Organometallics **2001,** *20,* 663−666

Nickel Indenyl Complexes as Catalysts for the Dimerization and Polymerization of Ethylene

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Received October 12, 2000

The nickel indenyl compounds Ind(PR_3)Ni-X (Ind = indenyl and its substituted derivatives; R = Ph, Cy, Me; X = Cl, Me, CCPh) can dimerize and/or polymerize ethylene in the presence of suitable activators. For example, poly(methylaluminoxanes) (PMAO) combine with these Ni precursors to produce catalytically active species for both the dimerization and polymerization of ethylene. The polymers obtained from these reactions are mostly linear polyethylenes which contain a small number of ethyl branches and exhibit molecular weights in the range of $M_w = 10^5$ (M_w/M_n ca. 2). On the other hand, using activators such as $AgBF_4$, $AlCl_3$, and $B(C_6F_5)_3$ leads to the exclusive formation of butenes. It is proposed that the latter activators convert the Ni precursors to the highly electrophilic cations $[IndNi(PR_3)]^+$, which efficiently catalyze the dimerization of ethylene to butenes; in contrast, Ni/PMAO combinations give both the aforementioned cationic species as well as neutral species bearing a Ni-(μ-Me)Al core, which is thought to be the active site for the polymerization reactions.

Introduction

The recent emergence of highly active, late-transition-metal-based catalysts for polymerizing ethylene has introduced a new dimension in the search for novel olefin polymerization catalysts. These catalysts operate under less stringent reaction conditions and can tolerate polar functional groups in the monomer; hence, they have the potential to widen the scope of polyolefins accessible by metal-based catalytic technology. The first examples of effective late-metal-based systems featured N-based auxiliary ligands such as the bidentate α-diimines (with Ni and Pd)[1] and the tridentate bis(imino)pyridines (with Fe and Co).[2] The operating mechanisms of these catalysts are believed to involve cationic intermediates derived from the interaction of the initial precursors with PMAO-type activators (PMAO = poly(methylaluminoxane)).[3] A more recently reported Ni system, which features salicylaldimine type ligands, has been shown to operate via neutral intermediates generated in the absence of activators.[4] This is a significant development because it demonstrates that cationic species are not essential for generating high turnover frequencies in olefin polymerizations and emphasizes the crucial role of ligand architecture for tuning the reactivity of the metal center and controlling the mechanism of its action.

The present paper reports the results of our studies on the dimerization and polymerization of ethylene catalyzed by a new family of nickel-based catalyst precursors which incorporate indenyl and phosphine ligands. Although the dimerization reaction is catalyzed by cationic species, it appears that the polymerization of ethylene in this system is catalyzed by a neutral species.

Results and Discussion

Previous studies[5] on the structures and reactivities of nickel complexes ligated by indenyl and phosphine ligands have shown that some of these compounds, when combined with various activators, can oligomerize or polymerize substrates such as $PhSiH_3$[6] and PhCCH.[7]

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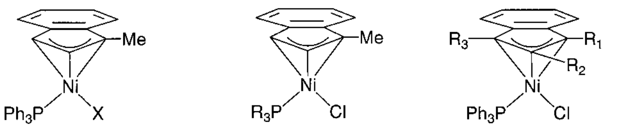
10.1021/om000872+ CCC: $20.00
Publication on Web 01/17/2001

Chart 1



X = Cl (**1**)
= Me (**2**)
= CC-Ph (**3**)

R = Me (**4**)
= Cy (**5**)

	R1	R2	R3
6	Me	H	Me
7	Me	Me	H
8	H	Ph	H
9	Me	Ph	Me
10	$SiMe_3$	H	H
11	i-Pr	H	H

Table 1. Reactivities of (R-Ind)(PR_3)NiX with Ethylene

run	[Ni]	initiator/cocatalyst (ratio to [Ni])	activity[a] (kg of PE/((mol of Ni) h atm))
1	**1**, **2**, or **3**		no reaction
2	**1**	$AgBF_4$ (1:1)	0 (only butenes)
3	**1**	PMAO (400:1)	8[b]
4	**4**	PMAO (400:1)	65[c]
5	**5**	PMAO (400:1)	62[d]
6	**6**	PMAO (400:1)	12
7	**7**	PMAO (400:1)	16
8	**8**	PMAO (400:1)	12
9	**9**	PMAO (400:1)	20
10	**10**	PMAO (400:1)	12
11	**11**	PMAO (400:1)	111[e]
12	**2**	PMAO (400:1)	55
13	**3**	PMAO (500:1)	110[f]
14	**11**	PMAO (800:1)	29[g]
15	**11**	PMAO (100:1)	2
16	**11**	PMAO (50:1)	0.6
17	**3**	PMAO (1000:1)	130[h]
18	**2**	PMAO-IP (400:1)	55
19	**2**	$AlMe_3$ (400:1)	4
20	**2**	MAD[i] (400:1)	no reaction

[a] Activities refer only to the production of PE and do not take into account the production of butenes, even though this constitutes the major reaction pathway in most cases. Strictly speaking, the activity numbers are underestimated because only a small fraction of the Ni-containing species is involved in the polymerization. [b] M_w ca. 4.0×10^5. [c] M_w ca. 5.8×10^5, $M_w/M_n = 1.73$. [d] M_w ca. 4.6×10^5, $M_w/M_n = 1.89$. [e] M_w ca. 3.8×10^5, $M_w/M_n = 2.37$. [f] M_w ca. 4.5×10^5, $M_w/M_n = 2.50$. [g] M_w ca. 4.7×10^5, $M_w/M_n = 2.12$. [h] M_w ca. 4.8×10^5, $M_w/M_n = 1.95$. [i] MAD = MeAl{O(1,6-(tBu)$_2$C$_6$H$_2$-4-Me)}$_2$.

Analogous studies with ethylene as substrate showed that the reactivity of these systems is strongly dependent on the nature of the activator used. For instance, the 1:1 combination of (1-Me-Ind)(PPh_3)NiCl (**1**; Chart 1) and $AgBF_4$ in ethylene-saturated 1,2-dichloroethane ($P_{ethylene} \approx 5$ atm) leads to ethylene uptake at the rate of ca. 11 000 kg/((mol of Ni) h) and produces a mixture of mostly butenes (by GC-MS analysis) with only traces of higher oligomers (run 2, Table 1). In contrast, combinations of **1** with PMAO type reagents lead to the concomitant formation of high-molecular-weight polyethylenes (PE) as well as butenes. For example, combining 6 μmol of **1** with an excess of PMAO (150 mg) in ca. 300 mL of ethylene-saturated toluene (concentration of **1** ca. 20 μM) gave 0.132 g of PE ($M_w \approx 4 \times 10^5$ g/mol) in 30 min (run 3, Table 1). This reaction also produced an undetermined amount of butenes found in the filtrate; indeed, only about 5−10% of the ethylene consumed was converted into PE (vide infra). Analysis by $^{13}C\{^1H\}$ NMR of the PE formed in this system showed it to be mostly linear with only a small number of Et branches (but no Me branching), corresponding to the incorporation of ca. 5 mol % of the 1-butene produced in situ.

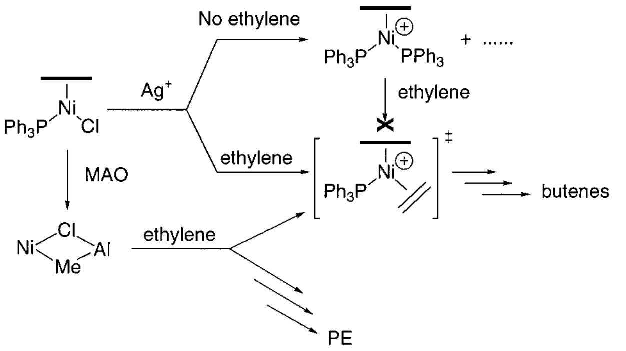
The amount of PE obtained increases when precursors containing trialkylphosphines are used. For instance, under similar conditions, (1-Me-Ind)(PMe_3)NiCl (**4**) and (1-Me-Ind)(PCy_3)NiCl (**5**) gave about 1 g of PE (runs 4 and 5, Table 1). The Ind substituents also affect the catalyst activity (runs 6−11, Table 1), with (1-(Pr^i)Ind)(PPh_3)NiCl being the most active. Higher activities are also obtained with (1-Me-Ind)(PPh_3)NiMe (**2**) and (1-Me-Ind)(PPh_3)NiCCPh (**3**) (runs 12 and 13, Table 1). It should be emphasized that all of the polymerizations catalyzed by these compounds show very short induction periods, which can be attributed to the rate-limiting diffusion of the activator to the Ni complex. In addition, all experiments displayed ethylene flow profiles with very similar curve shapes, the main difference among the various runs being the area under the flow vs time curves. These characteristics imply that the different levels of activities are representative of actual rates of polymerization, so that the different activities observed with the precatalysts **4**−**11** might be interpreted to indicate that the phosphine and Ind ligands remain coordinated to Ni during the catalysis.

The optimal Ni:PMAO ratio seems to be about 1:400 for the Ni−Cl precursors (runs 11 and 14−16, Table 1), but the NiCCPh analogue maintains its activity with higher ratios (run 17, Table 1). Using PMAO-IP (PMAO containing very low levels of residual $AlMe_3$) instead of PMAO did not alter the effectiveness of the catalytic system, whereas substituting $AlMe_3$ for PMAO led to a lower polymerization activity (compare runs 12, 18, and 19, Table 1). This suggests that it is the PMAO itself, rather than the $AlMe_3$ present in PMAO samples, which is responsible for activating the precatalyst.

We have examined the interaction of the Ni precursors with various initiators/ cocatalysts in stoichiometric or near-stoichiometric reactions in the hopes of understanding why the Ni/Ag^+ system leads to the almost exclusive production of butenes whereas the Ni/PMAO system gives both butenes and PE. Thus, **1** reacts with chloride abstracting agents such as $AgBF_4$, $AlCl_3$, and $ClAlMe_2$ to give the cationic complexes [(1-Me-Ind)(PPh_3)$_2$Ni]$^+$X$^-$ in low yields;[5d] these bis(phosphine) cations are completely inert toward ethylene. In contrast, the species generated from **1**/Ag^+ *in an ethylene-saturated medium* remains highly active in the production of butenes, as long as the ethylene concentration remains high (no decrease in activity levels observed over 2 h). Catalytically active cations can also be generated by protonating the Ni−Me precursor **2** or reacting **1** with $B(C_6F_5)_3$; under the catalytic reaction conditions, these activators led to oligomerizations similar to those observed with Ag^+, albeit at a much slower rate. It is worth emphasizing that no polymerization is observed with any of these cationic initiators and that even the oligomerization proceeds only if ethylene is present prior to the initiation.

The outcomes of both stoichiometric and catalytic experiments are quite different when PMAO is used in conjunction with the Ni precursors. Thus, NMR experi-

Scheme 1



ments have shown that **1** reacts rapidly with 1 equiv or more of PMAO to give a species which displays the same ^{1}H and ^{31}P{^{1}H} NMR resonances as those of the independently prepared complex **2**, (η^3-1-Me-Ind)(PPh_3)-NiMe.[5c] Moreover, interaction of complex **2** with up to 50 equiv of PMAO has virtually no effect on the NMR spectra and definitely shows no detectable quantities of the cationic species for up to 6 h. On the other hand, monitoring the NMR samples prepared from **1**/PMAO and **2**/PMAO for longer periods showed the gradual emergence of the cations [(Ind)Ni(PR_3)$_2$]$^+$. It is important to recall that combinations of [Ni]/PMAO convert ethylene to butenes as well as PE and that mixtures of PMAO and the Ni precursors can be prepared prior to the polymerization experiments and remain stable in the absence of ethylene; introduction of ethylene leads to the formation of butenes and PE. These observations demonstrate that the interaction of PMAO with the Ni precursors is qualitatively different from that observed with the cationic initiators such as Ag$^+$. We propose that ethylene polymerization in the PMAO/Ni system involves noncationic intermediates generated by the interaction of Ni−X (X = Cl, Me, CCPh) with PMAO while the ethylene oligomerization is catalyzed by small quantities of the highly electrophilic, coordinatively unsaturated cationic intermediate [(1-Me-Ind)(PPh_3)-Ni]$^+$; the latter species can undergo a redistribution reaction in the absence of a sufficiently high concentration of monomer to give the unreactive [(1-Me-Ind)-(PPh_3)$_2$Ni]$^+$ and other unidentified byproducts (Scheme 1). It should be emphasized that even under the conditions of polymerization experiments most of the monomer is converted to butenes and only a small amount ends up in the isolated PE. This may be explained by the much higher reactivity of the cationic species.

The above mechanistic conclusions raise the question of how PMAO activates these Ni precursors toward ethylene polymerization. We have considered the possibility that, in analogy to the mechanism of action for the Grubbs catalysts, PMAO might assist in the removal of the phosphine ligand, thereby opening a coordination site for ethylene uptake. NMR experiments indicate, however, that the phosphine ligand remains coordinated to Ni in the presence of a large excess of PMAO. In addition, among the phosphine ligands tested, the higher activities are obtained with the ones more strongly coordinated to Ni.[8] Therefore, phosphine dissociation seems unlikely. The removal of the Ind ligand by PMAO can also be ruled out, at least at the initial stages of the reaction, on the basis of the above-discussed NMR experiments and the fact that the Ind substituents influence reactivities without changing induction periods. This leads us to conclude that the action of PMAO involves the Ni−X bond. Given that the Ni−Me precursor does not undergo insertion in the absence of PMAO (Scheme 1), we speculate that the role of PMAO is to weaken the Ni−Me bond without actually abstracting the Me ligand. At this stage, we envisage a bridging interaction between Ni−Me and Al−X moieties, similar to Ni(μ-X)$_2$Al species proposed in a number of other Ni/Al systems;[9] the uptake of ethylene in this intermediate would presumably be facilitated by the slippage of Ind to an η^1 mode.[10] In this sense, PMAO is more appropriately viewed as a cocatalyst rather than an initiator, as its presence is probably necessary at every insertion step. This proposal is consistent with the observation that highly Lewis acidic reagents ionize the Ni−X bond and promote the oligomerization reaction, while insufficiently Lewis acidic reagents such as $AlMe_3$ decrease polymerization activities as a result of insufficient weakening of the Ni−X bond. Moreover, Lewis acidic but bulky reagents such as MeAl{O(1,6-(tBu)$_2$$C_6H_2$-4-Me)}$_2$[11] do not promote ethylene insertion (run 20, Table 1) presumably because of the hindered Ni(μ-X)$_2$Al interaction.[12]

Conclusion

The complexes Ind(PR_3)NiX combine with PMAO to produce primarily noncationic intermediates which can polymerize ethylene into fairly high molecular weight poly(ethylene) chains at a modest level of activity. Cationic intermediates are also formed in these reactions and lead to efficient dimerization of ethylene. Some of the 1-butene thus produced is then incorporated into the growing polymer chain to give PE which is mostly linear but contains a small number of ethyl branches. When cationic initiators such as Ag$^+$ are reacted with the Ni−Cl precursors, ethylene dimerization is the only catalysis observed. Future studies will pursue the optimization of this system and will explore the mechanistic issues discussed above.

Experimental Section

The Ni complexes were prepared according to published procedures.[5,7] A typical experimental procedure for the polymerization runs is as follows. A 1 L autoclave was dried under vacuum at 373 K for several hours, refilled with dry N_2, and allowed to cool to 303 K. The vessel was then charged with 300 mL of dry and deoxygenated toluene under a positive

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[8] Complex **1** undergoes a facile and irreversible displacement of PPh_3 in the presence of trialkylphosphines such as PCy_3, PBu_3, and PMe_3. The results of a detailed study on the ligand exchange reactions in these systems will be reported shortly.

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[12] NMR experiments reveal that the Ni complex **2** undergoes a very slow reaction (3 days) with MAD at room temperature to form, inter alia, the cationic bis(phosphine) complex [(1-Me-Ind)Ni(PPh_3)$_2$]$^+$; under catalytic conditions, neither ethylene polymerization nor oligomerization is observed after 30 min at room temperature using complex **1** or **2** in the presence of 300 μM of MAD.

pressure of N_2, and then saturated with ethylene at ca. 5 atm. For experiments involving single-component activators, a solution of MAD (Me-Al{O(1,6-(tBu)$_2$C$_6$H$_2$-4-Me)}$_2$) in toluene (10 mL) was introduced using a small sampling vessel overpressurized with N_2 to give a final concentration of 300 μM. After the mixture was stirred for 1 h, solutions of the cocatalyst (1.2 equiv) and the Ni precursor (1.0 equiv) in toluene (20 mL each) were sequentially introduced in the same manner as for MAD; the final concentration for the Ni precursor was ca. 6 μM. A similar procedure was adopted for polymerizations using PMAO in that the required amount of PMAO was added to the reactor followed by the Ni complex. Ethylene uptake was monitored using a calibrated mass flow meter; constant monomer flow was observed typically within 5 min after catalyst introduction. The temperature was controlled using an external cooling jacket connected to a recirculating heating/cooling bath and was monitored by an RTD sensor placed in a thermocouple well in contact with the reactor contents. Polymerization experiments were conducted for 20−30 min following attainment of steady-state conditions (constant T and ethylene flow) in the reactor. An excess of MeOH was added to the final mixture through an overpressurized sample vessel, the reactor was then vented, and the polymer slurry was drained from the reactor through a bottom drain valve. In many cases, additional PE had to be removed by scraping of the reactor walls and stirrer assembly. A small aliquot (ca. 0.5 mL) of the polymer slurry was removed and analyzed by GC-MS while polymer samples were isolated by filtration, washed with MeOH, and dried prior to weighing. Polymer characterization by ^{13}C NMR spectroscopy and by high-temperature GPC was accomplished by methods described in detail elsewhere.[13]

Acknowledgment. D.Z. is grateful to the NSERC, FCAR, and Ministère de l'Éducation (Québec) for financial support of this work, to Drs. D. Harrison and Q. Wong of Nova Chemicals Ltd. of Calgary, Alberta, Canada, for evaluating the catalytic properties of some of the complexes discussed in this work, and to F. Fontaine and L. Groux for their contributions to some of the experiments. S.C. is grateful to the NSERC and Nova Chemicals for financial support of this work.

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