Facile Preparation and Activation of High-Productivity Single-Site Nickel Catalysts for Highly Linear Polyethylene

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

A easy-to-prepare series of nickel complexes are reported, which, upon activation with near-stoichiometric alkylating agents, polymerize ethylene with turnover number (TON) of over 10^5, which brings the catalyst into the range of commercial single-site catalysts based on early transition metals. However, in contrast to the usual metallocenes, the catalyst shows the same activity in coordinating solvents such as THF and dioxane as it shows in toluene. Moreover, the polymer produced is highly linear, which, together with the long catalyst lifetime, suggests that the combination of the nickel catalyst and a *Lewis* acid suppresses formation of nickel hydrides.

Introduction. – Polymerization of ethylene and other olefins with transition-metal catalysts is a process of considerable academic as well as industrial interest¹). The original *Ziegler–Natta* catalyst systems – heterogeneous catalysts activated *in situ* – have been continually improved, leading to highly active systems that produce nearly 100 million tons/year of polyolefins. Originally conceived as homogeneous models for the heterogeneous catalysts, single-site catalysts (SSC), principally metallocenes, have evolved into commercially important catalysts for high-performance polymers in which the fine degree of molecular-level control afforded by the structurally well-defined organometallic complexes can be used to produce superior products, *e.g.*, stereoregular polymers. Nevertheless, the metallocene and related catalysts of the current generation of SSCs suffer from several disadvantages. First, the activated catalysts are exceedingly sensitive to poisoning by impurities that contain coordinating heteroatoms. Second, the metallocenes themselves are expensive compounds, being prepared in a multistep process. Lastly, the activation of metallocenes is typically done with methylalumoxane (MAO) – partially hydrolyzed $AlMe_3$ – which plays a triple role as sacrificial drying agent, alkylating reagent, and *Lewis* acid. Molar excesses of MAO over metallocene between 100 and 1000 are normal, which becomes a substantial cost factor [2] despite the low unit cost of MAO. An ideal alternative would be a SSC based on an inexpensive late transition metal that would show greater tolerance for heteroatoms, removing the need for MAO as a sacrificial drying agent. A neutral, as opposed to cationic, complex would not need MAO in its role as *Lewis* acid. Alkylation by inexpensive stoichiometric metal-alkyls would be desirable. Lastly, the well-established coordina-

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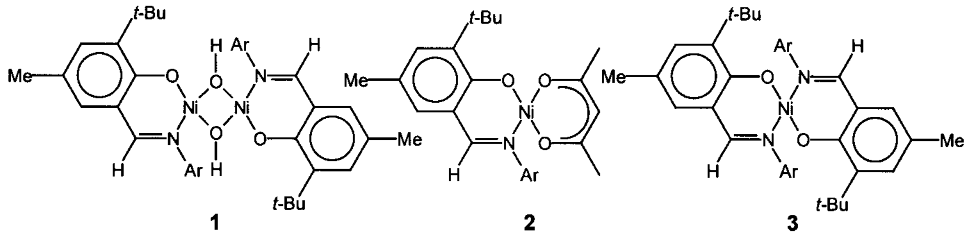
¹) A complete overview of *Ziegler–Natta* polymerization can be found in [1].

tion chemistry of late transition metals should simplify the synthesis of the catalyst. The use of neutral, late transition metal complexes as polyolefin catalysts has been limited, though, by the decidedly modest turnover number (TON) of known systems, *i.e.*, TON of *ca.* 10^3 as opposed to the $10^5 - 10^6$ for Ti and Zr-based catalysts. We report the synthesis and polymerization reactions of a family of simple Ni^{II} coordination complexes, **1**–**3**, containing at least one salicylaldimine ligand.

Ar = 2,6-diisopropylphenyl



1 **2** **3**

These catalysts are easily prepared from readily available Ni complexes and salts, and can be activated by near-stoichiometric amounts of almost any metal-alkyl or hydride to form a SSC that tolerates heteroatoms in that it shows the same high activity for ethylene polymerization in THF or dioxane solution as it does in toluene. Moreover, in contrast to previous systems in the literature, at least one member of the new family is chemically robust. It shows high stability and long catalyst lifetime after activation, leading to outstanding catalyst productivity, with turnover numbers (TON) on the order of 10^5 in the production of highly linear polyethylene.

Experimental. – All manipulations were done under Ar with either standard *Schlenk* techniques or in an *MBraun 'Unilab'* glove box unless otherwise specified. Analysis by ^{1}H-NMR was performed with a *Varian Mercury 300* spectrometer. Electrospray ionization mass spectrometry (ESI-MS) was performed with a *Finnigan MAT LCQ Deca* ion-trap mass spectrometer with a dynamic nanospray source. Infrared (IR) spectra were recorded with a *Perkin-Elmer 1600 Series FTIR*. Toluene, THF, and 1,4-dioxane solvents were purified by distillation from alkali metal. Ethylene, *N35* (> 99.95%) grade, was purchased from *Air Liquide* and used as received. MeLi (*Fluka*, 1.6M in Et_2O), and BuLi (*Fluka*, 2.7M in heptane) were titrated prior to use to establish their true concentration. Methylalumoxane (MAO, *Witco*) was used as received. The titer of MAO, in terms of methide equivalents, varied from batch-to-batch and according to manufacturer, so the MAO results should be considered to be less quantitatively accurate. $BH_3 \cdot THF$ complex was purchased from *Fluka* (1M in THF) and used as received.

Polymerizations were performed in two different reactors. The 'small' reactor was constructed from thick-walled, 25-mm OD *Pyrex* pressure tubes (*Ace Glass Inc.*) fitted with a *Bourdon*-tube manometer on a stainless-steel head fitted with high-pressure valves (*Whitey SS-43MA-S4*, specified for up to 200 bar). The soln. was magnetically stirred with or without external temp. control. The stirring requires some comment; the soln. in the reactor tube was stirred with a 50-mm long, vertically-oriented, magnetic stir-bar spinning at 1500 rpm so that the soln. formed a thin, rapidly moving annulus extending up the walls of the reactor tube. This measure was needed to ensure rapid transfer of ethylene from the gas-phase into soln. When stirring was inefficient, mass transport, rather than chemical kinetics, limited the rate of the overall reaction. The rate of polymerization was then quantified either by the amount of polyethylene produced at the end of the reaction, or by the (near) isobaric rate of ethylene consumption. For the former measurement, the polymerization reaction was quenched by release of the ethylene overpressure and pouring of the soln. into a large excess (typically 10 ×) of acidified methanol to precipitate polyethylene. The solid material was collected by filtration on a glass frit, and then dried under vacuum to constant weight. Measurement of the polymerization rate by the (near) isobaric rate of ethylene consumption was done by periodic isolation of the reactor tube from its constant-pressure ethylene source and measurement of the time needed for the pressure to drop by a fixed amount, usually 0.5 bar or less. In cases of pressure changes, or at the onset of a reaction, measurements were started only after 5 min. to exclude artifactual pressure changes due to re-equilibration between the gas- and solution-phase. The integrity of the apparatus was tested up to 6 bar and found to be tight – negligible pressure drop – for periods up to 48 h, so it can be assumed that the measured pressure drop is due to polymerization. The duration of polymerization was limited by either the catalyst lifetime or, more usually in these experiments, the increase in viscosity of the soln. For the more active systems under the conditions used in this series of experiments, the soln. became viscous enough to essentially stop reaction after *ca.* 2 h.

Polymerizations in larger reaction volumes were conducted in a custom-made stainless-steel autoclave (*DC2*, *NWA GmbH*), designated further is the 'large' reactor. The mechanically-stirred inner volume of 100 ml was temp.-controlled by means of a digital thermometer connected to an electrical heater. Injection of reagents and withdrawal of samples could be done under pressure – the entire autoclave was tested up to 300-bar total pressure. The larger-scale polymerizations were conducted with the similar absolute amounts of catalyst and activator as in the small reactors, but with solvent volumes between 50 and 100 ml. With the reactor connected to a constant pressure ethylene source, ethylene consumption could be monitored by means of pressure drop upon brief isolation of the reactor from the source. The gauge, however, was not suitable for quantitative work at an accuracy comparable to that in the small reactors, but isobaric ethylene consumption could nevertheless be used as an indicator that the catalyst was still producing polymer.

Synthesis of **1** *from [Ni(cod)$_2$].* A suspension of 1.21 g (4.41 mmol) [Ni(cod)$_2$] in 150 ml of Et_2O was cooled to $-116°$ and 380 µl (534 mg, 1.0 equiv.) of allyl bromide were added with stirring. The mixture was allowed to warm to r.t. and stirred until all [Ni(cod)$_2$] had dissolved. The resulting dark red soln. was cooled to $-5°$ and 1 equiv. (1.65 g) of the Na salt of the salicylaldimine ligand, prepared by condensation of the salicylaldehyde and 2,6-diisopropylaniline, both from *Aldrich* and used as received, was added in 150 ml of THF. The mixture was allowed to reach r.t. and stirred for 18 h. After the soln. was filtered, the solvent was removed under reduced pressure. Recrystallization of the brown residue from EtOH yielded between 0.8 – 1.1 g (42 – 60%) of **1** as brown crystals. X-Ray diffraction by single crystals of **1** yielded a structure that is described in the *Supplementary Material* (available upon request). IR (KBr): 3603*m*, 2959*m*, 1618*s*, 1597*s*, 1536*s*, 1457*m*, 1430*s*, 1384*m*, 1352*m*, 1328*s*, 1236*m*, 1204*m*, 1166*s*, 937*w*, 870*s*, 544*m*. ^{1}H-NMR ($CDCl_3$): 7.12 (*dd*, $^1J = {}^2J = 7.3$, 2 H); 7.02 (*d*, $J = 7.3$, 4 H); 6.84 (*d*, $J = 11.6$, 4 H); 6.55 (*s*, 2 H); 4.52 (*sept.*, $J = 6.7$, 2 H); 2.1 (*s*, 6 H); 1.96 (*d*, $J = 6.7$, 12 H); 1.17 (*d*, $J = 6.7$, 12 H); 0.78 (*s*, 18 H); -8.3 (*s*, 2 H). ESI-MS (THF/CH_3CN, $c = 0.1$ mg/ml, spray voltage 2.5 kV, 150 µl/h, capillary voltage 10 V, tube lens offset 15 V): 851 – 857 (100, $[M + H]^+$, cluster of Ni isotopes), 833 (65, $[M + H - 18]^+$), 440 (35), 424 (45), 407 (55), 394 (32), 351 (30).

Synthesis of **1** *from $NiBr_2 \cdot 6\ H_2O$.* A soln. of 219 mg (1.0 mmol) $NiBr_2 \cdot 6\ H_2O$, 351 mg (1 equiv.) of salicylaldimine ligand and 147 µl (150 mg, 1 equiv.) of DBU in 10 ml of toluene was heated to reflux for 4.5 h. After cooling to r.t., the amount of solvent was reduced to 5 ml under reduced pressure and the residue was diluted with 5 ml of pentane. The resulting mixture was filtered and the solvent removed. The brown residue was recrystallized from Me to yield 31 – 123 mg (7.3 – 30%) of **1** as brown crystals, identical to those described above.

Synthesis of **2** *from [Ni(acac)$_2$].* A soln. of 512 mg (2.0 mmol) [Ni(acac)$_2$] and 704 mg (1 equiv.) salicylaldimine ligand in 20 ml of mesitylene was heated to reflux. The resulting excess of acetylacetone was removed by azeotropic distillation with the solvent for 4 h; 10 ml of fresh solvent were added to the mixture two times as the distillation proceeded. The remaining solvent was removed under reduced pressure. The solid residue was dissolved in pentane and filtered through *Celite*. Removal of the solvent and recrystallization from pentane yielded 203 – 355 mg (40 – 70%) of **2** as a brown powder. IR (KBr): 2963*s*, 2870*m*, 1618*m*, 1581*s*, 1523*s*, 1464*s*, 1431*s*, 1382*s*, 1356*m*, 1331*m*, 1164*m*, 777*w*, 764*w*. ^{1}H-NMR ($CDCl_3$): 7.37 – 7.04 (*m*, 5 H); 6.69 (*dd*, $^1J = 2.2$, $^2J = 1.0$, 1 H); 5.17 (*s*, 1 H); 4.32 (*sept.*, $J = 6.8$, 2 H); 2.23 (*s*, 3 H); 1.47 (*d*, $J = 6.8$, 6 H); 1.44 (*s*, 6 H); 1.36 (*s*, 9 H); 1.21 (*d*, $J = 6.8$, 6 H). ESI-MS (EtOH, $c = 0.1$ mg/ml, spray voltage 2.7 kV, 150 µl/h, capillary voltage -20 V, tube lens offset -70 V): 508 (100, $[M + H]^+$, cluster of Ni isotopes), 352 (30), 198 (37).

Synthesis of **3** *from 1,2-Dimethoxyethanenickel(2+) Dibromide.* To a soln. of 1.0 g (2.8 mmol) salicylaldimine ligand in 10 ml of THF, a soln. of 1 equiv of MeLi in Et_2O (1M) was added. After the evolution of gas had ceased, 439 mg (0.5 equiv.) of Ni^{II}-dibromide 1,2-dimethoxyethane (DME) complex dissolved in 10 ml of THF were added, and the resulting mixture was stirred for 18 h. After the solvent was removed under reduced pressure, the brown residue was dissolved in toluene and the soln. was filtered. Removal of the toluene and recrystallization by slow evaporation from pentane yielded 600 mg (56%) of dark brown crystals. IR (KBr): 2962*s*, 1619*m*, 1580*s*, 1534*s*, 1459*m*, 1386*m*, 1362*m*, 1322*m*, 1234*m*, 1206*w*, 1166*s*, 1098*w*, 935*w*, 764*w*. ^{1}H-NMR ($CDCl_3$; due to the paramagnetic properties of the compound, all signals were very broad and no coupling was registered): 54.5 (*s*, 2 H); 43.5 (*s*, 2 H); 24.8 (*s*, 6 H); 22.8 (*s*, 2 H); 20.8 (*s*, 2 H); 12.7 (*s*, 2 H); 9.8 (*s*, 18 H); 9.0 (*s*, 6 H); 5.8 (*s*, 6 H); 2.4 (*s*, 6 H); 1.4 (*s*, 4 H); -1.2 (*s*, 6 H); -6.9 (*s*, 2 H). ESI-MS (THF (abs.), $c = 0.1$ mg/ml, spray voltage 2.5 kV, 150 μl/h, capillary voltage 21 V, tube lens offset -10 V): 759 (100, $[M + H]^+$, cluster of Ni isotopes), 444 (12), 424 (14), 410 (11), 352 (59).

In situ *Preparation and Polymerization by the Catalytic Formulation from* $(CH_3OCH_2CH_2OCH_3)NiCl_2$ (**4**). To a soln. of 20 mg (53.4 μmol) Na salt of the salicylaldimine in 10 ml of THF, 11.7 mg (1 equiv.) Ni^{II} chloride DME complex were added. The resulting soln. was stirred for 20 min at r.t. and 305 ml (1 equiv.) of 0.175M soln. of MeLi in THF were added. After stirring at an ethylene pressure of 4 bar for 30 min, the soln. was worked up as usual. The yield of polyethylene was 1.8 g.

Preparation of Grubbs *Catalyst* **5**. Catalyst **5** was prepared according to the published procedure [3]. Spectroscopic data agreed well with published values.

Results. – Three compounds, representative of a general structural motif, were prepared. The μ-OH bridged complex, **1**, is an uncommon structure for Ni^{II}, although μ-alkoxy-bridged complexes are known. Characterization of **1** by X-ray crystallography on single crystals shows an approximately C_2-symmetric structure (*Fig. 1*). Particularly diagnostic is the chemical shift of the OH H-atom in the ^{1}H-NMR spectrum. The H-atom lies in the shielding region 2,6-diisopropylphenyl group, directly over the ring, giving rise to the very large upfield shift to -8.3 ppm.

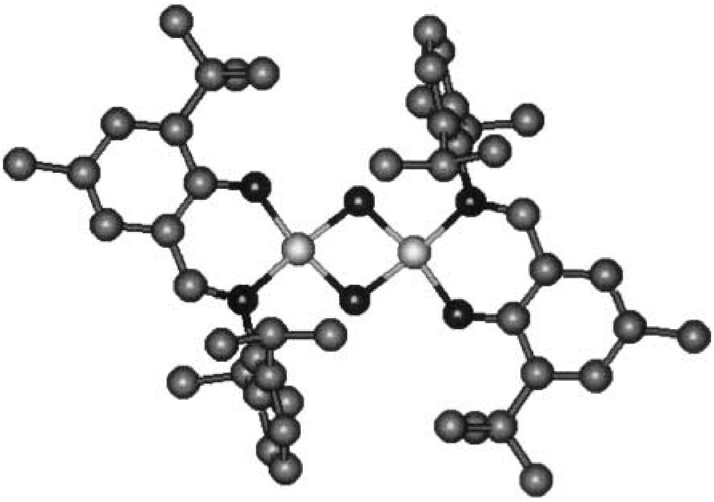
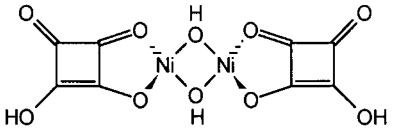


Fig. 1. *X-Ray structure of* **1**, *showing non-H-atoms.* The μ-bridging OH group H-atoms are situated directly above the aromatic ring of the *Schiff* base, leading to the characteristic upfield shift for those H-atoms in the ^{1}H-NMR. A detailed description of the structure is available from the *Cambridge Crystallographic Data Centre* (*CCDC*), deposition No. CCDC-198689.

Interestingly, **1** appears to be an unusually favorable structure, being produced by nearly any synthetic route in which the components, *i.e.*, Ni^{II} and salicylaldimine ligand, are reacted in the presence of traces of H_2O. The structure was assigned by X-ray diffraction of single crystals. Compound **1** is a brown complex that is stable under normal handling conditions in ambient air. It can be stored as a solid in a sealed vessel for months without noticeable change. Associated β-diketonate-alkoxo-Ni^{II} complexes with presumed structures similar to that of **1** have been reported by *Baranwal* and *Mehrotra* [4]. Analogous dinuclear Ni^{II} [5] and Pd^{II} [6] complexes with μ-aryloxy bridging ligands have also been published. Perhaps most relevant are two structures, **6** and **7**, that have been previously reported [7]. The structures were originally assigned on the basis of spectroscopic and magnetic-susceptibility data; **7** has subsequently been crystallographically characterized.



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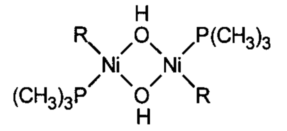

R = alkyl, aryl

7

Both binuclear Ni complexes show the μ-OH groups. The Ni-centers in **6** show tetrahedral coordination. An X-ray structure of **7** shows each Ni to be square planar. More importantly with respect to the structure of **1**, the complexes **6** and **7** indicate that the μ-OH groups are neither so basic that they are cleaved by relatively acidic groups (in **6**), nor so acidic that they themselves protonate off Ni alkyls (in **7**).

Complexes **2** and **3** are related in that they are salicylaldiminato-Ni^{II} complexes in which the remaining two coordination sites are occupied by a bidentate monoanionic ligand. Characterization by ^{1}H-NMR, ESI-MS, and IR support the structural assignments. Complex **2** is formed by treating anhydrous [Ni(acac)$_2$] with 1 equiv. of the salicylaldimine ligand in mesitylene, followed by azeotropic distillation to remove the more-volatile acetylacetone. Similarly, **3** is prepared by combination of the anhydrous $NiBr_2 \cdot DME$ complex with 2 equiv. of the Li salt of the salicylaldimine ligand. Both **2** and **3** are stable in air in the solid state under normal handling conditions. Exposure to traces of H_2O in solution leads to slow conversion of **2** or **3** to **1**, as can be seen by ^{1}H-NMR.

All three complexes can be activated with respect to ethylene polymerization by treating dilute solutions of **1**–**3** in toluene with near-stoichiometric amounts of BuLi, MAO, $BH_3 \cdot THF$, or MeLi in the presence of 1–75 bars of ethylene. Catalyst productivity was found to be broadly similar for all three complexes with all of the activators. As a control experiment, the catalyst productivity, as determined by total polyethylene formed after workup, was compared to the productivity computed by integrating the isobaric rate of ethylene consumption. The resulting graph (*Fig. 2*) shows that the two are linearly correlated, making either measurement a suitable indicator of total productivity.

The experiment validates the utility of the isobaric rate of ethylene consumption as a measure of instantaneous catalyst activity at a given point of the reaction. The last two activators listed above introduce *Lewis* bases that normally poison single-site catalysts – the borane includes 1 equiv. of THF, and MeLi comes as a dilute solution in THF due to its insolubility in hydrocarbon solvents. Neutral Ni^{II} complexes of *Grubbs* and coworkers [3] show broad tolerance for ethers, so the activation of **1**–**3** was attempted in THF or 1,4-dioxane as solvent in the presence of ethylene. Not only did polymerization proceed, but the productivity in the coordinating solvents was hardly different from that in toluene. While one might expect some tolerance for heteroatoms in a late transition metal SSC, insensitivity to strongly coordinating solvents is rare.

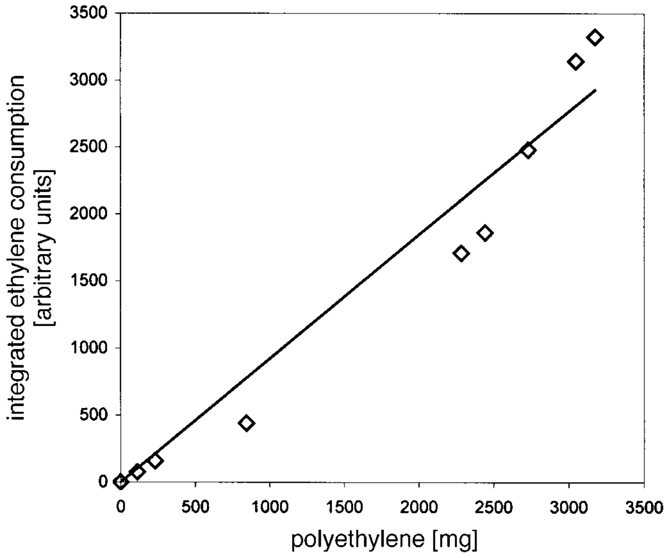

Fig. 2. *Correlation of the integrated isobaric ethylene consumption against isolated polyethylene after workup for polymerizations in the 'small' reactor.* The linear relationship indicates that both measurements may be used to characterize catalyst activity. It also indicates that the ethylene is polymerized rather than oligomerized because the polyethylene yield was measured after removal of all volatile components.

Interestingly, the activity of the catalyst depends strongly on the amount of the alkylating or hydride-transfer agent. In general, the maximum activity occurs for slightly more than 1 equiv. of alkylating agent per nickel (*Fig. 3*).

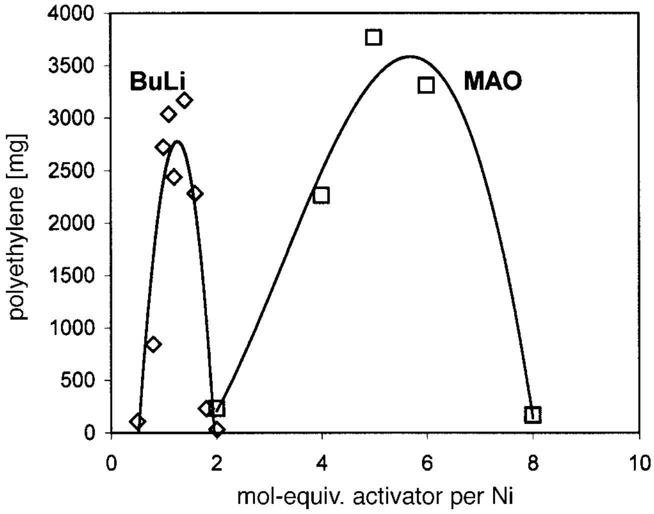

Fig. 3. *Dependence of catalyst productivity on the mol-equiv. per Ni of the activator for the case of BuLi and MAO.* The solid lines represent polynomial fits to the data points. The concentration of BuLi was standardized by titration. MAO was assumed to have its nominal concentration as delivered.

With much more than 1 equiv., the activity rapidly goes to zero, as shown in *Fig. 3*. For MAO, productivity of the catalyst shows a similar maximum, although the curve is shifted to a higher number of equiv. In the case of MAO, it cannot be excluded that all of the Me equiv. are not equally available; nevertheless, the general conclusion that a large excess of alkylating (or hydride transfer) agent deactivates the catalyst is clearly demonstrated. Comparable curves were obtained for all activators and catalysts **2** and **3**. In all cases, near-stoichiometric amounts of activators gave maximum productivity; more than a few equiv. resulted in no activity. One should note that complex **3**, termed 'the 2 : 1 complex' in the study of *Grubbs* and co-workers, was reported to be inactive in either oligomerization or polymerization of ethylene when activated by MAO. Presumably, the customary large molar excess of MAO was employed, which we have confirmed to result in deactivation of the catalyst.

The catalytic formulation produced by activation of **1**, and, to a lesser extent, **2** and **3**, is chemically robust and long-lived. *Fig. 4* shows the isobaric ethylene consumption by activated **1** under 4 bar of ethylene at 25° and 40°, as well as under adiabatic conditions where the reactor temperature was allowed to rise due to the reaction exothermicity. As is clear from the data, the activated catalyst is long-lived in that there is no deactivation process, at least on the timescale of 1 h. The drop in activity that is typically observed in the 'small' reactors (10–20 ml of solvent) comes because the solution becomes too viscous for efficient stirring, slowing and, eventually, preventing

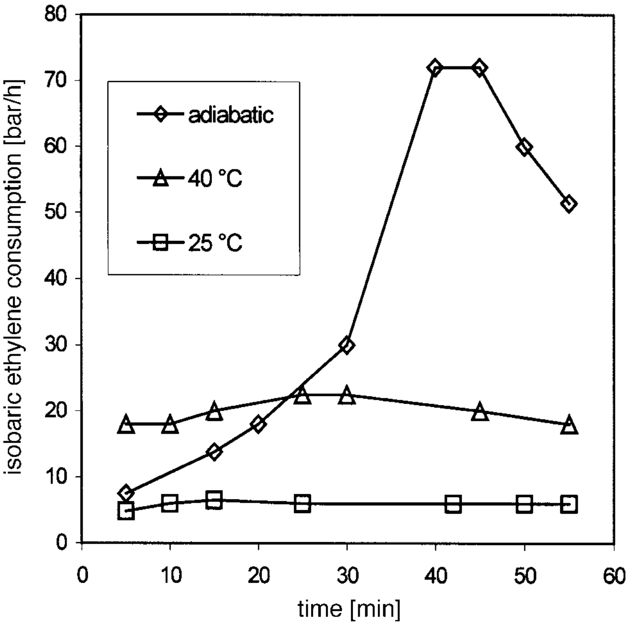

Fig. 4. *Isobaric ethylene consumption for polymerization of ethylene in the 'small' reactor at 25°, 40°, and under adiabatic conditions.* In the latter case, the temperature typically rose from room temperature to over 50°. Standard conditions were 20 mg of catalyst **1** in toluene, activated with 1.2 equiv. (per Ni) BuLi and 4 bar ethylene.

transfer of ethylene from the gas-phase into solution. As further evidence for the chemical stability of the catalyst, we find that the polymerization in the 'small' reactor could be interrupted by replacement of ethylene by CO_2 (three evacuation–refilling–equilibration cycles) for a period of time, typically *ca.* 1 h. Upon replacement of CO_2 with ethylene, polymerization recommenced with no break in the activity of the catalyst as measured by isobaric ethylene consumption. Furthermore, if the ethylene source is closed off from the 'small' reactor so that all ethylene in the reactor is consumed after polymerization has commenced, the resulting solution will continue polymerization upon re-introduction of ethylene after interruptions of up to *ca.* 1 h.

The pressure dependence of the polymerization reaction is easily seen in *Fig. 5*. With the isobaric ethylene consumption instead of final polyethylene yield after workup, the instantaneous activity can be ascertained. An approximately linear dependence of activity on ethylene pressure was observed. The pressure dependence as well as the catalyst lifetime could be further verified by bulk polymerization experiments in the 'large' reactor (50–100 ml of solvent). The *Table* summarizes catalyst productivities in both reactors under a variety of conditions. *Entries 10–15* were performed with the 'large' reactor. The increased productivity in *Entry 10* appeared to be consistent with the 'small' reactor results when the higher temperature and ethylene pressure were considered. With successive decreases in the amount of catalyst, *e.g.*, *Entries 11–13*, it becomes apparent that the TON of 22,000 represents the chemically-limited productivity for **1** with MeLi activation even as ethylene pressure is further increased. In particular, ethylene consumption ceased after 2 h in *Entry 12* without solidification of the reaction solution (which happened, *e.g.*, in *Entry 10*), indicating that catalyst deactivation had finally become limiting.

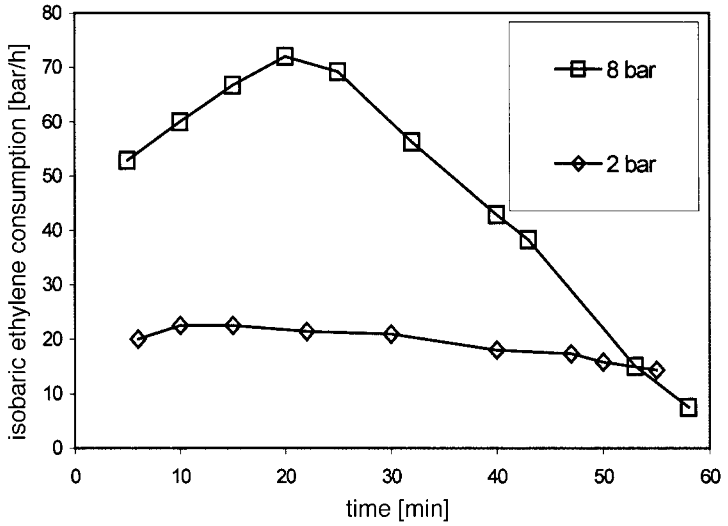

Fig. 5. *Pressure dependence of the isobaric ethylene consumption rate at two pressures under reaction conditions as in* Fig. 4 *for a polymerization at room temperature*

Table. *Polyethylene (PE) Production in the 'Small' Reactor* (*Entries 1–9*) and the *'Large' Reactor* (*Entries 10–15*) *by Catalysts* **1**–**4**. The amount of activator is given in mol-equiv. per Ni. Turnover number (TON) is defined as mol ethylene converted to PE divided by mol nickel. Note that catalyst **1** contains 2 mol Ni per mol catalyst.

Entry	Catalyst ([mg])	Activator	Solvent ([ml])	*P* [bar]	*T* [°]	*t* [h]	PE [g]	TON
1	**1** (20)	BuLi (1.2 equiv.)	toluene (15)	4	25	2	2.4	1,900
2	**1** (10)	MAO (6.0 equiv.)	toluene (15)	4	40	1	3.3	5,100
3	**2** (26)	BuLi (1.9 equiv.)	toluene (20)	3.5	25	1.5	4.5	3,100
4	**3** (20)	MeLi (1.0 equiv.)	THF (12)	4	25	4	2.3	3,200
5	**1** (10)	MeLi (1.2 equiv.)	THF (10)	4	25	0.5	1.0	1,600
6	**1** (10)	MeLi (1.2 equiv.)	dioxane (10)	4	25	0.5	1.0	1,600
7	**2** (20)	MeLi (1.0 equiv.)	dioxane (10)	4	25	2	3.6	3,200
8	**1** (15)	BH_3 (1.0 equiv.)	THF (10)	4	25	1.5	2.2	2,300
9	**4** (12)	MeLi (1.0 equiv.)	THF (10)	4	25	0.5	1.8	1,200
10	**1** (20)	MeLi (1.2 equiv.)	toluene (70)	75	55	2.5	28	22,000
11	**1** (10)	MeLi (1.2 equiv.)	toluene (50)	40	40	2	14	22,000
12	**1** (5)	MeLi (1.2 equiv.)	toluene (50)	40	40	2	7	22,000
13	**1** (5)	MeLi (1.2 equiv.)	toluene (50)	75	50	2.5	7	22,000
14	**1** (5)	MAO (5 equiv.)	toluene (56)	75	40	overnight	20	63,000
15	**1** (2.3)	MAO (5 equiv.)	toluene (45)	75	40	overnight	16	104,000

The final lines, *Entries 14* and *15*, show the same experiment, but with MAO instead of MeLi as activator. MAO had, in 'small' reactor trials, generally given higher productivity than MeLi. The reactor was left overnight in these cases because the polymerization continued to run for several hours. For both *Entries 14* and *15*, the increased TON of 63,000 or 104,000, respectively, represent lower bounds because the reactor was completely filled with a solid mass in each run, blocking the ethylene inlet. It should be noted that the polymerizations under higher pressures occur in a regime where ethylene is supercritical²), which affects the TON in that the viscosity of the medium is reduced and diffusion is enhanced³).

The properties of the related catalyst **5**, from *Grubbs* and co-workers, have been reported in several publications [3] and a patent [10]. Similar systems **8**, from *Mecking* and co-workers [11], have also been reported. These catalysts show TON values that range from a few hundred to a few thousand for **5**, and similar levels for **8**. The particular *Grubbs* catalyst with almost the same salicylaldimine ligand as **1** shows a TON of 1600. Although **1**–**3** resemble **5** and **8**, the TON for **1** in toluene, activated with MAO, exceeds 10^5. It is also clear that the TON can be further improved by alterations in either the catalyst structure or process design; the filling of the reactor limited TON in *Entries 14* and *15*. The very high productivity for **1** begins to reach the level for the current generation of high-activity *Ziegler*–*Natta* catalysts in which the TON values of *ca.* 10^5–10^6 mean that catalyst residues are low enough to simply leave in the polymer. The substantially higher TON for **1**–**3** derives not from higher turnover frequency (TOF), but rather from a significantly longer catalyst lifetime with respect to deactivation.

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²) The critical temperature and pressure for ethylene is 9° and 50 bar, respectively [8]. Polymerization throughout the reactor at higher temperature and pressure occurs because the supercritical ethylene fills the entire volume of the reactor. However, as in the case of polymerization in toluene solution, the reaction ceases, when the polymer concentration becomes so high as to inhibit transport.

³) For a review of polymerization in supercritical media, see [9].

Given the structural similarity between **1**–**3** and **5**, the increased lifetime and the concomitantly increased TON must be due to the presence or absence of some other component. As a control experiment, **5** was prepared and tested as shown in *Fig. 6*. When activated by 1.5 equiv [Ni(cod)$_2$] in THF, **5** began to consume ethylene after an induction period of 12 min. In this particular example, ethylene consumption continued for *ca.* 25 min, and then ceased. The same amount of **5**, activated identically, but with the addition of 10 equiv. of $LiClO_4$, consumed ethylene at a significantly higher rate, but, more importantly, continued to consume ethylene even after 1 h when viscosity problems began, as usual, to impact catalyst productivity. While full quantitative characterization is not yet complete, one can see qualitatively that the activated species from **1** is longer-lived than those from **2** or **3**, and that the lifetime is generally longer in toluene solvent than in THF or dioxane. While there may be other factors that may also be important, the activated forms of **1**–**3** likely owe their increased lifetimes to the presence of *Lewis* acidic metal cations in low molar excess.

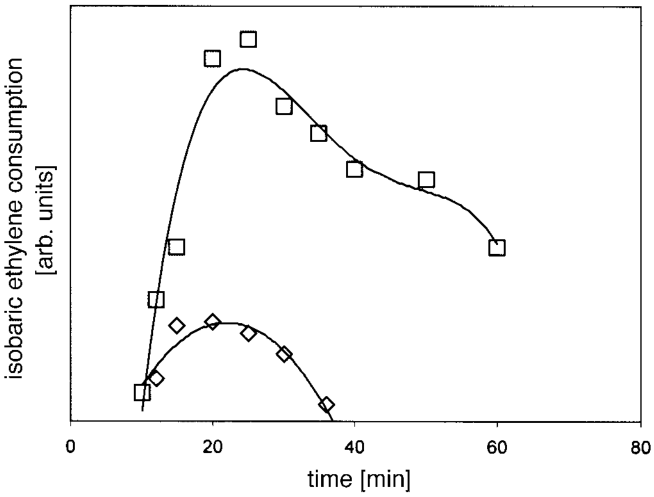

Fig. 6. *Isobaric ethylene consumption by a solution of 10 mg* (13.3 μmol) **5** *and 6 mg* (1.5 equiv.) *[Ni(cod)$_2$] in 10 ml of THF at an ethylene pressure of 4 bar, with* (□) *and without* (◇) *the addition of 10 equiv $LiClO_4$*. Addition of [Ni(cod)$_2$] as a phosphine scavenger defines the zero in time.

The polyethylene produced in *Entries 13* and *14* was characterized by GPC and viscometry[4]). For the two samples, the molecular weight and polydispersity, M_w and M_w/M_n, were 14,000 and 1.91, and 24,000 and 1.93, respectively. The catalyst of *Grubbs* with almost the same ligand gave 11,400 and 1.8 for M_w and M_w/M_n. Interestingly, while the catalyst of *Grubbs* produced polyethylene with 55 branches per 1000 C-atoms, the polyethylene from *Entries 13* and *14* was completely linear with no detectable branching.

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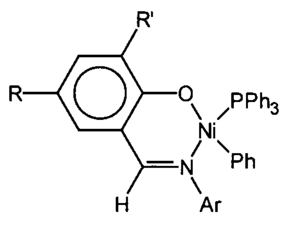
[4]) Polymer characterization was done at *Bayer AG*, Leverkusen, with a *Waters 150C GPC* (*o*-dichlorobenzene, 140°) by differential refractometric and viscometric detection. Branching was determined by comparison of *Mark-Houwink* parameters to suitable reference samples.

Given that **1**–**3** are simple coordination compounds that are subsequently activated with near-stoichiometric alkylating or hydride-transfer agents, one may question the necessity of prior isolation of the catalysts at all. *Entry 9* in the *Table* shows the results for the *in situ* preparation of a catalytic formulation by reaction of the DME complex of $NiCl_2$, **4**, with the Na salt of the salicylaldimine in THF, followed directly by MeLi activation with no isolation or purification of intermediates. The productivity of the catalyst is within a factor of 2–3 of that for the isolated and purified catalysts under comparable conditions. The successful *in situ* catalyst preparation and activation may present interesting practical possibilities, but also opens the way to high-throughput screening of pooled catalyst libraries [12].

Discussion. – Late-transition-metal SSCs have recently become the focus of intense investigation due to the possibility that one may be able to circumvent some of the diadvantages of the early-transition-metal catalysts, notably, metallocenes. The return, especially to Ni, is ironic, given that the coordination oligomerization and polymerization of ethylene was originally discovered a half-century ago with adventitious Ni as the catalytic metal [13]. Several of the first- and second-row late transition metals, as well as a large variety of ligands, have now been shown to yield moderate-to-very good catalysts for olefin polymerization[5]).

Importantly, *Brookhart* and co-workers [15][16] have reported extensive mechanistic studies of the Ni^{II} diimine catalysts, **9,** in which it was established that the olefin π-complex, directly observed by low-temperature NMR, is the resting state in the catalytic cycle, *i.e.*, the turnover-limiting step is insertion of the olefin into the metal–alkyl bond. Similar catalysts have been reported by *Gibson* and co-workers [17]. Also, *Grubbs* and co-workers [3][10], building on SHOP-like [18] systems from *Cavell* and co-workers [19], *Keim* and co-workers [20] and *Ostoja-Starzewski* and *Witte* [21], have shown that neutral Ni^{II} complexes can effectively polymerize ethylene with substantially improved tolerance for heteroatoms. A thorough review of Ni^{II} systems has been published [22]. The tolerance of Ni^{II} systems is sufficient for their use in toluene/H_2O emulsions, as has been shown by *Mecking* and co-workers [11], for the production of polyolefin latexes.



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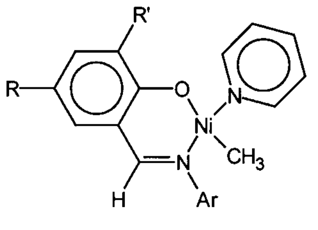

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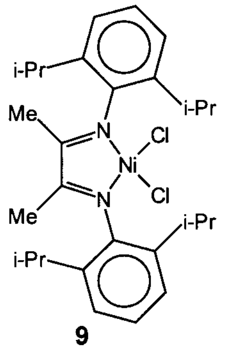

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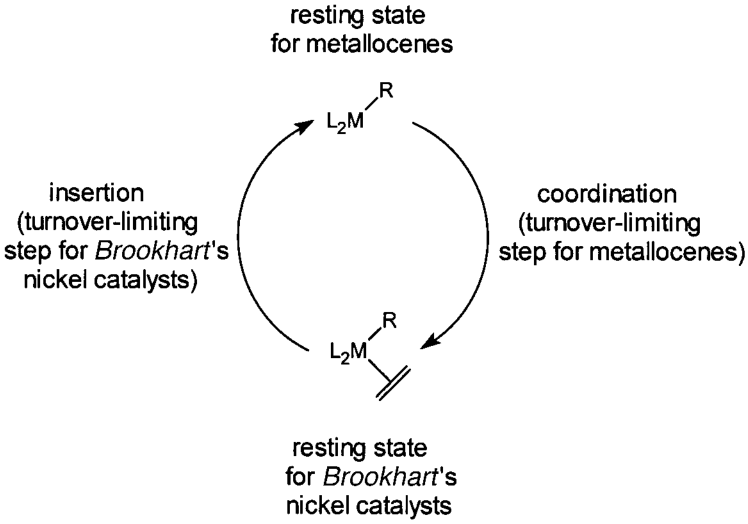
[5]) A review of new catalysts and ligands is found in [14].

Looking at the minimum mechanism for ethylene polymerization according to the *Cossee–Arlman* model [23], one sees that, aside from chain transfer, there are two fundamental steps in the catalytic cycle: ethylene π-coordination and insertion (*Scheme 1*). If insertion is turnover-limiting, as is observed for the *Brookhart* catalysts, then the polymerization rate is necessarily zero-order in ethylene, as is indeed observed for those systems. Tolerance for coordinating solvent is expected, though, because there is no competition for a coordination site by solvent at the turnover-limiting transition state. On the other hand, the turnover-limiting step in metallocene-catalyzed polymerization of ethylene is π-coordination of the incoming olefin; the resting state of the catalyst is computed to be the metal alkyl with the fourth coordination site on the metal filled by an agostic C–H bond [24]. Accordingly, the kinetics of polymerization are first-order in ethylene, which is desirable in practice, but any strongly coordinating solvent can occupy the fourth site and inhibit turnover.

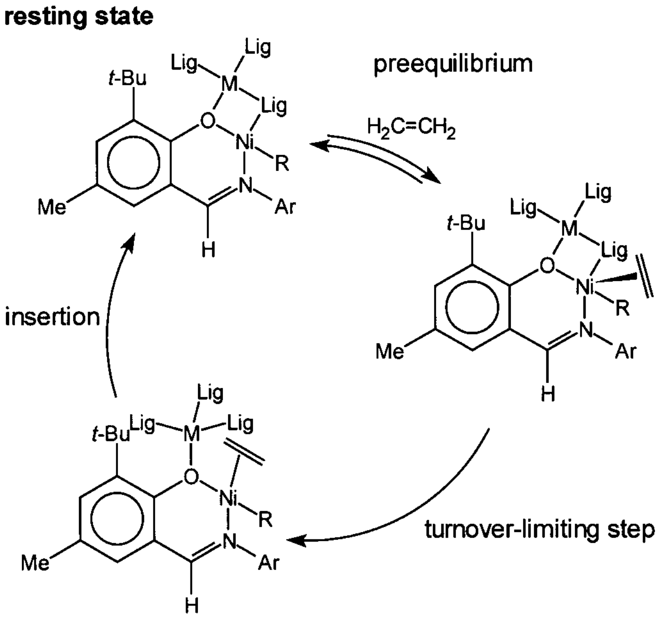
Scheme 1



One expects, therefore, that two desirable features, first-order kinetics and tolerance for heteroatoms, should be mutually exclusive. Given that complexes **1**–**3** show both first-order kinetics with respect to ethylene and tolerance for heteroatoms, the mechanistic picture must necessarily be more complicated than that shown in *Scheme 1*.

Complex **5** of *Grubbs* and co-workers [3], and several other similar complexes [11][25], are the closest analogs to **1**–**3**. All of the complexes are neutral in their active form, and are based on Ni^{II}; **1**–**3** and **5** have moreover the same salicylaldimine ligand. Nevertheless, there are some differences in chemical behavior, which shed light on the mechanism by which **1**–**3** operate. The increase in both activity and lifetime, when $LiClO_4$ is added to a polymerization catalyzed by **5**, suggests that the complexation of the *Lewis*-acidic alkali-metal cation, presumably to two O-atoms of OH or alkoxy moieties may be largely responsible for the significant improvement in catalyst performance. This observation supports a proposed structure for the resting state in the catalytic cycle for activated forms of **1**–**3**, shown in *Scheme 2* for which the additional ligands (Lig) on the second metal (M = Li, Al, B) are a (salicylaldiminato)Ni moiety, acetylacetonato, or salicylaminato ligands, or solvent, or a combination thereof.

Scheme 2



In contrast to the tetrahedral d^0 metallocenes, the resting state in *Scheme 2* is a square planar d^8 complex, which most likely performs ligand exchange predominantly according to an associative mechanism [26] involving coordination of the incoming ethylene to form a five-coordinate intermediate, followed by departure of one of the original four ligands. The pre-equilibrium in the proposed catalytic cycle – the first step in the associative ligand exchange – yields overall first-order kinetics with respect to ethylene, and the assignment of the turnover-limiting step to the departure of an oxy ligand is consistent with the acceleration of turnover by the presence of Li or oxophilic *Lewis* acids. Moreover, unless a nucleophile, including solvent, were to coordinate more strongly than does the entropically favored Li-bound aryloxy moiety, that nucleophile should exercise no adverse effect on the turnover rate. The mechanism is similar to the associative pathway proposed by *Cavell* and co-workers [19]. For the rate acceleration in the polymerization reactions of **5** in THF with $LiClO_4$, coordinated THF occupies at least some of the 'Lig' positions in *Scheme 2*. Heterobimetallic complexes with μ-bridging heteroatom ligands have been reported in several contexts, providing precedent for the structural hypothesis in *Scheme 2*. *Uhlig* and co-workers have characterized several Fe^{II}, Co^{II}, and Ni^{II} acac complexes in which a second cation is bound by μ-bridging oxy ligands [27]. Even more relevant are examples by *Floriani* and co-workers [28], and others [29] in which aryloxy ligands in a late transition metal salicylaldimato complex have bound a second electrophilic metal. Overall, the postulated active species is chemically reasonable, and provides an explanation for all of the experimental observations in this catalyst system.

The last issue concerns the characteristic of **1** that most strongly contributes to its practical potential. The TON of *ca.* 10^5 achieved by **1** brings it into the range of productivity needed for commercial manufacture of polyolefins. Given that TON for similar complexes **5** and **8** are lower by 2–3 orders of magnitude – *Brookhart* and coworkers also mention [22] that none of his Ni-based SSCs shows TON over a few thousand – one is compelled to speculate as to the role of additional components in producing this dramatic effect. While the experiments do not yet support an unambiguous explanation for catalyst deactivation in **5** and **8**, and, conversely, the suppression of catalyst deactivation in **1**, one can make a suggestion. The associative mechanism proposed above works with a switching between four-coordinate and five-coordinate intermediates. An alternative dissociative mechanism would work *via* three-coordinate and four-coordinate structures. Even if an associative mechanism were to be predominant, a small contribution by a dissociative mechanism would mean that three-coordinate Ni alkyls would be present, at least to a small extent. If these intermediates were to undergo β-hydride elimination to form Ni hydrides, as expected for three-coordinate Ni-alkyls, then the presence of basic reagents, present as additives in **5** and **8**, could lead to deprotonation – effectively reduction – with concomitant deactivation. Bidentate complexation of a *Lewis* acid may largely shut down the alternative dissociative mechanism for polymerization, leading to longer catalyst lifetimes. The observed stability of activated **1**, even when no ethylene is present, supports the hypothesis; other Ni^{II} catalysts typically deactivated irreversibly and formed black precipitates when starved of ethylene. If β-hydride elimination is shut down, chain-transfer could still occur for activated **1** by a β-hydride transfer mechanism without the formation of hydrides. Because hydride intermediates have been suggested to play an integral role in the chain-walking mechanism for branch formation [22], one would expect **1** to form highly linear polyethylene as a necessary consequence of the mechanistic hypothesis for the increased catalyst lifetime. The observation of linear polyethylene with no detectable chain-branching provides additional support for the postulated mechanism. Further work is underway to clarify the mechanistic aspects of this new catalyst system.

Lastly, **5** and **8** have been shown to copolymerize ethylene with polar monomers as well as norbornene⁶). One expects that **1** should do so as well. These studies are also underway.

Conclusions. – A family of Ni^{II} coordination complexes are reported for which activation by stoichiometric amounts of ordinary metal alkyls produce efficient, highly productive, polyolefin catalysts. The kinetic order and an unusually high tolerance for heteroatoms leads to a proposed catalytic cycle in which the key species are heteronuclear complexes involving Ni^{II} and a second electrophilic metal cation. The second metal center, with associated bridging ligands functions to suppress catalyst

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6) Preliminary results show that norbornene is, in fact, incorporated.

deactivation, leading to TON exceeding 10^5. With further optimization, higher productivities are likely to be achievable.

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