

Chromium allyl and alkyl catalysts for the vinyl polymerization of norbornene and ethylene–norbornene copolymerizations

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Abstract

Homoleptic allyl complexes of divalent metals, $M^{II}[1,3-C_3H_3(SiMe_3)_2]_2$ (**1**, M=Cr; **2**, M=Fe; **3**, M=Ni; **4**, M=Co) activated with methylaluminoxane (MAO) have been tested as catalysts for the polymerization of norbornene. Whereas the iron and cobalt systems were poorly active, both the nickel and chromium complexes were very productive and gave high molecular weight poly(norbornene)s, although the polymers generated by Cr and Ni differed significantly in the degree of stereoregularity. $Cr^{II}[1,3-C_3H_3(SiMe_3)_2]_2$ polymerized ethylene in the absence of any cocatalyst but, surprisingly, was deactivated by MAO, whereas $1/B(C_6F_5)_3$ showed moderate activity at 20 °C under 1 bar of ethylene. NMR experiments suggest that $B(C_6F_5)_3$ acts as a one-electron oxidant to generate the $[Cr^{III}(allyl)_2]^+$ cation. Although ethylene/norbornene copolymerizations were possible with $1/B(C_6F_5)_3$, the activity was much lower than in ethylene homopolymerizations, and only limited amounts of norbornene could be incorporated. The catalytic behavior of this Cr(II) precursor contrasts sharply with that of the Cr(IV) alkyl complex $Cr(CH_2SiMe_3)_4$ (**5**)/MAO which polymerizes ethylene but reacts with norbornene to give oligomers, mostly trimers–pentamers. On the other hand, (**5**)/MAO is highly active for ethylene/norbornene copolymerizations and gives high molecular weight copolymers. Significantly, catalyst activity increases with increasing norbornene concentration. The copolymers show block-structure, and incorporated norbornene is present at the least as di-norbornene units, even at incorporation levels as low as 10 mol%. At higher norbornene concentrations, NNN sequences prevail.

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1. Introduction

Bicyclo[2,2,1]hept-2-ene, better known as norbornene (NB), can be homo-polymerized via three distinct pathways, each leading to polymers with different structures and properties [1]. Of these three processes, the ring-opening metathesis polymerization (ROMP) has been most widely investigated [2]; it generates a polymer with an unsaturated backbone and high solubility in a wide range of organic solvents. Cationic and radical polymerizations result in low molecular weight oligomers with 2,7-connectivity of the monomer [3]. Lastly,

vinyl addition polymerization of norbornene results in a saturated polymer which retains the bicyclic structural unit [4]. Polynorbornenes (PNBs) produced in this manner show high chemical resistance, high optical transparency, a low dielectric constant and high glass transition temperatures (T_g up to 370 °C). Typically, complexes of nickel, cobalt, titanium, zirconium and palladium have been employed for the vinyl polymerization of norbornene [1,5].

Ethylene–norbornene (E–N) copolymers were first obtained with metallocene–methylaluminoxane based catalysts [6]. The resulting amorphous E–N copolymers are of great interest owing to their transparency, high water vapor resistance and biocompatibility [6,7]. This combination of properties suggests potential applications in optics, such as

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compact disc coatings and also as pharmaceutical packaging. The most widely reported ethylene–norbornene copolymerization catalysts are metallocene [6,8,9], half sandwich [10] or constrained geometry (CGC) based systems [11–13], in combination with MAO. With these catalysts, copolymers with up to ca. 70 mol% norbornene content have been described, although catalytic activity decreases with increasing norbornene concentration. These catalysts show no or only very low activity in norbornene homopolymerizations [10,11b].

Despite the widespread use of heterogeneous chromium catalysts for the polymerization of ethylene, for example the Phillips process [14], only a limited number of homogeneous chromium catalysts for ethylene polymerization have been reported, almost exclusively based on bulky cyclopentadienyl and chelating N- and O-donor ligands [15–20]. Only one system for ethylene–norbornene copolymerization has been described; Heitz et al. recently reported that the Cr(III) catalysts $[\text{Cp}^R\text{CrMeCl}]_2$ activated with MAO at 0 °C affords highly linear, high molecular weight polyethylene, with activities in the range 1.4–4.7 kg PE (mol Cr)⁻¹ h⁻¹ bar⁻¹ (at 3 bar) ($\text{Cp}^R = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5, \text{Ind}, \text{Flu}$), as well as norbornene/ethylene copolymers. The crystallinity of PNB was comparatively low but said to increase with the bulkiness of the Cp ligands [21].

The use of sterically demanding silyl substituents has recently allowed the isolation of the first monomeric homoleptic bis(π -allyl)metal(II) complexes CrL_2 (**1**) and FeL_2 (**2**) ($\text{L} = 1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2$) [22]. Despite the low formal electron count, these complexes are thermally stable at room temperature and can be purified by sublimation at 65 °C/10⁻² mmHg. Although some effort to explore the chemistry of these complexes with donor ligands such as PMe_3 and PPh_3 has been made, no polymerization chemistry has yet been reported. We report here the behavior of this Cr(II) catalyst precursor in ethylene and norbornene polymerizations. The results provide an interesting contrast with the Cr(IV) system $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4/\text{MAO}$ which shows good activity both for ethylene and norbornene homopolymerizations, as well as for E–N copolymerizations.

2. Experimental

2.1. General procedures

All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk line techniques. Solvents were distilled under nitrogen from sodium (toluene), sodium benzophenone (tetrahydrofuran), sodium–potassium alloy (light petroleum, bp 40–60 °C). Deuterated solvents were degassed by several freeze–thaw cycles and stored over 4 Å molecular sieves. NMR spectra were recorded on a Bruker DPX300 spectrometer. ¹H NMR spectra (300.1 MHz) were referenced to residual solvent protons of the deuterated solvent used; ¹³C NMR spectra (282.2 MHz) were referenced

internally to the D-coupled ¹³C resonances of the NMR solvent. FeL_2 (**2**) [22] and $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ (**5**) [23] were prepared according to published procedures. Norbornene was stirred over molten potassium at 80 °C under nitrogen for 4 h and distilled. Ethylene was dried by passing through a column of supported P_2O_5 , followed by a column of activated 4 Å molecular sieves and finally a silicone oil bubbler containing $\text{Et}_2\text{AlO}(\text{CH}_2)_7\text{CH}_3$.

2.2. Preparation of $\text{Cr}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]_2$ (**1**)

In a variation of the published procedure [22], a suspension of CrCl_2 (2.20 g, 17.9 mmol) in tetrahydrofuran (120 mL) was treated with portions of solid $\text{K}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]$ (8.00 g, 35.6 mmol) over 15 min. The grey CrCl_2 dissolved slowly, and after stirring for 16 h the solution had become deep red-orange, with a large quantity of precipitate. The volatiles were removed in vacuo. Extraction of the residue with light petroleum (3 × 40 mL), and removal of the volatiles afforded the title compound as a deep red-orange powder, yield 5.67 g (74.9%). The ¹H NMR spectrum of **1** in benzene-*d*₆ could not be assigned owing to the paramagnetic nature of the complex. However the following signals were observed: ¹H NMR (benzene-*d*₆, 20 °C): δ 53.7 (br s, 6H), 9.04 (br s, 9H), 1.35 (br s, 3H).

2.3. Preparation of $\text{Ni}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]_2$ (**3**)

A solution of $\text{K}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]$ (5.00 g, 22.3 mmol) in tetrahydrofuran (40 mL) was added dropwise to solution of $\text{Ni}(\text{acac})_2$ (2.60 g, 10.1 mmol) also in tetrahydrofuran (60 mL) at –78 °C. The dark colored solution was allowed to warm to room temperature, at which time the solution had become dark red. After a further 16 h, the volatiles were removed in vacuo and the residue was extracted with light petroleum (100 mL). Evaporation of volatiles left an oil which slowly crystallized on standing. The product was obtained as orange crystals, yield 1.78 g (41.2%) and was characterized by single-crystal X-ray diffraction. The structure is reported elsewhere [24].

2.4. Preparation of $\text{Co}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]_2$ (**4**)

A solution of $\text{K}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]$ (7.02 g, 31.3 mmol) in diethyl ether (50 mL) was added dropwise to suspension of $\text{Co}(\text{acac})_3$ (3.36 g, 9.43 mmol) also in diethyl ether (100 mL) at –78 °C. The reaction was allowed to warm slowly to room temperature, during which time the color changed from green to orange, until all the $\text{Co}(\text{acac})_3$ had dissolved. The volatiles were removed in vacuo and the resulting orange powder was extracted with light petroleum (100 mL). The extract was concentrated to ca. 5 mL placed at –30 °C to give **4** as orange crystals, yield 1.33 g (32.8%). Anal. Calcd. for $\text{C}_{18}\text{H}_{42}\text{Si}_4\text{Co}$: C, 50.30; H, 9.85. Found: C, 50.50; H, 9.88%. The identity of the product was confirmed

by X-ray diffraction analysis which is reported elsewhere [24].

2.5. Reaction of $\text{Cr}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]_2$ with AlMe_3 (1:10)

An NMR tube containing 20 mg of **1** (0.047 mmol) in 0.5 mL benzene- d_6 was treated with AlMe_3 (0.05 mL, 0.038 g, 0.52 mmol). The color of the solution remained deep red. The ^1H NMR spectrum showed the same features as the spectrum of **1** in benzene- d_6 and a large single peak at -0.35 ppm can be assigned to AlMe_3 , thus indicating that no reaction had occurred.

2.6. Reaction of $\text{Cr}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]_2$ with Et_2AlCl (1:10)

An NMR tube containing 20 mg of **1** (0.047 mmol) in 0.5 mL benzene- d_6 was treated with Et_2AlCl (0.06 mL, 0.057 g, 0.47 mmol). The color of the solution immediately faded to pale pink and a large amount of precipitate formed. It was not possible to obtain a ^1H NMR spectrum from this sample, owing to problems with shimming. After allowing the precipitate to settle, the supernatant was transferred by syringe to another NMR tube. The ^1H NMR spectrum of this solution showed clear signs of an aluminum complex bearing the 1,3- $\text{C}_3\text{H}_3(\text{SiMe}_3)_2$ ligand, with a triplet at 8.37 ppm and a doublet at 3.74 ppm ($J_{\text{HH}} = 17.1$ Hz) assigned to the allyl protons [25]. The SiMe_3 protons were obscured by the large AlCH_2CH_3 signals, and the reaction product could not be definitively identified.

2.7. Reaction of $\text{Cr}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]_2$ with $\text{B}(\text{C}_6\text{F}_5)_3$ (1:1)

To an NMR tube containing **1** (12 mg, 0.028 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (15 mg, 0.029 mmol) was added 0.5 mL toluene- d_8 (0.5 mL). A brown solution formed and some dark colored precipitate was seen. The ^1H NMR spectrum did not contain the signals associated with **1**; rather a new set of signals assigned to the $[\text{Cr}\{1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}_2]^+$ cation were observed. The ^{11}B NMR spectrum had a broad signal at δ 65.1 owing to some unreacted $\text{B}(\text{C}_6\text{F}_5)_3$, and a small signal at δ -17.8 due to $[\text{B}(\text{C}_6\text{F}_5)_4]^-$. This signal grew in intensity with time. The broad signal assigned to unreacted $\text{B}(\text{C}_6\text{F}_5)_3$ had a prominent shoulder, suggesting a peak at around δ 60. The ^{19}F NMR spectrum contained resonances of $\text{B}(\text{C}_6\text{F}_5)_3$ and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, as well as a significant further set of signals at δ -134.2 , -147.4 and -165.6 which are as yet unidentified. ^1H NMR (toluene- d_8 , 20°C): δ 6.19 (br m, 1H, allyl), 5.46 (br, 1H, allyl), 3.92 (br, 1H, allyl), 0.03 (s, 18H, SiMe_3). The unidentified product is characterized by the following spectroscopic parameters: ^{11}B NMR (toluene- d_8 , 20°C) δ 60.0. ^{19}F NMR (toluene- d_8 , 20°C): δ -134.2 (m, 2F, *o*-F), -147.4 (m, 1F, *p*-F), -165.6 (m, 2F, *m*-F).

2.8. Reaction of $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ with $\text{B}(\text{C}_6\text{F}_5)_3$

To an NMR tube containing $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ (14 mg, 0.035 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (18 mg, 0.035 mmol) was added benzene- d_6 (0.5 mL). The solution was very dark purple. The ^1H NMR spectrum showed signals of unreacted $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$, and the ^{11}B and ^{19}F NMR spectra were identical to those of $\text{B}(\text{C}_6\text{F}_5)_3$. ^1H NMR (benzene- d_6 , 20°C): δ 0.28 (m s, 8H, CH_2SiMe_3), -2.27 (br s, 36H, CH_2SiMe_3). ^{11}B NMR (benzene- d_6 , 20°C): δ 65.1 ($\text{B}(\text{C}_6\text{F}_5)_3$). ^{19}F NMR (toluene- d_8 , 20°C): δ -129.5 (m, 6F, *o*-F), -148.5 (m, 3F, *p*-F), -161.3 (m, 6F, *m*-F).

2.9. Reaction of $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ with AlMe_3 (1:12)

An NMR tube containing $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ (17 mg, 0.042 mmol) in benzene- d_6 (0.5 mL) was treated with AlMe_3 (0.05 mL, 0.038 g, 0.52 mmol). The color of the solution remained deep purple. The ^1H NMR spectrum showed the same features as the spectrum of $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ in benzene- d_6 and a large single peak at δ -0.37 can be assigned to AlMe_3 , thus indicating that no reaction had occurred.

2.10. Reaction of $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ with Et_2AlCl (1:13)

An NMR tube containing $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ (14 mg, 0.035 mmol) in benzene- d_6 (0.5 mL) was treated with Et_2AlCl (0.05 mL, 0.057 g, 0.47 mmol). The color of the solution remained deep purple, although some precipitate was observed. The ^1H NMR spectrum showed the presence of unreacted $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ and Et_2AlCl with small shoulders on the ethyl signals and a small peak at δ -0.53 suggesting that some degree of ligand exchange had occurred between the complexes. ^1H NMR (benzene- d_6 , 20°C): δ 1.12 (br m, 80H, AlCH_2CH_3), 0.22 (br m, 59H, AlCH_2CH_3 and $\text{CrCH}_2\text{SiMe}_3$), -2.31 (br s, 36H, CH_2SiMe_3).

2.11. Polymerization details

Norbornene polymerizations were carried out as follows. The monomer was transferred into the reactor vessel, toluene and MAO were added. The catalyst precursor as a solution in toluene was then injected via syringe. The reaction was terminated by the addition of methanol (ca. 2 mL). The poly(norbornene) (PNB) was precipitated into acidified methanol (200 mL), filtered and dried at 50°C to constant weight.

Ethylene polymerizations were carried out in a 500 mL round-bottomed flask charged with toluene (50 mL), MAO (5 mmol) under 1 bar of ethylene. For copolymerizations, the required amount of norbornene was added at this stage. The precatalyst was injected as a solution in toluene. The polymerizations were terminated by the injection of methanol (ca. 2 mL) and worked up as described.

3. Results and discussion

The synthesis of the metal allyl complexes is depicted in Scheme 1. As described by Hanusa and co-workers [22], the chromium(II) and iron(II) allyl complexes **1** and **2** are readily obtained from the metal dichlorides and 2 equiv. of $K[1,3-C_3H_3(SiMe_3)_2]$ as a dark red solid and orange crystals, respectively. The nickel complex **3** was prepared from $Ni(acac)_2$ and 2 equiv. of $K[1,3-C_3H_3(SiMe_3)_2]$ in tetrahydrofuran. The complex was obtained from the reaction as an orange oil which crystallized on standing at room temperature. The cobalt complex **4** was prepared from $Co(acac)_3$ and 3 equiv. $K[1,3-C_3H_3(SiMe_3)_2]$ in diethyl ether and formed orange crystals from a very concentrated solution in light petroleum at $-30^\circ C$. The single-crystal X-ray structures of **3** and **4** have been determined and are reported elsewhere [24].

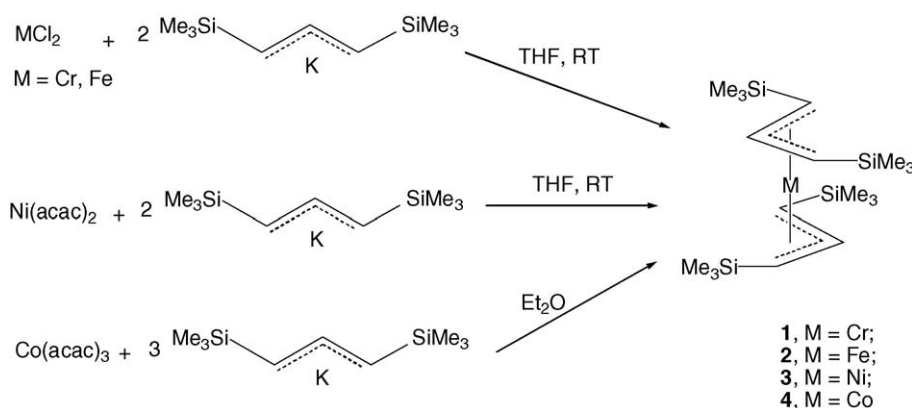
The elucidation of the organometallic chemistry involved in the polymerization chemistry discussed here is necessarily complicated by the paramagnetism of the complexes. For instance, the 1H NMR signals of **1** are very broad and cannot be easily interpreted. Nevertheless, NMR scale reactions did provide some useful information. The reaction of **1** with typical catalyst activators was investigated. The allyl complex does not react with $AlMe_3$ in benzene- d_6 at room temperature, with the 1H NMR spectrum showing only starting materials. There is however a rapid reaction of **1** with Et_2AlCl , and the deep red color of the solution fades to very pale orange, with formation of a large quantity of a grey precipitate. It proved impossible to obtain NMR spectra from this sample, although the 1H NMR spectrum of the clear supernatant showed signs of an aluminum allyl species, with a triplet at δ 8.37 and a doublet at δ 3.74 ($J_{HH} = 17.1$ Hz) assigned as the allyl protons [25]. Apparently ligand exchange occurs readily in this case, with formation of Al allyls and $CrCl_2$.

Of most interest was the reaction of **1** with $B(C_6F_5)_3$ in toluene- d_8 . The color of the reaction immediately changed from the deep red of **1** to brown. The 1H NMR spectrum was much simpler than that of **1**, containing three discrete signals

for the allylic protons at δ 6.19, 5.46 and 3.92 and one for the silyl methyl protons at δ 0.03. The ^{19}F NMR spectrum showed resonances due to excess $B(C_6F_5)_3$ as well as peaks at δ -134.2 , -147.4 and -165.6 , while the ^{11}B NMR spectrum had a signal at δ 65 with a prominent shoulder at approximately 60 ppm. The identity of this major product is as yet unknown. The data suggest a one-electron oxidation of **1** to generate the $[Cr(allyl)_2]^+$ cation, with the concurrent formation of the tris(pentafluorophenyl)borane radical anion, $[B(C_6F_5)_3]^{\bullet-}$. $B(C_6F_5)_3$ has been shown to provide a one-electron oxidation of an η^2 -vinyl molybdenum complex, and it is also reported that an azazirconacyclobutene undergoes a one electron oxidation in the presence of this borane, although in both cases the radical anion could not be detected [26]. The EPR and UV spectra of the radical anion have been recorded following the reaction of Cp^*_2Co and $B(C_6F_5)_3$ [27]. The radical anion $[B(C_6F_5)_3]^{\bullet-}$ has been shown to have a limited lifetime (about 5 min at $0^\circ C$ in THF) [27], and it seems likely that the unidentified product results from its decomposition. The $[B(C_6F_5)_4]^-$ anion is also formed as a by-product, and the ^{11}B and ^{19}F NMR signals for the anion increased in intensity with time. The formation of this tetra(aryl)borate anion was also observed as a decomposition product in the reaction of Cp^*_2Co and $B(C_6F_5)_3$ [27].

3.1. Norbornene homopolymerizations

Nickel(II) complexes are well known as excellent norbornene polymerization catalysts, typically when activated with methylaluminoxane (MAO) [28]. As can be seen in Table 1, **3**/MAO at an Al/Ni ratio of 100 at $20^\circ C$ afforded PNB in high conversions over a relatively short time period. The polymer obtained was amorphous and moderately soluble in trichlorobenzene. NMR and IR analysis confirmed that it was formed exclusively by vinyl polymerization [29]. Increasing the monomer/Ni ratio from 400:1 to 2100:1 increased the PNB molecular weight from $\bar{M}_w = 583,000$ to 1,260,000, with little increase in polydispersity \bar{M}_w/\bar{M}_n from 1.9 to 2.2. A five-fold increase in the monomer/Ni ratio led to



Scheme 1.

Table 1
Norbornene homopolymerization with Cr, Fe, Co and Ni catalysts^a

Entry	Catalyst	Cat (μmol)	MAO (mmol)	NB (g)	Time (min)	Polymer yield (g)	Conversion (%)	M_w^b	M_n^b	M_w/M_n^b
1	3	50	5	1.9	10	1.77	93.2	583000	313000	1.9
2	3	10	0.5	2.0	20	1.09	54.5	1260000	582000	2.2
3	2	50	2.5	2.0	960	0.025	1.2	309000	29400	10.6
4	1	50	5	1.9	30	1.90	100	nd	nd	nd
5	1	25	2.5	1.9	30	1.65	86.8	nd	nd	nd
6	1	10	1	2.0	30	1.13	56.5	nd	nd	nd
7	4	30	3	2.0	180	0.011	0.6	nd	nd	nd
8	5	50	5	1.95	10	1.345	69.0	500	290	1.7
9	5	25	2.5	1.92	15	0.581	30.3	470	280	1.7

^a Conditions: metal 5×10^{-5} mol, toluene (20 mL), 20 °C, MAO activator.

^b Determined by GPC relative to polystyrene standards.

a doubling of the molecular weight. The initiation efficiency of this system was low, however (e.g. only 11% for entry 1, based upon a calculated \bar{M}_n of 37,600).

Neither of the iron and cobalt allyls **2** and **4** treated with MAO under the same conditions afforded an active catalyst, with only traces of polymeric material being produced in each case. By contrast, the Cr(II) complex **1** activated with MAO was found to exhibit high activity, comparable to that of the nickel complex. Thus a mixture of **1**/MAO (50 μmol Cr, Al/Cr=100) and 400 equiv. of norbornene at 20 °C gave complete conversion in 30 min (Table 1). In contrast to the PNB produced with the nickel catalyst, the chromium-derived PNB was totally insoluble in organic solvents; this precluded molecular weight determinations and NMR analysis. However, IR studies showed the absence of bands at 1680–1620 cm^{-1} , indicative of a fully saturated polymer, and confirmed that the polymer was produced by vinyl polymerization. By contrast, **1**/ $\text{B}(\text{C}_6\text{F}_5)_3$ did not homopolymerize norbornene, so that it seems likely that polymerization is dependent on the formation of a Cr–Me bond capable of inserting norbornene.

As mentioned in Section 1, norbornene polymerization with half-sandwich chromium(III) catalysts of the type $[\text{Cp}^R\text{CrMeCl}]_2/\text{MAO}$ has been reported, where Cp^R = substituted cyclopentadienyl, indenyl or fluorenyl [29]. In that case the authors suggested that the stereoregularity and crystallinity of the polymer increased with steric demand of the Cp ligands, from 0 to 30%. In the case of **1**/ AlMe_3 there is evidence for at least partial exchange of the allyl ligands, as discussed above, to give presumably sterically much less encumbered species. The formation of highly crystalline PNB from such a catalyst was therefore surprising.

We were interested in comparing the behavior of the Cr(II) catalyst precursor with other oxidation states of chromium, such as the Cr(IV) complex $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ (**5**)

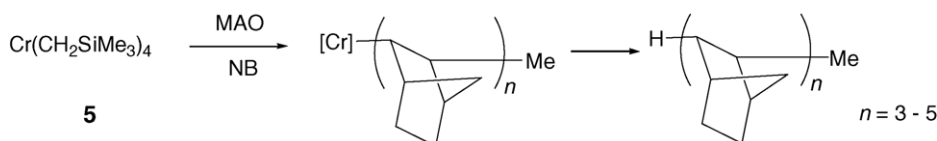
is readily synthesized from $\text{CrCl}_3(\text{THF})_3$ and 4 equiv. of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in tetrahydrofuran [23].

$\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ in benzene- d_6 does not react with either AlMe_3 or $\text{B}(\text{C}_6\text{F}_5)_3$; in both cases the NMR spectra (^1H , ^{11}B and ^{19}F) are essentially identical to those of the starting materials. However, with Et_2AlCl there was some evidence of ligand exchange, with a precipitate formed in the NMR tube. The ^1H NMR spectrum had signals for both starting materials, although the ethyl signals of Et_2AlCl had shoulders suggesting that another compound was also present. It appears that $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ reacts with Et_2AlCl or MAO under ligand exchange, as an entry to catalyst activation.

Consistent with this observation, a mixture of **5** and MAO readily reacted with norbornene, with high conversion (Table 1, entries 8 and 9). However, in contrast to the polymer produced from **1**, the product obtained with **5**/MAO was soluble in 1,1,2,2-tetrachloroethane- d_2 and 1,2,4-trichlorobenzene and was found to consist of NB oligomers, mostly trimers–pentamers. There was no evidence of unsaturated end groups (^1H NMR); however, NMR and mass spectrometric evidence showed that the oligomers contained methyl end-groups and must thus have arisen by norbornene insertion into Cr–Me bonds, followed by rapid transfer to aluminum (Scheme 2).

3.2. Ethylene polymerizations and E/N copolymerizations

$\text{Cr}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]_2$ (**1**) was found to polymerize ethylene in the absence of any cocatalyst, albeit with modest activity (Table 2, entry 1). Surprisingly, when MAO was added, the catalytic activity was drastically reduced, and only traces of polymer were obtained. Et_2AlCl was also found to reduce the activity. In both these cases it seems likely that allyl transfer to aluminum may lead to deactivation. By



Scheme 2.

Table 2
Ethylene homopolymerizations with Cr(II) and Cr(IV) catalyst precursors^a

Entry	Catalyst	Cocatalyst	Time (min)	Polymer yield (g)	Activity ^b	M_w^c	M_w/M_n^c
1	1	–	60	0.032	630	nd	nd
2	1	B(C ₆ F ₅) ₃	60	0.557	1110	739000	52
3	1	2Et ₂ AlCl	60	0.016	320	nd	nd
4	1	MAO	60	Traces	–	–	–
5	5	MAO	30	0.025	100	418000	31
6	5	MAO	60	0.059	118	475000	14

^a Conditions: Cr 5.0×10^{-5} mol, MAO/Cr = 100, ethylene pressure 1 bar, 50 mL toluene, 20 °C.

^b In g PE mol⁻¹ h⁻¹ bar⁻¹.

^c Determined by GPC relative to polystyrene standards.

contrast, treating **1** with B(C₆F₅)₃ resulted in much higher ethylene polymerization activity (Table 2, entry 2). As discussed above, NMR experiments suggested that this reaction involves a one electron oxidation of Cr(II) by B(C₆F₅)₃, with the formation of the [Cr(allyl)₂]⁺ cation which is presumably responsible for the observed activity.

Cr(CH₂SiMe₃)₄/MAO was also active for ethylene polymerization (Table 2, entries 5–6). The polyethylene was found to possess high molecular weight but a broad polydispersity. This was in good agreement with the reported productivity of Cr(CH₂SiMe₃)₄ when activated with 2 equiv. of AlCl₃ (1.1×10^3 g PE (mol Cr)⁻¹ h⁻¹ bar⁻¹) [23b].

Both the Cr(II) allyl and the Cr(IV) alkyl systems were tested for ethylene–norbornene copolymerizations. The polymerizations were conducted under one bar ethylene, with varying starting concentrations of NB. As had been found for ethylene homopolymerizations, the addition of ethylene to the norbornene polymerization catalyst **1**/MAO led to deactivation. With the borane system **1**/B(C₆F₅)₃ the activity was much reduced, with only small quantities of polymer obtained, regardless of the initial concentration of norbornene. The polymer was shown to contain only limited levels of incorporated norbornene, up to 11 mol%.

In contrast to the behavior of Cr(II) allyl precursors, the activity of **5**/MAO was not depressed by ethylene, and good E–N copolymerization activities were observed. Unlike group 4 metallocene catalysts, the activity of this Cr system actually *increased* with increasing NB feed, and at higher [NB] (e.g. 0.32 mol L⁻¹) the activity exceeded that of ethylene homopolymerizations with this catalyst by almost one order of magnitude. The level of norbornene incorporation could be varied within wide limits, depending on the initial NB feed concentration, with incorporation levels ranging from 8 to 60% being produced from [NB]₀ of between 0.11 and 0.32 mol L⁻¹ (Fig. 1).

The ¹³C NMR spectra of ethylene–norbornene copolymers can be very complex, due to the presence of two stereogenic carbon atoms per norbornene unit (Fig. 2), the possibility of isomers with exo and endo connectivity, and the formation of blocks of varying lengths, e.g. –ENE–, –ENNE–, –ENNNE– moieties [1]. The main structural features of E–N copolymers produced with titanium and zirconium metallocene catalysts have been assigned [8, 11b, 12b, 30–32].

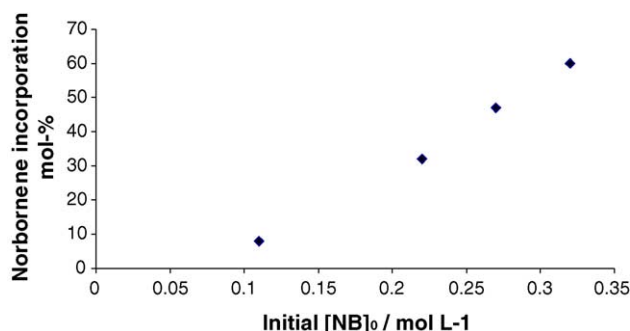


Fig. 1. NB incorporation levels (mol%) as a function of initial NB feed concentration [NB]₀ in E–N copolymerizations with **5**/MAO.

When E–N copolymers contain either alternating units or isolated norbornene units, the spectra are comparatively simple, with a perfectly alternating structure featuring only five peaks. Indeed, E–N copolymers produced with “constrained-geometry” titanium catalysts contain almost exclusively isolated norbornene units and show only traces of –ENNE– norbornene diads [11]. The copolymers produced with the Cr(II) catalyst **1**/B(C₆F₅)₃ showed these characteristics (see Fig. 3) and in this respect are similar to the copolymers produced using [Cp^RCrMeCl]₂/MAO, where at low incorporation levels (up to 35%) mainly alternating or isolated norbornene units were found [21b]. By contrast, the copolymers produced with **5**/MAO all contained norbornene blocks, even at low levels of norbornene incorporation.

The ¹³C NMR spectrum of the copolymer generated from **5**/MAO (Al/Cr = 1000) with [NB]₀ = 0.32 mol L⁻¹ (Table 3 entry 7) is shown in Fig. 4. The signals were assigned in comparison with the spectra of norbornene-rich E–N copolymers obtained with ansa-zirconocenes [30–32]. The three signal

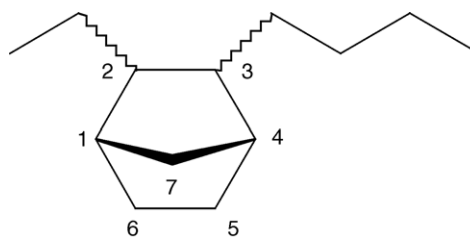


Fig. 2. Section of an ethylene–norbornene copolymer with the labeling of the norbornene unit.

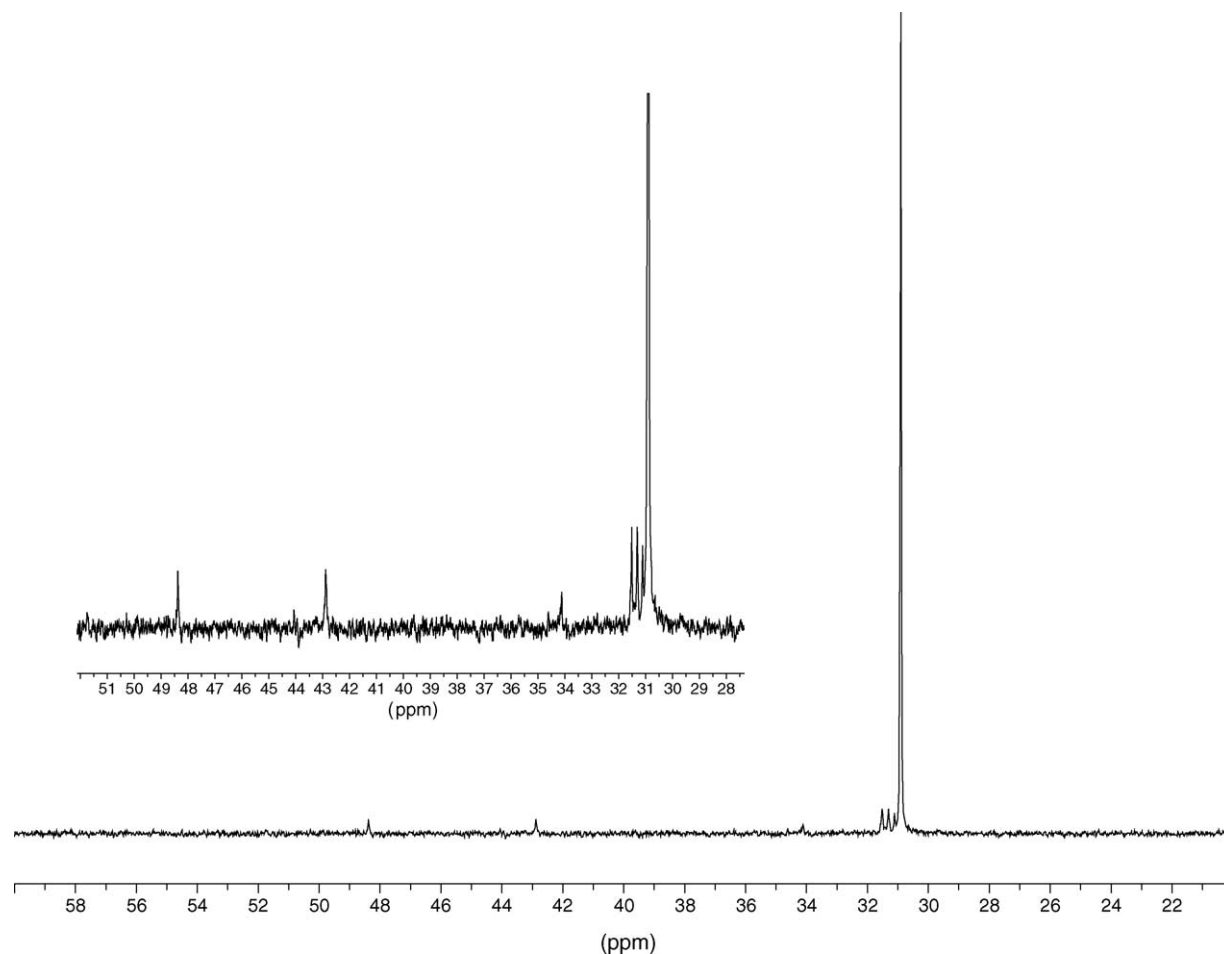


Fig. 3. ^{13}C NMR spectrum of an ethylene–norbornene copolymer prepared with $1/\text{B}(\text{C}_6\text{F}_5)_3$; 20°C , 1 bar ethylene, $[\text{NB}]_0 = 0.11 \text{ mol L}^{-1}$; NB incorporation 6.0 mol%.

groups for carbon atoms C1–C4 and C7 (see Fig. 2) ranging from δ 32–50 show complex splitting and indicate the presence of at least diblock units. This is confirmed by the presence of a signal at δ 28.3, which has been assigned as characteristic of –NN– units by comparison with the spectra of norbornene dimers and trimers [11b]. The small signals between δ 34 and 41.5 and also between δ 43 and 47 are indicative of –NNN– sequences.

The two copolymers with the lowest NB content showed molecular weights of ca. 200,000, with comparatively narrow polydispersities (for example entry 4, $\bar{M}_w = 220,000$, $\bar{M}_w/\bar{M}_n = 4.1$). The polydispersity increased significantly at higher norbornene incorporation levels; this is not least due to facile polymer precipitation during reactions with higher $[\text{NB}]_0$. The GPC traces for these two polymer samples showed bimodal distributions.

Table 3
Ethylene–norbornene copolymerizations^a

Entry	Catalyst	Cocatalyst	$[\text{NB}]_0$ (mol L ⁻¹)	Time (min)	Polymer yield (g)	Activity ^b	Norborne incorp. ^c (mol%)	M_w^d	M_n^d	M_w/M_n^d
1	1	MAO	0.21	25	Traces	–	–	–	–	–
2	1	$\text{B}(\text{C}_6\text{F}_5)_3$	0.11	60	0.020	400	6.0	684000	15100	45
3	1	$\text{B}(\text{C}_6\text{F}_5)_3$	0.33	60	0.036	720	11	744000	8120	92
4	5	MAO	0.11	60	0.083	1660	8.0	220000	53100	4.1
5	5	MAO	0.21	60	0.419	8380	32	190000	39100	4.9
6	5	MAO	0.27	60	0.265	5300	47	618000	41500	15
7	5	MAO	0.32	60	0.475	9500	60	205000	7950	26

^a Conditions: Cr 5.0×10^{-5} mol, Al/Cr = 100, ethylene pressure 1 bar, 50 mL toluene, 20°C .

^b In g polymer mol⁻¹ h⁻¹ bar⁻¹.

^c Determined by analysis of the ^{13}C NMR spectra in 1,1,2,2-tetrachloroethane- d_2 at 110°C .

^d Determined by GPC relative to polystyrene standards.

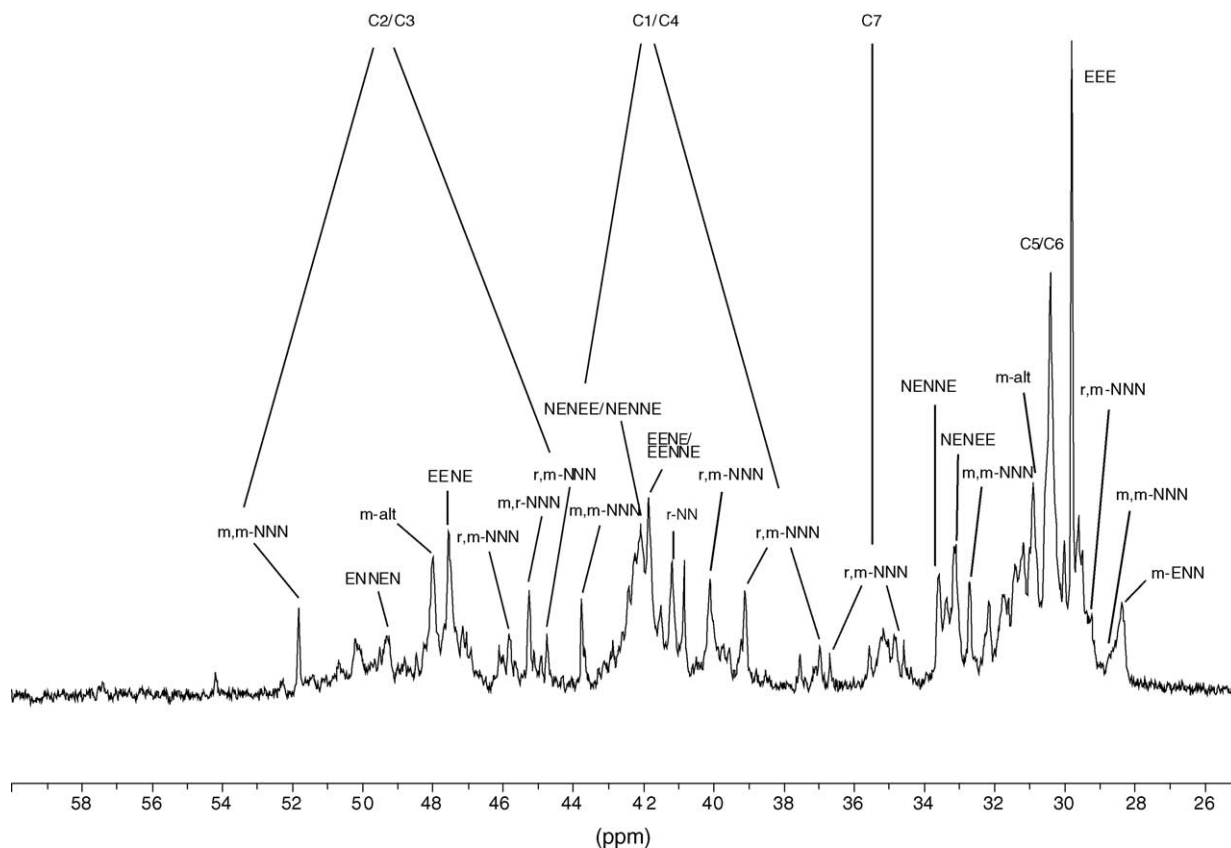


Fig. 4. ^{13}C NMR spectrum of an ethylene–norbornene copolymer. Catalyst **5**/MAO (Al/Cr = 1000); 20 °C, 1 bar ethylene, $[\text{NB}]_0 = 0.32 \text{ mol L}^{-1}$; norbornene content of the copolymer 60 mol%.

The block structure of these copolymers was confirmed by the determining the reactivity ratios for ethylene and norbornene, r_E and r_N , by means of ^{13}C $\{^1\text{H}\}$ NMR spectroscopy. Measurements were taken over the (admittedly limited) compositional range. Data were analyzed assuming a first-order Markovian model. Although the determination of the copolymer compositions proved difficult at high norbornene incorporation (>40 mol%), there was good agreement between the Fineman–Ross and Kelen–Tüdös methods, giving $r_E \approx 10$, $r_N \approx 2.5$, and $r_E r_N \approx 25$.

The disparity between the behavior of the two systems **1**/MAO and **1**/ $\text{B}(\text{C}_6\text{F}_5)_3$ is striking. The reluctance of **1**/ $\text{B}(\text{C}_6\text{F}_5)_3$ to homopolymerize norbornene explains the lower activities encountered in ethylene–norbornene copolymerization. With this catalyst, multiple NB insertions are evidently disfavored, as no ENNE units were found in these copolymers. With the Cr(IV) system **5**/MAO, no such problems were encountered, and even at low comonomer enchainment levels multiblock norbornene units were observed.

3.3. Heterogeneous polymerization with $\text{Cr}(\text{L}^1)_2$ on silica

One approach to the modelling of Phillips catalysts has been the preparation of silica immobilized chromium alkyl complexes via the reaction of chromium alkyls

and partially dehydroxylated silica [33]. For example tetrakis(neopentyl)chromium(IV) reacts with the hydroxy groups of amorphous silica (dehydroxylated at 200 °C) to give a bis(neopentyl)chromium(IV) surface complex [33b,33c]. We were interested in the effect of heterogenization on the Cr(II) precursor **1**.

A sample of silica (Vulkasil® S, with a surface area of $175 \pm 20 \text{ m}^2/\text{g}$) was partially dehydroxylated at 500 °C for 3 h. It has been estimated that under these conditions only isolated silanol groups remain, with an average surface concentration of between 5.5 and 1 nm^{-2} [34]. The supported catalyst was prepared by suspending a portion of this silica (typically 0.3–0.4 g) in a light petroleum solution of **1** (0.084 g, 200 μmol) for 30 min. During this time the dark red color of the solution transferred onto to the solids, so that on settling the supernatant was colorless. The solids were dried in vacuo, giving a pale red powder. The filtrate was shown to contain $1,3\text{-C}_3\text{H}_4(\text{SiMe}_3)_2$, formed from the reaction with surface-OH.

The results of ethylene and ethylene–norbornene polymerization trials with the supported complex are assembled in Table 4. Polymerizations were carried out at 7 bar and 60 °C. In the absence of an aluminum cocatalyst no polymer was obtained under these conditions. With MAO at Al/Cr = 1000 or with 10 equiv. of Et_2AlCl , polyethylene was produced with an activity of $\sim 4.8 \times 10^3 \text{ g}(\text{mol Cr})^{-1} \text{ h}^{-1} \text{ bar}^{-1}$. This

Table 4
Ethylene polymerization with **1** supported on silica^a

Entry	Silica (g)	Cocatalyst	[NB] ₀ (mol L ⁻¹)	Time (min)	Polymer yield (g)	Activity ^b	Norborne incorp. ^c (mol%)	M _w ^d	M _n ^d	M _w /M _n ^d
1	0.380	MAO	0	50	5.77	34600	–	818000	94700	8.6
2	0.345	Et ₂ AlCl	0	50	5.65	33900	–	515000	40600	13
3	0.365	MAO	2.0	50	2.05	1000	0.0	889000	23900	37

^a Conditions: Cr 2.0 × 10⁻⁴ mol, ethylene pressure 7 bar, 300 mL toluene, 20 °C.

^b In g PE mol⁻¹ h⁻¹ bar⁻¹.

^c Determined by analysis of the ¹³C NMR spectra in 1,1,2,2-tetrachloroethane-d₂ at 110 °C.

^d Determined by GPC relative to polystyrene standards.

figure is low compared to supported chromium(III) alkyl complexes, for example Cr[CH(SiMe₃)₂]₃ on silica showed an activity of 4.5 × 10⁶ g (mol Cr)⁻¹ h⁻¹ bar⁻¹ at 100 °C and 14 bar [33f]. The low activity of the current system may be due to a less facile insertion into the chromium allyl bond, or it may reflect the lower activity of a chromium(II) catalyst [35]. An attempted ethylene–norbornene copolymerization ([NB]₀ = 6.4 mmol L⁻¹) did produce some polymer, although ¹³C NMR analysis in 1,1,2,2-tetrachloroethane-d₂ did not show any norbornene units, suggesting that if any incorporation had occurred, it was below the level of detection. The polyethylene was found to be of high molecular weight, with a broad polydispersity. The polyethylene produced with Et₂AlCl as cocatalyst had very similar characteristics.

4. Conclusions

Both Ni(II) and Cr(II) allyl complexes in combination with MAO give active catalysts for the polymerization of norbornene. While this is not unexpected for nickel, the chromium system represents, to our knowledge, only the second norbornene polymerization catalyst with this metal, and the first example of a Cr(II) complex. There was a pronounced dependence of activity on the metal oxidation state: the Cr(II) system **1**/MAO was active for norbornene homopolymerization but inactive for ethylene polymerization, and in the presence of ethylene the norbornene polymerization was also suppressed. However the system **1**/B(C₆F₅)₃ was active for ethylene polymerization but not for norbornene. In E–N copolymerization experiments with this catalyst much lower activity was found than for ethylene homopolymerization, and it seems likely that insertion of a norbornene monomer significantly hinders further monomer insertion. NMR experiments suggest that the reaction of Cr^{II}[1,3-C₃H₃(SiMe₃)₂]₂ with B(C₆F₅)₃ proceeds via a one electron oxidation of the metal to give the [Cr{1,3-C₃H₃(SiMe₃)₂]₂⁺ cation, with the concurrent formation of the [B(C₆F₅)₃]^{•-} radical anion.

Although an active heterogeneous ethylene polymerization catalyst could be prepared by reacting a solution of Cr[1,3-C₃H₃(SiMe₃)₂]₂ in light petroleum with dehydroxylated silica, the catalyst was not active in the absence of either Et₂AlCl or MAO as cocatalysts, and the activity does not reach the values seen for other systems prepared from Cr(III) or Cr(IV) alkyls and silica.

By contrast, the chromium(IV) complex Cr(CH₂SiMe₃)₄/MAO shows good activities for ethylene homopolymerization and norbornene oligomerization, as well as for E–N copolymerizations. The level of norbornene incorporated in the polymer can be varied over a wider range than is possible with group 4 catalysts, and norbornene incorporation levels of 8–60 mol% were obtained from initial norbornene concentrations of 0.11–0.32 mol L⁻¹. In contrast to metallocene catalysts, the activity of this chromium catalyst rises with increasing norbornene concentration. There is a tendency towards the formation of oligo(norbornene) block structures; thus even at low incorporation levels there was little evidence for isolated norbornene units, and NN or higher units predominate. At higher norbornene incorporation levels the polymer microstructure was consistent with the formation of mainly NNN blocks.

Acknowledgments

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