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Aluminum bis(iminophosphorano)methanide and methandiide complexes—transition metal-free ethylene polymerization cationic catalyst precursors

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Abstract

The catalytic activity of a new family of aluminum bis(iminophosphorano)methanide and methandiide complexes (**1**–**5**) toward olefin polymerization has been evaluated. The complexes (**1**–**3**) are monomeric methanide complexes of the form $[\kappa N, \kappa N'-\{(Me_3SiN=P(Ph)_2)_2CH\}Al(Cl)R]$ (R = Et) (**1**) or $[\kappa N, \kappa N'-\{(Me_3SiN=P(Ph)_2)_2CH\}AlR_2\}$ (R = Me, Bu) (**2**, **3**) which have a structure reminiscent of $R_2Al(acac)$ complexes. These systems are moderately effective as transition metal-free ethylene polymerization catalysts when activated by trityl tetrafluoroborate yielding slurry polymerization activities in the range of 3–68 g polymer/(mmol Al h) (normalized to 1 atm) under normal industrial conditions. A remarkable bis(iminophosphorano)methandiide complex $[\kappa C, \kappa C, \kappa N, \kappa N'-\{(Me_3SiN=P(Ph)_2)_2C\}(R_2Al)_2]$ (R = Me) (**4**) which is based on a spirocyclic carbon center subtended by two $AlMe_2$ units (each of which is further coordinated with an imine group) gave, under similar catalytic activation and reaction conditions, very high polymerization activity (2×10^3 g polymer/(mmol Al h)) for ethylene. Solution polymerization activity was also high. This system also co-polymerized ethylene and 1-octene. The analog **5** wherein R = Bu was not so effective. These latter complexes indicate that dialuminum species may provide effective transition metal-free olefin polymerization systems.
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1. Introduction

Single site catalyst technology has made a dramatic impact on the polyolefin industry, providing access to materials with new and improved performance parameters compared with the polyolefin polymers produced by traditional Ziegler heterogeneous titanium-$MgCl_2$ catalysts [1].[1] A continuing interest in the pursuit of discovery and development of new families of catalysts for olefin polymerization exists and many different systems have been explored. In particular, complexes of nitrogen-based ligands, such as a variety of Schiff base complexes, metal amides, metal amidinates, metal guanidinates, etc. have been the focus of much recent attention. Most of these complexes

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[1] Extensive surveys and reviews have been published on the subject the most extensive being the series of articles in the theme issue of Chem. Rev. 100 (2000) 1167–1681.

contain elements of the transition metal family, in particular the early members. Although an Al co-catalyst is widely used (but its role is poorly understood) ([2], specifically pp. 1413–1414, for discussion of the role of alumoxane), a recent review of ([1a], Section 9) pointed to some early literature which employed Al as the only active metal nucleus for the catalytic process. Recently a resurgence in the chemistry of aluminum complexes [3–20] has occurred although most of the published activity refers to the synthesis of novel complexes and not to their catalytic applications. However, catalytic activity of Al systems is described in several recent papers [17,21–24].

We recently reported syntheses [8] and reactivity [9] of some alkyl aluminum complexes containing monoanionic bis(iminophosphorano)methanide and dianionic bis(iminophosphorano)methandiide ligands. Herein, we report olefin polymerization studies [25] with these new compounds.

2. Experimental

2.1. General procedures

All experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques or an argon-filled glovebox with an efficient recirculator. Solvents were dried and distilled under argon prior to use. Hexane and toluene were distilled from Na–K and Na, respectively. NMR solvents benzene-d_6 and toluene-d_8 were freshly vacuum transferred from Na–K. Triisobutylaluminum solution was obtained as 25.2 wt.% solution. Aluminum compounds **1**, **2** and **4** were prepared as described earlier, [8] complexes **3** and **5** by similar methods [26]. Infrared spectra at the University of Alberta were recorded on a Nicolet 7199 infrared spectrometer and those at NOVA Chemicals Corporation with a Nicolet model 750 Magna IR spectrometer.

All the polymerization experiments described below were conducted using a 500 ml Autoclave Engineers Zipperclave reactor equipped with an air driven stirrer and an automatic temperature control system. The reactor uses a programmable logic control (PLC) system with Wonderware 5.1 software for the process control.

Anhydrous toluene was purchased from Aldrich and passed through a series of purification beds (various absorption media) to remove the impurities. 1-Octene

was purchased from Aldrich and purified over a series of purification beds (containing various absorption media). [CPh$_3$][B(C$_6$F$_5$)$_4$] was purchased from Asahi Glass Inc.; lot # 980224. PMAO-IP was purchased from Akzo Nobel. This product contains 13.9 wt.% aluminum. Polymer grade ethylene was purchased from Praxair. All the chemicals (solvent, catalyst and co-catalyst materials) were fed into the reactor batch-wise, except ethylene which was fed on demand. No product was removed during the polymerization reaction. All the feed streams were purified prior to introduction into the reactor by contact with selected absorption media to remove catalyst poisoning impurities, such as water, oxygen, sulfur and polar materials. All components were stored and manipulated under an atmosphere of purified argon or nitrogen.

The initial polymerization temperature was systematically varied. In comparative experiments the initial (setting) polymerization temperature was in the range 50–120 °C for slurry polymerizations (Table 1) and approximately 160 °C for solution polymerizations (Table 2). The polymerization reaction time varied from 4 to 40 min for each experiment. The temperature of the reaction mixture initially increased as the exothermic reaction commenced and then gradually dropped to a steady-state value after a few minutes (Fig. 1). Temperatures reported in Tables 1 and 2 are the average temperatures of each experiment. The reaction was terminated by adding 5 ml of methanol to the reactor and the polymer was recovered by evaporation of the volatiles including toluene and by drying the residue in vacuum. Time averaged polymerization activities were calculated based on the weight of the polymer produced over the duration of the run.

Polymer molecular weights and molecular weight distributions were measured by GPC (Waters 150 °C) at 140 °C in 1,2,4-trichlorobenzene calibrated using polyethylene standards. DSC was conducted on a DSC 22 C from Seiko Instruments. The heating rate was 10 °C/min from 0 to 200 °C. All results are summarized in Tables 1 and 2.

2.2. Testing for transition metal contamination of the reactor

2.2.1. Solution polymerization with the Al catalyst (**4**)
Toluene (216 ml) was transferred into the reactor with 0.05 ml of PMAO-IP (1 mmol/l) as a

Table 1
Slurry polymerization data[a]

Aluminum catalyst precursor	Co-catalyst	Average temperature (°C)	Run time (min)	Polymerization activity (g polymer/(mmol Al h))	M_w ($\times 10^{-3}$)	PD	MP (°C)
1	PMAO-IP[b,c]	56.3	30	15.5	1255.0	2.4	137.9
1 + [CPh$_3$][BC$_6$(F$_5$)$_4$)][d]	PMAO-IP[d] in situ alkylation	54.8	30	68.1	1397.0	2.0	141.1
2	[CPh$_3$][B(C$_6$F$_5$)$_4$][e]	53.8	40	3.5	1252.0	1.8	142.3
4	[CPh$_3$][B(C$_6$F$_5$)$_4$][e]	120.4	4	2886.8	721.9	3.7	135.2
4	[CPh$_3$][B(C$_6$F$_5$)$_4$][f] co-polymerization	50.5	20	8.1	840.1	1.7	105.0
5	[CPh$_3$][B(C$_6$F$_5$)$_4$][g]	53.8	35	378.4	1526.0	1.6	134.3

[a] General homopolymerization conditions: reactor temperature initially set at approximately 50 °C; 300 psig of C$_2$; catalyst concentration 300 mmol/l; 216 ml of toluene as solvent.

[b] A polymethylaluminoxane.

[c] PMAO-IP activation at Al/Al ratio = 60.

[d] In situ alkylation plus trityl borate activation: reactor temperature initially set at approximately 50 °C; PMAO-IP as an alkylation reagent with Al/Al ratio = 20; trityl borate as co-catalyst at B/Al ratio = 1.05; PMAO-IP at 1 mmol/l as a scavenger.

[e] Trityl borate activation: trityl borate as a co-catalyst at 315 μmol/l and PMAO-IP at 1 mmol/l as a scavenger.

[f] Co-polymerization conditions: 100 psig of C$_2$; 30 ml of 1-octene; trityl borate activation, trityl borate as a co-catalyst at 315 μmol/l and PMAO-IP at 1 mmol/l as a scavenger.

[g] Trityl borate activation at 630 μmol/l, other conditions are as described in the general polymerization conditions.

scavenger. The solution was heated to 160 °C and saturated with 140 psig of ethylene. Complex **4** (43.2 mmol, 36.64 mg) was dissolved in toluene and injected into the reactor. At the same time, [CPh$_3$][B(C$_6$F$_5$)$_4$] (90.72 mmol, 83.68 mg) dissolved in toluene (12.2 ml), was injected into the reactor. A 5 °C temperature rise was observed. The polymerization reaction was finally terminated by adding 5 ml of MeOH. After evaporating the solvent, 14.9 g of polyethylene was collected.

2.2.2. Blank

A blank run was conducted under the exact conditions described above but omitting the Al catalyst charge. Thus, 216 ml of toluene along with 1 mmol/l

PMAO-IP (0.216 mmol of Al) were loaded into the reactor which was then heated to 160 °C with stirring. The reactor was then saturated with 140 psig of ethylene and 200 μmol/l (43.2 mmol) of trityl borate was injected. No ethylene consumption was observed. After evaporating the solvent a trace amount of white solid was isolated which was identified as aluminum oxides.

3. Results and discussion

The complexes of interest (**1**–**5**; Scheme 1) fall into two categories, those in which the aluminum is coordinated by a bis(iminophosphorano)-

Table 2
Solution polymerization data[a]

Aluminum catalyst precursor	Co-catalyst	Average temperature (°C)	Run time (min)	Polymerization activity (g polymer/mmol (Al) h)	M_w ($\times 10^{-3}$)	PD	MP (°C)
4	[CPh$_3$][B(C$_6$F$_5$)4]	158.3	10	1028.3	251.7	8.3	133.9
4	[CPh$_3$][B(C$_6$F$_5$)4][b]	163.5	10	6491.7	164.7	2.9	133.4
4	[CPh$_3$][B(C$_6$F$_5$)4][c]	165.7	10	4530.3	77.8	2.4	107.1
5	[CPh$_3$][B(C$_6$F$_5$)4][b]	159.0	10	840.4	557.2	2.2	134.4

[a] General homopolymerization conditions: borate activation; reactor temperature initially set at 160 °C; 200 psig of C$_2$; catalyst concentration 200 mmol/l; trityl borate as co-catalyst at B/Al ratio = 0.525; PMAO-IP at 1 mmol as a scavenger, 216 ml of toluene as solvent.

[b] B/Al ratio = 1.05.

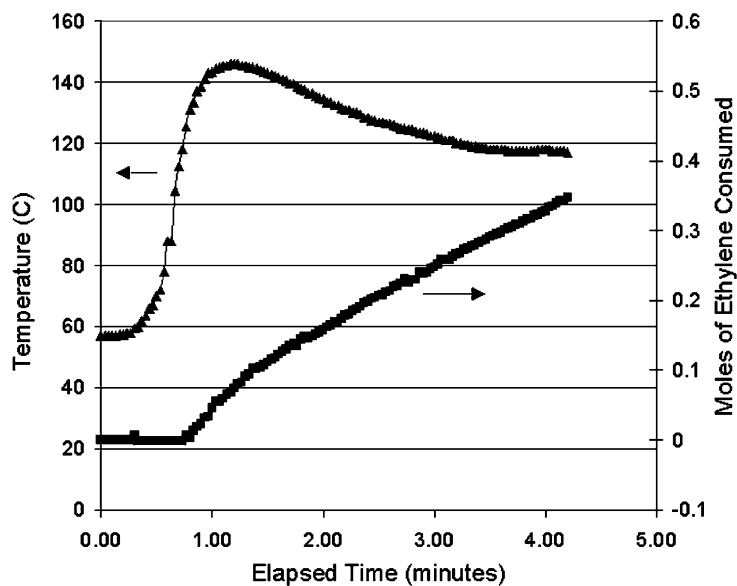[c] Ethylene and 1-octene co-polymerization with 38 ml of 1-octene, B/Al ratio = 1.05.

Fig. 1. Ethylene uptake and temperature rise profile for the reaction of **4** under conditions described in Table 1.

methanide ligand offering a structure reminiscent of an acetylacetonate complex and a remarkable bis(iminophosphorano)methandiide ligand complex (R = Me) (**4**) which is based on a spirocyclic carbon center subtended by two AlMe$_2$ units, each of which is further coordinated by an imine nitrogen. This complex arises simply from the high temperature reaction of bis(iminophosphorano)methane with the appropriate ratio of AlMe$_3$ (Scheme 2). Lower temperature
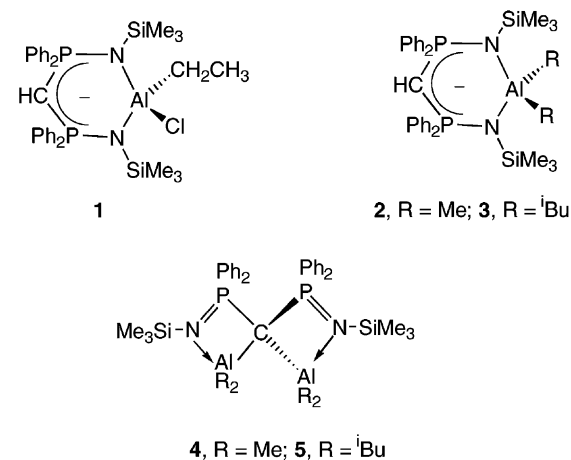
reaction with equimolar stoichiometry yields the aforementioned bis(iminophosphorano)methanides which can be converted to the diide complex [8]. Similar procedures with the butylated aluminum precursor lead to **5**.

The catalytic reactivity of all complexes was evaluated (Table 1) with the overall result that methandiide complexes of the form **4** and **5** proved to be much more
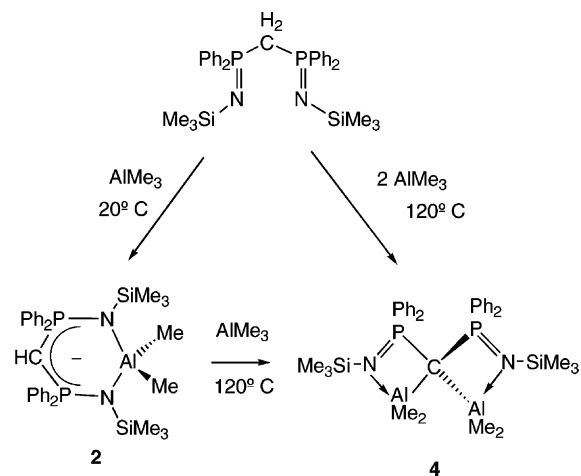
Scheme 1.

Scheme 2.

active than those with the methanide structure (**1–3**). Interestingly, the increased bulk of ligands pendant to the Al nuclei provided by **5** was not beneficial to the process; **4** had much higher activity than **5**. However, the polymer produced using **4** had a lower molecular weight and a lower melting point than that produced using **5**. The catalytic activity of the methanides **1–3** is similar to some of the best examples provided by other single aluminum systems [22,23,27].

The roles of the aluminum catalyst precursor and the activator were examined through comparison tests using **1**. In the first set of tests the catalyst system comprised only **1** without addition of PMAO-IP as an activator. Trityl borate was added as activator in a second set of tests. In no cases were good reaction rates obtained. The activity of the system increased four-fold when trityl borate activation was included. However, no benefit was found from inclusion of PMAO-IP. The data strongly suggest that the activity of complexes of the types **1–3** as catalyst precursors does not arise from conventional alumoxane type activation. Rather, the data suggest that the activity of these systems depends directly on the functionality of the aluminum catalyst precursor complexes themselves. These results contrast with findings for other Al-based polymerization catalysts, including those listed in Table 3. It is noteworthy that the present complexes **1–3** are comparable in structure with the diimines except that there is less steric constraint on one side of the complex and as a consequence they are not particularly catalytically effective structures.

The highly constrained complexes **4** and **5** provide a totally different structural form of the catalyst precursor and **4** is especially active as a precursor to an ethylene polymerization catalyst. However, attempts to co-polymerize ethylene with either propylene or octene using a slurry system at low temperatures were less successful (Table 1). In contrast, ethylene and octene were successfully co-polymerized in solution at 165 °C. We compare the utility and reaction conditions required for our solution system in Table 3 to data from previously reported aluminum diimine [22] and Schiff base [23] catalytic systems. Complexes **4** and **5** are active when used at an average reaction temperature between 50.5 and 163.5 °C (Tables 1 and 3). The range of available reaction temperatures for these systems and the stability and sustained activity of **4** at high reaction temperatures are both noteworthy.

A reaction profile for use of **4** as catalyst in a slurry reactor is shown in Fig. 1. A blank run under identical conditions without the Al catalyst (**4**) produced no polymer, thus possible transition metal contamination from the reactor can be ruled out. The initial reaction rate appears to be low at the starting temperature of (in this case) 57 °C. At this stage, the reaction is proceeding with only the dissolved ethylene in the solution and no fresh feed of ethylene is entering the reactor—hence the flat line for the consumption curve. After about 15 s, a rapid exotherm is apparent which raises the temperature of the reaction mixture by about 90 °C over a period of 45 s. Rapid polymerization occurs and the consumption of the initial ethylene charge starts

Table 3
Comparison with literature (solution polymerization)[a]

Aluminum catalyst precursor	Co-catalyst	Average temperature (°C)	Run time (min)	Polymerization activity[a] (g polymer/(mmol Al h bar))	M_w ($\times 10^{-3}$)	PD	MP (°C)	Reference
Al–amidinate complex	$[CPh_3][B(C_6F_5)_4]$[b]	85	30–60	3	184.7	2.3	138	[22]
Al–Schiff base complex	$B(C_6F_5)3$[c]	40	60	0.10	23	2.9	?[d]	[23]
4	$[CPh_3][B(C_6F_5)_4]$[e]	163.5	10	477	164.7	2.9	133.4	This work

[a] Normalized to 1 atm C_2 feedstock pressure.

[b] Polymerization done at 2 atm ethylene pressure.

[c] Polymerization done at 5 atm ethylene pressure.

[d] Information not supplied.

[e] General homopolymerization conditions: trityl borate activation; reactor temperature initially set at approximately 50 °C; 200 psig of C_2; catalyst concentration 200 mmol/l; trityl borate as co-catalyst at B/Al ratio = 1.05; PMAO-IP at 1 mmol as a scavenger 216 ml of toluene as solvent.

the flow of ethylene into the reactor which evident in the steep increase of the molar consumption curve. The temperature then gradually drops to a steady-state value that is considerably higher than the initial temperature of the reactor. This steady-state temperature is maintained until termination of the reaction. The rate of ethylene uptake varies approximately linearly with inverse temperature from about 1 min after the initiation to termination of the reaction. The apparent activation energy over this period is 6.6 kcal/mol. The present systems appear to have higher activation energy than the previously reported systems [22,23], however, kinetics of polymerization of olefins is complex [28] and so the apparent activation energy is a composite value for the overall process [29]. Nevertheless, the value of the apparent activation energy suggests that the rate controlling step in this region of the reaction profile is the propagation step.

It is notable that the dialuminum complexes **4** and **5** are much more effective catalysts than the single metal species **1**–**3** (or that of Kim et al. [27]) which lends support to the proposal derived from a recent theoretical analysis [30] that dinuclear aluminum systems should be better catalysts than the single aluminum species. This new dinuclear mechanism may be inhibited by the presence of bulky substituents on the Al and this would explain the reduced activity of **5** versus **4**.

The dependence of catalytic activity on the structure of the catalyst precursor alone, and not on an alumoxane activator, the range of operating conditions available, and the high polymerization activity found to date show that the present complexes represent a new type of useful transition metal-free polymerization catalyst. The structures of the complexes allow systematic variation of the steric and electronic environments of the catalytic center and therefore, offer the opportunity for development of new polymerization and co-polymerization catalyst systems. The provision of dinuclear aluminum systems which offer high polymerization activity opens new directions in the development of new, simple, aluminum-based ethylene polymerization catalysts.

Acknowledgements

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