Dimerization and polymerization of ethylene catalyzed by nickel complexes bearing multidentate amino-functionalized indenyl ligands

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Abstract

The combination of the neutral compound $(\eta^3:\eta^0\text{-Ind}(CH_2)_2NMe_2)Ni(PPh_3)Cl$ (**1**) and methylaluminoxane (MAO) produces catalysts for the dimerization and the polymerization of ethylene. On the other hand, activation of the cationic complex $[(\eta^3:\eta^1\text{-Ind}(CH_2)_2NMe_2)Ni(PPh_3)][BPh_4]$ (**2**) by MAO or trimethylaluminum leads to a system which dimerizes ethylene with high turnover frequencies ($2 \times 10^3 \, s^{-1}$), but does not promote its polymerization. The effects of parameters such as ethylene pressure, reaction temperature and time, solvent type, and the type and amount of activator used have been studied in order to optimize the conditions for the formation of polyethylene. In addition, a number of reactions have been studied by NMR and GC–MS analysis in an effort to identify the catalytically active species. The results of these studies point to the involvement of cationic species in the dimerization of ethylene, whereas, the active catalyst for the polymerization of ethylene appears to be a non-cationic species.
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1. Introduction

The recent success of late transition metal systems, especially those of Group 10 metals, in the polymerization of ethylene has opened new vistas in the development of the next generations of catalysts for olefin polymerization [1]. Unlike the catalysts based on early transition metals, late metal-based catalysts tolerate polar functional groups in the monomers. It is anticipated that this characteristic will expand the range of polyolefins accessible by catalysis. The key element for an efficient system is the choice of the ligand. For example, a family of bidentate α-diimine ligands has been used in the development of highly efficient Ni and Pd systems for the polymerization of ethylene and propylene. These catalysts operate through cationic intermediates formed by the action of MAO-type activators [2,3]. On the other hand, recent reports on the chemistry of nickel complexes containing salicylaldimine ligands have shown that neutral intermediates could also be active and effective for the polymerization of ethylene [4].

We have shown [5,6] that the complexes $(Ind)(PR_3)$-NiX (Ind: indenyl and its substituted derivatives; R:

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Ph, Me or Cy, X: Cl, Me, CCPh) react with MAO to generate both cationic and neutral intermediates which convert ethylene to mostly butenes (>90%) as well as some polyethylene (M_w ca. 5×10^5). On the other hand, studies carried out on the polymerization of styrene and norbornene have shown that an amino alkyl substituent on the Ind ligand has a major influence on the course of the polymerization: polymers with high weight average molecular weight (M_w) were obtained with styrene, whereas, only oligomers were formed with norbornene [7]. With these results in mind, we set out to study the polymerization of ethylene catalyzed by complexes bearing chelating aminoindenyl ligands [8].

The present article reports the results of our investigation on the dimerization and polymerization of ethylene catalyzed by the neutral complex ($\eta^3:\eta^0$-Ind(CH$_2$)$_2$NMe$_2$)Ni(PPh$_3$)Cl (**1**) and the cationic complex [($\eta^3:\eta^1$-Ind(CH$_2$)$_2$NMe$_2$)Ni(PPh$_3$)][BPh$_4$] (**2**), Fig. 1. The effects of ethylene pressure, reaction temperature, time, activator, and solvent on these reactions have been studied. The results of NMR studies on the reactivity of these complexes with the activators MAO and AlMe$_3$, both in the presence and absence of ethylene, are also presented. GC–MS
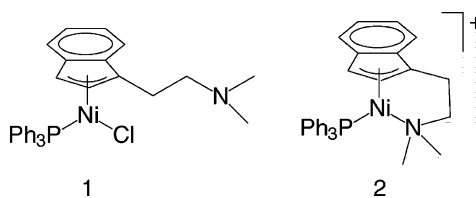

Fig. 1.

analyses were performed on the resulting solutions in order to track the reaction and decomposition products, thus providing clues on the reaction mechanism.

2. Results and discussion

2.1. Polymerization of ethylene with the neutral complex **1**

The outcome of the polymerization experiments with the neutral pre-catalyst **1** are summarized in Table 1. Most of these experiments resulted in the predominant formation of butenes, but various quantities of polyethylene (PE) representing ca. 1–4% of the total mass of ethylene consumed were also

Table 1
Reactivities[a] of ($\eta^3:\eta^0$-Ind(CH$_2$)$_2$NMe$_2$)Ni(PPh$_3$)Cl (1) with ethylene

Run	AlMe$_3$ (Eq.)	MAO (Eq.)	Solvent (300 ml)	P (psi)	T (°C)	Total activity (kg C2/(mol Ni h))	Activity (kg PE/(mol Ni h))	M_n (× 10^{-5} g/mol)	PDI (M_w/M_n)
1	–	50	Toluene	75	40	84	0	–	–
2	–	200	Toluene	75	40	2270	0	–	–
3	–	1000	Toluene	75	40	2350	90	1.1	2.3
4a	–	1000	Toluene	175	40	8400	144	2.6	2.5
4b						4790	360		
4c						2920	695		
5	–	1000	Toluene	175	60	8190	89	1.3	2.1
6	–	1000	Toluene	175	80	3980	121	0.7	1.9
7	2000	–	Toluene	175	60	460	0	–	–
8	2000	200	Toluene	175	40	5090	25		
9	–	1000	Toluene	270	40	10950	108		
10	–	1000	Hexanes	175	40	8080	0	–	–
11	–	1000	DCE[b]	175	40	12970	23	1.7	2.1
12	–	1000	DCE[b]	175	60	11270	182	0.3	2.0
13	–	1000	DCE[b]	175	80	15330	516	C14–22	–
14	–	100	ClBz[b]	175	40	1820	0	–	–
15	–	1000	ClBz[b]	175	40	19810	77	1.6	2.0

[a] Reaction time, 30 min except for runs 3 and 13 (60 min), and runs 4b (10 min) and 4c (4 min).
[b] DCE, dichloroethane; ClBz, chlorobenzene.

produced. The PE thus obtained has high molecular weights and low polydispersity index ($M_w \approx 10^5$; $M_w/M_n = 1.9$–2.5), and is essentially linear with a small number of ethyl branches exclusively.

Runs 1–3 of Table 1 focused on the determination of the optimum amount of activator. Examination of the effect of pressure (runs 3, 4a and 9) led us to select the conditions of run 4a (1000 equivalent of MAO, 300 ml toluene, 175 psi of ethylene, 40 °C for 30 min) as the standard run to which all the others would be compared. Next, we studied the effect of replacing MAO by AlMe$_3$ (runs 7 and 8), varying the reaction time (runs 4a–c), and temperature (runs 4a, 5, 6 and 11–13), and finally the choice of solvent (polar and non-polar, aromatic and aliphatic). The results of these studies are described later.

2.1.1. Effect of activator

The dimerization of ethylene can be catalyzed by complex **1** in the presence of only a few equivalents of MAO or a large excess of AlMe$_3$, whereas, only MAO (in large excess) is an effective co-catalyst for the production of PE (runs 4–6, 9, 11–13 and 15). It is not clear why such a large excess of MAO is needed to activate the pro-catalyst for the polymerization reaction, but some of this excess is likely used to eliminate all poisoning residues. This is illustrated by run 8 which shows that if AlMe$_3$, which does not activate the polymerization reaction, is first used to clean the solvent, then a smaller amount of MAO can be used as activator (compare runs 2, 4, 7 and 8). A number of NMR experiments were carried out in order to shed light on the role of MAO in these reactions, as described next.

2.1.2. NMR studies with complex **1**

The reactions of compound **1** with various amounts of MAO (2, 7, 14, 20, 30 and 100 equivalents; in the absence of ethylene) were monitored by ^{31}P and ^{1}H NMR spectroscopy (C$_6$D$_6$). Fig. 2 shows the conversion of complex **1** into various species as a function of MAO equivalents present in the reaction mixture. Some of the resulting species could be identified by comparison of their ^{31}P chemical shifts to those of known compounds[2] and the relative ratio of these

products was calculated from the integration of signal intensities.

Thus, reacting **1** with 2 equivalents of MAO forms the Ni–Me analogue (η^3:η^0-Ind(CH$_2$)$_2$NMe$_2$)Ni-(PPh$_3$)Me); this is evident from the characteristic ^{31}P NMR signal for the Ni–Me derivative (47.8 ppm) [9].[3] The same Ni–Me species is also obtained when **1** is reacted with AlMe$_3$ or MeLi. Experiments have shown that this Ni–Me species does not react with ethylene either on its own or when AlMe$_3$ is used as activator. On the other hand, MAO can activate the Ni–Me bond toward ethylene polymerization. We have proposed that the role of MAO is to weaken the Ni–Me bond, thereby promoting the insertion of ethylene.[4]

In order to determine the fate of the Ni–Me species, we monitored its reaction with increasing amounts of MAO. The ^{31}P{^{1}H} NMR spectra showed that the relative concentration of the Ni–Me species decreases as the concentration of MAO increases, and a new species (28.6 ppm) is formed in the presence of 7 equivalents of MAO. The chemical shift of this new species is very close to that of the cationic complex **2**, but its ^{1}H NMR spectrum reveals some differences. In fact, this same compound is also obtained upon reacting **2** with MAO and leads to the dimerization of ethylene. Increasing the quantity of MAO beyond 20 equivalent leads to the formation of a number of unidentified species (^{31}P: 46.1, 44.7, 41.0, 36.9, 30.4, and 27.5 ppm) one of which might well be the species producing polyethylene.

These results indicate that the Ni–Me species, which forms at the outset of the reaction between MAO and **1**, reacts further with MAO to produce a cationic species that is structurally very similar to **2**; the dimerization reaction is likely catalyzed by this homologue of **2**. The reaction of **1** with large excess of MAO also gives a number of unidentified species that show ^{31}P NMR signals in a region associated with neutral Ni–alkyl derivatives; we suspect that one or more of

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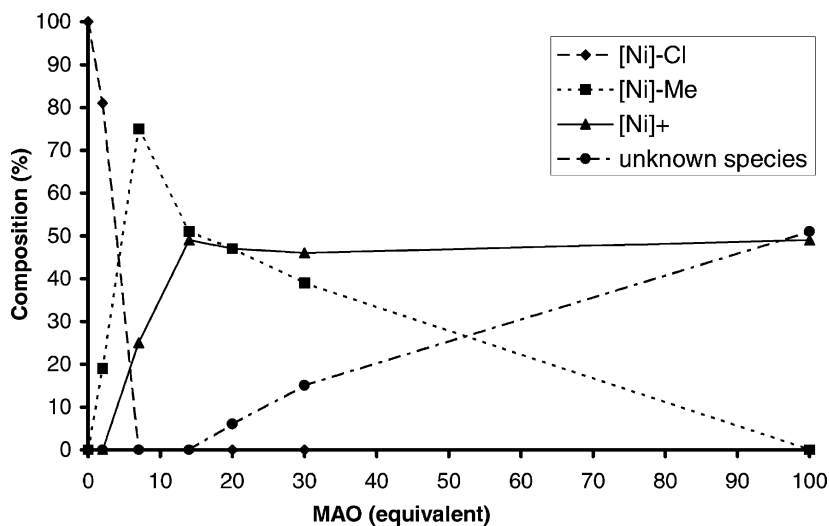
Fig. 2. [Ni] = $(Ind(CH_2)_2NMe_2)Ni(PPh_3)$. Reactivities of **1** with MAO in C_6D_6.

these species is involved in the polymerization reaction, but no firm conclusion can be drawn at this point.

2.1.3. Effect of reaction time

In order to get more information on the active species producing polyethylene, three runs were conducted under otherwise identical conditions, changing only the reaction time (run 4a–c; 30, 10 and 4 min, respectively). The polymerization activity per unit of time increases drastically from run 4a to 4c, implying that the active species is unstable and deactivates over time. Thus, it appears that 65% of the PE is produced during the first 4 min, 20% in the next 6 min and 15% in the last 20 min. On the other hand, the consumption of ethylene increases during the first 15 min (TOF goes from 25 to $100 s^{-1}$) and then stays constant over the last 15 min, during which the dimerization reaction is predominant.

2.1.4. Effects of pressure and reaction temperature

The total activity increases with pressure, but no significant increase has been observed on the formation of PE (runs 3, 4a and 9). Higher temperatures lead to higher activities and shorter chain lengths (runs 4–6 and 11–13). The TOF curves for runs 4 and 6 show that higher temperatures increase the reaction rate initially followed by a rapid deactivation of the catalyst.

The consumption of ethylene falls to nearly zero after 15 min at 80 °C in toluene. (Fig. 3).

2.1.5. Solvent effect

The total activity increases with the increasing polarity of the solvent (chlorobenzene > dichloroethane > toluene > hexanes), whereas, aromatic solvents tend to favor the polymerization activity (runs 4a, 10, 11 and 15). Polymers with the highest number average molecular weight (M_n) were produced in toluene with modest activity. On the other hand, polymers of lower M_n or even oligomers were obtained in dichloroethane (DCE). These observations are consistent with the idea that the dimerization reaction is catalyzed by cationic species that are expected to be more stable in a polar medium.

2.2. Dimerization of ethylene with the cationic complex **2**

The results of the attempted polymerization experiments with the cationic complex **2** are summarized in Table 2. Run 16 (40 °C) and run 17 (80 °C) were used to test the ability of complex **2** to react with ethylene without activator. The observed inertness of this complex is in contrast to its reactivity in the polymerization of norbornene and styrene at 80 °C [7]. As will
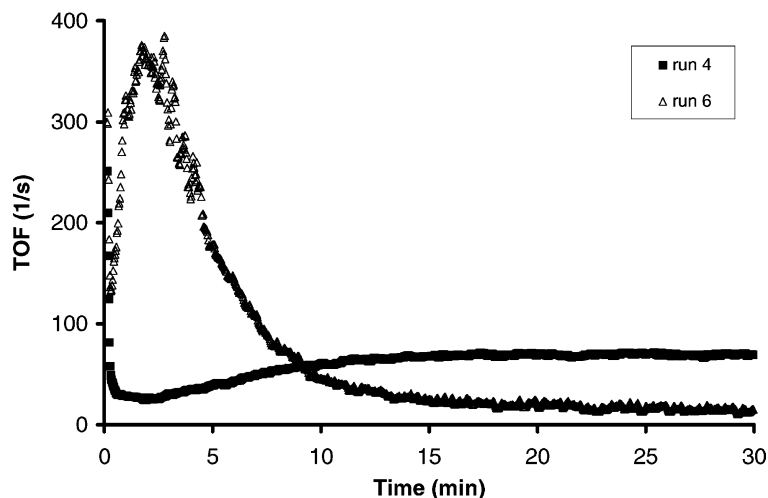
Fig. 3. Turnover frequencies plot for runs 4 and 6.

be discussed later, this implies a different mechanism for the polymerization of ethylene. The outcomes of runs 19–21 show that a rather large amount of MAO is needed to induce the dimerization of ethylene; no polymers were obtained.

A large excess of activator (either MAO or AlMe$_3$) is crucial for both removing the contaminants present in the reaction medium and also for binding the chelat-

Table 2
Reactivities[a] of $[(\eta^3:\eta^1\text{-Ind}(CH_2)_2NMe_2)Ni(PPh_3)][BPh_4]$ (**2**) with ethylene

Run	MAO	Solvent (300 ml)	Total activity (kg butenes[b]/(mol Ni h))
16	0	Dichloroethane	0
17	0	Dichloroethane	0
18	25	Dichloroethane	0
19	400	Dichloroethane	51700
20	1000	Dichloroethane	74800
21	2000	Dichloroethane	76000
22	2000[c]	Dichloroethane	3000
23	1000	Chlorobenzene	54400
24	1000	Toluene	20000
25	1000	Hexanes	20600
26	400[c]	Hexanes	4900

[a] 175 psi, 40 °C except for run 17 (80 °C); reaction time, 15–30 min.
[b] No solid isolated, only butenes are produced (^{13}C NMR, GC–MS analysis).
[c] AlMe$_3$ instead of MAO.

ing amino moiety in **2**; this binding frees a coordination site on the nickel center for ethylene. The cationic compound **2** in the presence of MAO (or AlMe$_3$) does not produce a Ni–Me species or catalyze the polymerization of ethylene. It is remarkable that no PPh$_3$–MAO adduct is formed even in the presence of a large excess of MAO (PPh$_3$–AlMe$_3$: δ −7.18 ppm (^{31}P {^{1}H} in C$_6$D$_6$)); [10] evidently, the phosphine is strongly bonded to the nickel center and does not dissociate.

By analogy to previously reported studies, the efficient dimerization of ethylene in the present system points to a mechanism involving the insertion of ethylene into a cationic Ni–H intermediate. The insertion of a second molecule of ethylene into the resulting Ni–ethyl bond, followed by β-H elimination would produce butene and regenerate the Ni–H species [11,12]. The initial formation of the cationic Ni–H species can occur by insertion of ethylene into the Ni–Ind bond followed by β-H elimination to give the corresponding vinyl indene, 1,1- or 1,3-(CH$_2$=CH–Ind–CH$_2$CH$_2$NMe$_2$). The involvement of such mechanism has been supported by the results of studies carried out on the analogous complex (1-*i*-Pr-Ind)Ni(PPh$_3$)OTf [13]. In contrast, GC–MS analysis of the reaction mixtures using complex **2** as catalyst failed to detect the postulated vinyl indene intermediate in our studies (reaction of **2** plus MAO and ethylene (1 atm)); as a result, the validity of

the above proposed mechanism in the present system cannot be confirmed.

3. Conclusion

The combination of the neutral nickel compound (**1**) and MAO can convert ethylene to butenes and linear PE. The performance of the catalysts and the characteristics of the resulting polymers were dependent upon the reaction parameters. It was observed that polar solvents favor the dimerization of ethylene versus its polymerization. On the other hand, activation of the cationic complex **2** by MAO or AlMe$_3$ leads to a system which only dimerizes ethylene with high activity. This result implies that a promising system for tandem production of linear low-density polyethylene (LLDPE) could be developed using a mixture of complex **2** and a selected catalyst for α-olefin polymerization [14].

4. Experimental section

4.1. General Comments

All manipulations, except for the gel permeation chromatography (GPC), were performed under an inert atmosphere of N$_2$ or argon using standard Schlenk techniques and a dry box. The polymerization experiments were carried out in oxygen free solvents (dried using 3 Å molecular sieves). AlMe$_3$ (2 M in toluene, Aldrich) and MAO (10 wt.% in toluene, Aldrich) were used as received. Solid MAO, obtained by evaporating the toluene solution to dryness, was used in the NMR experiments. CP grade ethylene and ultra high purity nitrogen (Praxair) were purified by passing through 3 Å molecular sieves and de-oxygenation catalyst beds. Syntheses of (η^3:η^0-Ind(CH$_2$)$_2$NMe$_2$)Ni(PPh$_3$)Cl, **1**, and [(η^3:η^1-Ind(CH$_2$)$_2$NMe$_2$)Ni(PPh$_3$)][BPh$_4$], **2**, have been reported previously [8].

4.2. Polymerization of ethylene

Ethylene polymerization was done using a 500 ml autoclave engineering stainless steel reactor. The temperature was controlled within ±0.5 °C of the set point

by heating an electrical jacket and circulation of cooling fluid through an internal coil. A four-blade impeller rotating at 800 rpm was used for stirring. Prior to each reaction, the reactor was heated to 140 °C and purged three times with nitrogen (10 bar), then placed under vacuum for 30 min, and purged again with nitrogen three more times. Using transfer needles, 295 ml of solvent and the co-catalyst were transferred in the reactor under a nitrogen flux. The stirring was turned on, and the reactor was stabilized at the set point temperature and fed with ethylene. The ethylene flux was monitored using a mass flow sensor (Brooks 5860E) until diluent saturation was reached. When the set-point temperature and ethylene saturation were attained, 5 ml of a solution containing $(2–10) \times 10^{-6}$ mol of complex **1** or **2** was transferred into the reactor using a catalyst injection bomb. After the desired reaction time had expired, 25 ml of ethanol was pumped inside the reactor to quench the polymerization, and then the reactor was vented. The liquid was poured onto 500 ml of ethanol and kept there for 24 h to ensure complete precipitation. The polymer was filtered, washed twice with ethanol, and dried under vacuum at 50 °C. The results are presented as shown in Tables 1 and 2.

4.3. Polymer characterization

The molecular weights (M_w) were determined by GPC using a Waters 150CV system equipped with three columns, differential viscometer, and refractive index detectors. The analyses were undertaken using 1,2,4-trichlorobenzene as solvent (with 0.5 g/l of Irganox 10/10 as antioxidant), at 140 °C, and M_w calculated using a universal calibration curve built with polystyrene standards. The results are reported as shown in Tables 1 and 2.

The polymers formed in our studies were shown to be linear PE with a small number of ethyl branches on the basis of ^{13}C {^{1}H} NMR spectroscopy (Bruker Avance 500 spectrometer, 125.75 MHz); the spectra recorded at 120 °C in C$_2$Cl$_4$D$_2$. For example, the ^{13}C {^{1}H} NMR spectrum of the PE obtained from run 14 shows the following signals (δ (integration, attribution [15,16])): 39.70 (1.0, brB$_2$), 34.07 (1.78, $^\alpha$B$_2$), 30.48 (2.71, $^\gamma$B$_2$), 30.00 (53.68, $^\delta$B$_2$), 27.32 (1.82, $^\beta$B$_2$), 26.74 (0.91, ^{2}B$_2$), 11.20 (1.20, ^{1}B$_2$) (Fig. 4). The branching is presumably due to
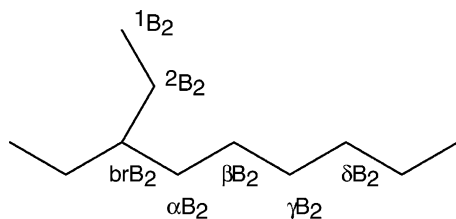
Fig. 4.

the co-polymerization of ethylene and the 1-butene formed in situ.

4.4. Reactivities of **1** with MeLi

Compound **1** (13.0 mg, 0.024 mmol) and MeLi (0.038 ml of a 1.5 M solution in Et$_2$O, 0.029 mmol, 2.4 equivalent) were mixed in C$_6$D$_6$. The ^{31}P {^{1}H} spectrum was recorded 15 min later, showing only one phosphorus-containing species (47.8 ppm) characteristic of (η^3:η^0-Ind(CH$_2$)$_2$NMe$_2$)Ni(PPh$_3$)Me. The ^{1}H NMR spectrum confirms the formation of this species with the characteristic doublet at −0.67 ppm ($^3J_{\text{P-H}}$ = 5.5 Hz) due to the Ni–Me moiety [9].

4.5. Reactivities of **1** with MAO

Compound **1** (20.1 mg, 0.037 mmol) and MAO (4.3 mg, 0.074 mmol assuming a M_w of 58) were mixed in C$_6$D$_6$. After 30 min, ^{31}P {^{1}H} and ^{1}H NMR

spectra were recorded on a Bruker AMXR400 spectrometer. The same procedure was repeated using 7, 14, 20, 30 and 100 equivalents of MAO. The resulting species were identified by their chemical shifts where possible (^{31}P {^{1}H}): 30.7 ppm (**1**), 47.8 ppm (η^3:η^0-Ind(CH$_2$)$_2$NMe$_2$)Ni(PPh$_3$)Me, 28.6 ppm (**2**), unidentified species: 46.1, 44.7, 41.0, 36.9, 30.4, 27.5 ppm) and the ratios calculated from the integrations. The results are presented as shown in Scheme 1 and Fig. 2.

4.6. Reactivities of **1** with AlMe$_3$

Compound **1** (13.0 mg, 0.024 mmol) and AlMe$_3$ (0.12 ml of a 2 M solution in hexanes, 0.24 mmol, 10 equivalent) were mixed in C$_6$D$_6$. The ^{31}P {^{1}H} spectrum was recorded after 15 min, showing two phosphorus-containing species (47.2 and 47.0 ppm) characteristic of new Ni–Me complexes: (η^3:η^0-Ind(CH$_2$)$_2$NMe$_2$)Ni(PPh$_3$)Me and (η^3:η^0-Ind-(CH$_2$)$_2$NMe$_2$AlMe$_3$)Ni(PPh$_3$)Me.

4.7. Reactivities of **2** with MAO

Compound **1** (9.5 mg, 0.011 mmol) and MAO (67 mg, 1.1 mmol assuming a M_w of 58, 100 equivalents) were mixed in CDCl$_3$. The ^{31}P {^{1}H} and ^{1}H NMR spectra were recorded 30 min later. Only one phosphorus-containing species was observed at 28.8 ppm.
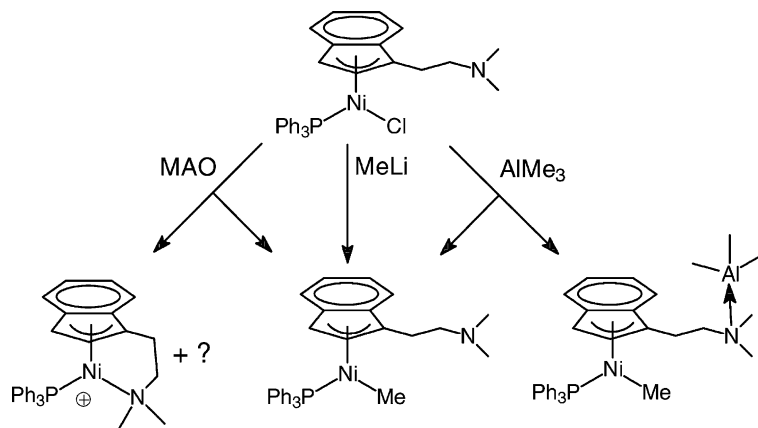
Scheme 1.

4.8. Reactivities of **2** with MAO in the presence of ethylene (10 psi)

Compound **1** (12.0 mg, 0.0145 mmol) and MAO (84 mg, 1.45 mmol assuming a M_w of 58, 100 equivalent) were mixed in $CDCl_3$ and the solution exposed to 10 psi of ethylene for a period of 10 min. The ^{31}P $\{^1H\}$, ^1H NMR and ^{13}C $\{^1H\}$ spectra were recorded on a Bruker AMXR400 spectrometer. One major phosphorus-containing species is observed at 28.8 ppm, whereas, traces of other phosphorus-containing species are observed at 37.9, 36.1, 26.7 and 24.0 ppm. The major products obtained were butenes (^{13}C $\{^1H\}$): Z-butene (12.5 and 124.7 ppm) and E-butene (18.0 and 126.0 ppm) in a 1:2 ratio [17].[5]

Acknowledgements

References

[1] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169 (references therein).

[2] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.

[3] L.K. Johnson, (DuPont) Int. Patent WO 96/23010 (1996).

[4] T.R. Younkin, E.F. Connor, J.L. Henderson, S.K. Friedrich, R.H. Grubbs, D.A. Bansleben, Science 287 (2000) 460 (references therein).

[5] M.-A. Dubois, R. Wang, D. Zargarian, J. Tian, R. Vollmerhaus, Z. Li, S. Collins, Organometallics 20 (2001) 663.

[6] R. Vollmerhaus, F. Bélanger-Gariépy, D. Zargarian, Organometallics 16 (1997) 4762.

[7] L.F. Groux, D. Zargarian, Organometallics 20 (2001) 3811.

[8] L.F. Groux, F. Bélanger-Gariépy, D. Zargarian, R. Vollmerhaus, Organometallics 19 (2000) 1507.

[9] T.A. Huber, M. Bayrakadarian, S. Dion, I. Dubuc, F. Bélanger-Gariépy, D. Zargarian, Organometallics 16 (1997) 5811.

[10] A.R. Barron, Organometallics 14 (1995) 3581.

[11] W. Keim, Ann. N. Y. Acad. Sci. 415 (1983) 191.

[12] A.M. Al-Jarallah, J.A. Anabtawi, M.A.B. Siddiqui, A.M. Aitani, A.W. Al-Saâd-Doun, Catal. Today 14 (1992) 1.

[13] R. Wang, L.F. Groux, D. Zargarian, Organometallics, 2002, in press.

[14] Z.J.A. Komon, G.C. Bazan, Macromol. Rapid Com. 22 (2001) 467.

[15] W. Liu, D.G. Ray III, P.L. Rinaldi, Macromolecules 32 (1999) 3817.

[16] G.B. Galland, R.F. de Souza, R.S. Mauler, F.F. Nunes, Macromolecules 32 (1999) 1620.

[17] R.M. Silverstein, G.C. Basseler, T.C. Morill, Spectrometric Identification of Organic Compounds, 4th ed., Wiley, New York, 1981, p. 263.

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[5] The observation in the polymer of exclusively ethyl branches implies a 1-butene/ethylene co-polymerization. On the other hand, complexes such as (1-*i*-Pr-Ind)(PPh₃)NiOTf, which is a precursor to the cation [(1-*i*-Pr-Ind)(PPh₃)Ni]⁺, isomerize 1-hexene to Z- and E-2-hexene [13]. Therefore, it is reasonable to assume that the initial product of the dimerization reaction is 1-butene, some of which is co-polymerized to give the polymer obtained the unreacted 1-butene is then isomerized to Z- and E-2-butene.