = 2.1 \times 10^{-5} \text{ s}^{-1}$, with $\Delta G^\ddagger = 21.8 \text{ kcal/mol}$. These barriers are considerably larger than those for insertion in previously studied Pd(II) α -diimine complexes.^{2,5} For example, the rate of insertion for ethylene into the Pd-Me bond for a typical α -diimine Pd(II) complex at -30 °C has been found to be $k_{\text{obs}} = 1.9 \times 10^{-3} \text{ s}^{-1}$, with $\Delta G^\ddagger = 17.2 \text{ kcal/mol}$.

Since polymerization of ethylene in the presence of ethyl acetate occurs with good activity, the use of **3** for copolymerization of ethylene and the polar comonomer methyl 10-undecenoate was examined. Exposure of **3**

to ethylene in the presence of methyl 10-undecenoate results in the formation of random copolymers (Table 3). In comparison to ethylene homopolymerization experiments (Table 1), productivities of the copolymerizations are greatly reduced and yield lower molecular weight material. Increasing the concentration of methyl 10-undecenoate in the reaction solution results in an increase in comonomer incorporation but a decrease in copolymer yield. An increase in ethylene pressure results in decreased comonomer incorporation, while an increase in reaction temperature has little effect on activity and methyl 10-undecenoate incorporation.

In summary, the Ni(II) and Pd(II) complexes described are active for the polymerization of ethylene but the Ni(II) allyl complex demonstrates very slow rates of initiation. The Ni complex exhibits very high activity at high ethylene pressures, generating linear PE of modest molecular weights. Pd catalysts **5** and **6** are an order of magnitude less active than **3**, forming low-molecular-weight PE oligomers in which the degree of branching decreases with increasing ethylene pressure. Complex **3** has been shown to copolymerize ethylene and methyl 10-undecenoate with polar comonomer incorporation of up to ca. 5%. The reason for the high insertion barrier in the Pd system relative to α -diimine catalysts is unclear and is a focus of our current investigations.

Acknowledgment. We thank DuPont and the National Science Foundation (Grant No. CHE-0107810) for financial support of this work.

Supporting Information Available: Text giving experimental details for the synthesis and characterization of complexes **2**–**7** and general polymerization procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0201516