New Highly Active and Selective Ethylene Oligomerization Catalysts Based on Cationic Diamide Zirconium Complexes

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SUMMARY: Group 4 complexes based on the diamide ligand, $[Me_3CN(SiMe_2)_2NCMe_3]^{2-}$, have been investigated as possible catalysts for olefin conversions. The dialkyl complexes, $(Me_2SiNCMe_3)_2ZrR_2$ (R = CH_2Ph, Me), were converted into zwitterionic (X-ray: $\{Me_2SiNCMe_3\}_2Zr(\eta^1\text{-Bz})\{\eta^n\text{-}BzB(C_6F_5)_3\}$), or cationic mono-alkyl compounds by reaction with $B(C_6F_5)_3$ or borate reagents. These electrophilic species catalyzed ethylene *oligomerization,* affording highly linear *alpha*-olefins under mild conditions (C_6 fraction > 99.5 % 1-hexene at 50 °C, 6 bar). The highest activities (290 Kg/g Zr.h) were obtained in toluene solvent using tri-*iso*-butylaluminium (TIBA) as scavenger. The catalyst exhibited activity decay in alkane solvent, which was countered by replacement of TIBA by more crowded trialkylaluminium scavengers or branched alkylaluminoxane scavengers. The product consisted primarily of linear alpha-olefins (LAO) with low levels of remote-branched AO's. These are formed by successive insertion of higher olefin and one or more ethylenes in a growing chain, followed by chain transfer.

Introduction

Group 4 complexes with dianionic diamide ligands[1-4) have received considerable attention as metallocene (and Constrained Geometry) alternatives, partly due to claims of living olefin polymerization.[5,6) The interest derives from the novel reactivity expected for highly electrophilic and sterically open cationic metal complexes of the form, $[N_2ZrR]^+$ (N_2^{2-} = $[RN\text{-bridge-}NR]^{2-}$; maximum 10-electron count), as well as the relatively facile synthesis of diamide ligands.

Our goal was to develop new Group 4 olefin polymerization catalysts by systematically varying the bridging group in the diamide complexes, $\{(Bridge)(NCMe_3)_2\}ZrX_2$ (Fig.1) so as to better understand the required ligand environment for catalysis by cationic metal-alkyl species. Cationic benzylzirconium complexes stabilized by the robust dimethylsilicon-bridged diamide ligand (**A**) were found to exhibit unusual *single* insertion of olefins and alkynes, but showed very low ethylene polymerization activity.[3) In contrast,

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the diamide ligand with a Si-C-Si bridge (**C**) was found to be susceptible to facile C-H bond activation involving the ligand methylene group.7) Benzyl group abstraction (with $B(C_6F_5)_3$ or on protonolysis) from the dibenzyl complex resulted in well-characterized ligand metallation products, such as $\{\eta^3\text{-}(Me_3CNSiMe_2CHSiMe_2NCMe_3)\}Zr\{\eta^n\text{-}PhCH_2B(C_6F_5)_3\}$. These electrophilic complexes were also inactive in ethylene polymerization. We postulated that complexes of the Si_2-bridged diamide ligand (**B**)8,9) would be less susceptible to metallation than those with the SiCSi-bridged ligand (**C**), whilst affording a more crowded environment (than in complexes with Si-bridged ligand, **A**) at the cationic active centre, hindering blocking coordination of Lewis base or anion.

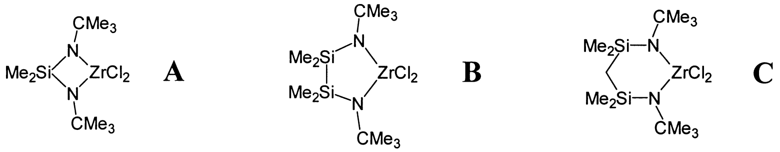


Fig.1: Variation of the bridging group in Group 4 diamide chemistry

Our attempts to develop new olefin polymerization catalysts by diamide ligand variation led to the unexpected discovery of a new class of active ethylene *oligomerization* catalysts based on complex family **B**, which is the subject of this report.10,11)

Cationic Group 4 Diamide Complexes

The bulky diamine ligand $Me_3CNH(SiMe_2)_2NHCMe_3$ was routinely prepared in 200 g amounts from hexamethyldisilane12) via the two-step synthesis (93 % and 86 % isolated yields, respectively) shown in Fig.2.9-12) Double deprotonation of the ligand and reaction with $ZrCl_4$ afforded the analytically pure $\{Me_2SiNCMe_3\}_2ZrCl_2(THF)$.7,10,11) Treatment of this complex with magnesium or lithium alkylating agents, followed by cooling pentane solutions, afforded the analytically pure crystalline dibenzyl (**1**) and dimethyl complexes (**2**), respectively (Fig.2)7,10)

An alternative larger scale preparation of the dibenzyl complex avoided purification of the zirconium dichloride intermediate. The crude toluene-soluble fraction of the reaction of the diamide dianion with $ZrCl_4$ was utilized in the reaction with $PhCH_2MgCl$ and the dibenzyl product (**1**) obtained by extraction and recrystallization from pentane on a 290 g scale in > 99.5 % NMR purity (yields in last two steps: 85 % and 78 %).

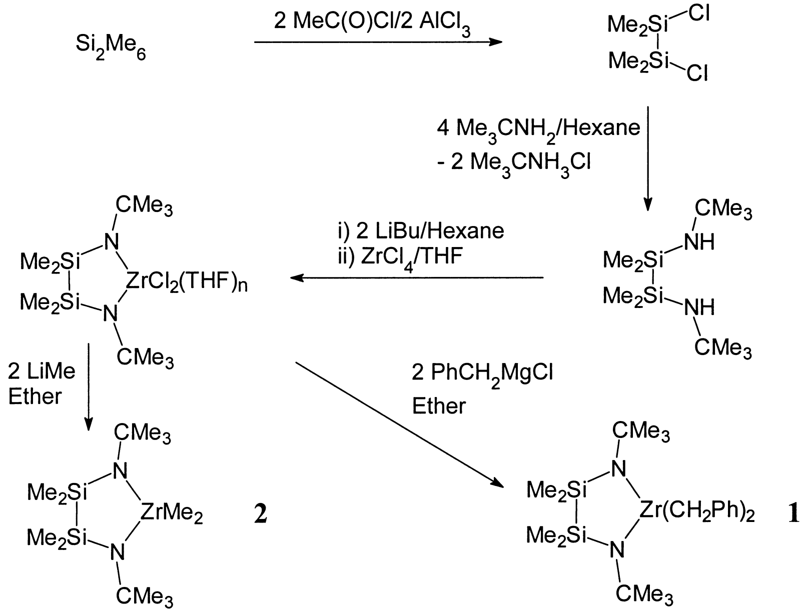


Fig.2: Preparation of dialkyl complexes supported by a diamide ligand

Zwitterionic complexes were cleanly obtained on reaction of the dialkyl complexes **1** and **2** with $B(C_6F_5)_3$ (Fig.3).7,10) Anion coordination to the cationic zirconium centre is clearly shown by multinuclear NMR studies, in particular the characteristic chemical shift difference between the *para* and *meta*-fluorines in the ^{19}F NMR spectrum (benzyl: $\Delta(\delta_p-\delta_m)$ = 3.50 ppm, 2.8 ppm in free anion; methyl $\Delta(\delta_p-\delta_m)$ = 4.35 ppm, 2.5 ppm in free anion).2-4)

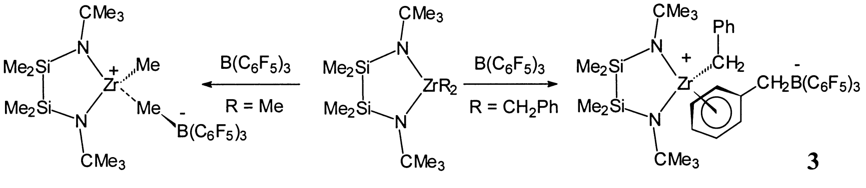


Fig.3: Alkyl group abstraction with $B(C_6F_5)_3$

Coordination of the benzylborate anion to zirconium in **3** in the solid state was also confirmed in the X-ray structure (Fig.4).7) The benzene ring exhibits an usual coordination which might best be described as eta-3, with three short Zr-C(ring) distances, which compares to η^5- and η^6-benzyl coordination in related zwitterionic species.12,13)

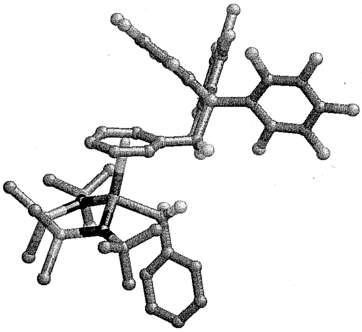


Fig.4: X-ray structure of $\{Me_2SiNCMe_3\}_2Zr(\eta^1\text{-}Bz)\{\eta^n\text{-}BzB(C_6F_5)_3\}$ (**3**). Key distances in Å. Zr-C_{para}, 2.630 (3); Zr-C_{meta}, 2.704(3); Zr-C_{ortho}, 2.845(2); Zr-C_{ipso}, 2.975(2). Zr-C_{benzyl}, 2.287(2). Zr-N, 2.031(2), 2.026 (2)

Treatment of complexes **1** and **2** with DAN-FABA ($[PhMe_2NH][B(C_6F_5)_4]$) or TRI-FABA ($[Ph_3C][B(C_6F_5)_4]$) resulted in clean alkyl abstraction.7) The initially formed alkylzirconium cations are stabilized by coordination of NMe_2Ph or, possibly, solvent (S). Although the aniline-coordinated benzyl cation **4** was stable at 25 °C, the other products were rapidly and cleanly converted to other species, as shown in Fig.5. The thermodynamic products of the TRI-FABA reaction are tentatively postulated to be dimeric dicationic complexes.3)

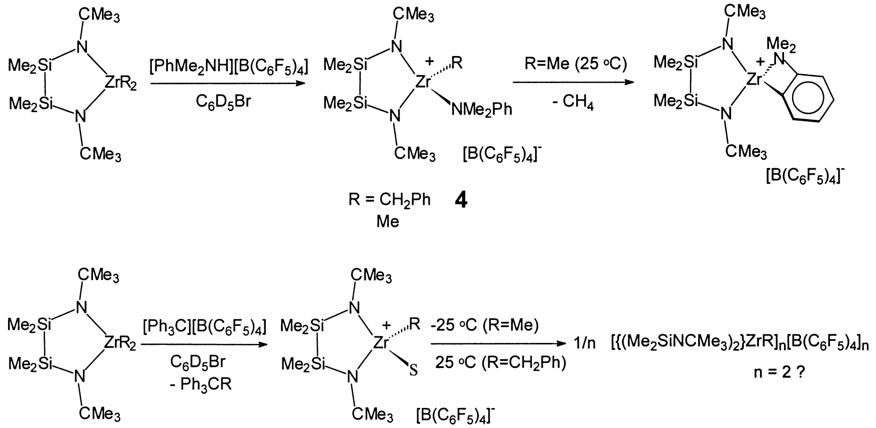


Fig.5: Preparation of cationic alkylzirconium complexes and postulated decay products

Reactivity with Olefins

Prior to the autoclave studies of the electrophilic diamide complexes, an NMR investigation of the olefin reactivity of the benzyl cations in C_6D_5Br solvent was performed. Reaction of the benzyl species obtained from **1** and $B(C_6F_5)_3$ or DAN-FABA, with a single equivalent of ethylene or propylene afforded clean mono-insertion products, $[\{Me_2SiNCMe_3\}_2Zr(\eta^1\text{-}CH_2CHRCH_2Bz)(L)]^{0/+}$ (R = H, Me; L = $[\eta^n\text{-}PhCH_2B(C_6F_5)_3]^-$ or NMe_2Ph).[3,7] Stronger coordination of the benzylborate anion or NMe_2Ph to the alkylzirconium cation than to the starting benzyl cations presumably lies behind the lower reactivity of the insertion products. However, in the case of ethylene, addition of a larger excess of olefin resulted in multiple insertion and (with > 10 equivalents ethylene) the formation of ethylene oligomers, including $PhCH_2(CH_2CH_2)_nCH{=}CH_2$. This contrasts to the dimethylsilicon-bridged diamide system, where only single olefin insertion occurred, presumably because the second equivalent of olefin could not displace the coordinated anion or Lewis base.[3]

Preliminary catalytic testing under higher ethylene pressures was undertaken with zirconium and hafnium alkyl complexes and three activators. As summarized in Table 1, catalytic ethylene oligomerization was observed, with the highest activities using DAN-FABA or TRI-FABA as activator.[7,10] Rather high catalyst intakes were required due to the lack of an additional scavenger, leading to high reaction exotherms (Table 1). The activities found therefore afford only a crude comparison of the effectiveness of the different catalyst systems.

In all cases a Schulz-Flory distribution of ethylene oligomers was found, characterized by a constant molar ratio $C_{n+2}^{=}/C_n^{=}$ (K factor). The K factor varied in a narrow range 0.69-0.77 for zirconium and 0.60-0.62 for hafnium. Product quality, as exemplified by the proportion of the $C_6^{=}$ product that is 1-hexene was, generally, very high for zirconium (> 99 %) and somewhat lower for hafnium. As shown in Fig.6, branched 2-ethyl-1-butene was the most significant contaminant, and internal olefins were present in very low amounts.[15-17] The nature of the olefin products, particularly the contaminants present in higher olefins, is discussed in more depth below.

Table 1. Ethylene oligomerization with Group 4 diamide cations in absence of alkylaluminium scavenger (7.1 bar ethylene, 190 mL toluene, 10-30 min)[a]

Complex	Activator	Intake (μmol)	Temp. (°C)[b]	Yld. $C_4^=$-$C_{30}^=$ (g)[c,d]	Activity $C_4^=$-$C_{30}^=$ (Kg/g Zr.h)	K factor[e]	Purity $C_6^=$ fraction (% 1-hexene)
N_2ZrBz_2 (**1**)	$B(C_6F_5)_3$	200	25 (49)	18.0	2.0	0.70	99.7
N_2ZrBz_2 (**1**)	$B(C_6F_5)_3$	200	50 (62)[f]	4.1	0.5	0.69	98.5
N_2ZrBz_2 (**1**)	DAN-FABA	100	25 (64)	41.9	28.0	0.71	99.9
N_2ZrBz_2 (**1**)	TRI-FABA	100	25 (66)	59.9	39.4	0.70	99.8
N_2ZrMe_2 (**2**)	$B(C_6F_5)_3$	200	25 (47)	9.0	1.0	0.77	99.0
N_2ZrMe_2 (**2**)	DAN-FABA	100	25 (43)	21.8	14.3	0.72	99.9
N_2HfBz_2	$B(C_6F_5)_3$	200	25 (28)	0.7	0.03	0.60	97.3
N_2HfBz_2	TRI-FABA	200	25 (79)	129.1	42.7	0.62	95.5

a) Oligomerizations performed in jacket-cooled, mechanically stirred 1L steel autoclave, with catalyst injection under pressure.
b) Figure in brackets is maximum reaction temperature
c) Yield by GC (n-hexylbenzene internal standard)
d) Variable low levels of insoluble residue obtained, mixture of less soluble higher olefins & polymer
e) Determined by GC analysis of $C_4^=$-$C_{30}^=$ range of olefins
f) 5.6 bar ethylene

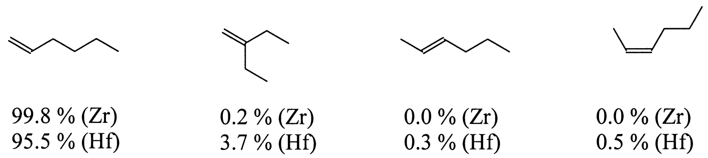


Fig.6: Typical distribution of $C_6^=$ products (TRI-FABA, 25 °C; Table 1, entries 4 and 8)

Ethylene Oligomerization in Presence of Alkylaluminium Scavengers

Ethylene oligomerization catalysis was studied in depth for the **1**/DAN-FABA catalyst. Application of tri-*iso*-butylaluminium (TIBA) as scavenger allowed much lower catalyst concentrations to be applied (resulting in isothermal conditions) without influencing the nature of the olefin product, as shown in Table 2. The existence of a catalyst threshold for activity is suggested by the lower activity with 2.5 μmol catalyst in comparison to 5 μmol.

Table 2. Ethylene oligomerization using TIBA as scavenger (**1**/DAN-FABA, 3 bar, 50 °C, 400 mL toluene, TIBA in premix and toluene ca. 1:3 ratio)

Catalyst (μmol)	TIBA (μmol)	Time (min)	Yld. $C_4^=$-$C_{30}^=$ (g)	Activity $C_4^=$-$C_{30}^=$ (Kg/g Zr.h)	Purity $C_6^=$ fraction (% 1-hexene)
30.1[a]	480	25	86.5	75.7	98.8
5.0	550	50	85.0	224.0	99.7
2.5	540	25	8.0	84.8	99.8

a) Effective ethylene pressure 1-2 bar due to high consumption & flow limitations

The effect of temperature and pressure on oligomerization catalysis was studied in the four experiments shown in Fig.7. GC analysis of samples removed from the autoclave at regular intervals allowed the dependence of yield and product quality on reaction time to be determined. Comparison of the yield-time relationship for the reactions at 3 bar and 6 bar (50 °C) shows that activity increases with pressure. Initial activity (at 6 bar pressure) also increases with temperature (35->50->70 °C), but catalyst decay is clearly higher at 70 °C. The highest activity over a 2 h period (290 Kg/g Zr.h) was observed at 50 °C/6 bar. The K factor shows a remarkable insensitivity to changes in temperature and pressure (range 0.74-0.76 in these experiments), whereas, as discussed later, product quality is highly sensitive to these factors.

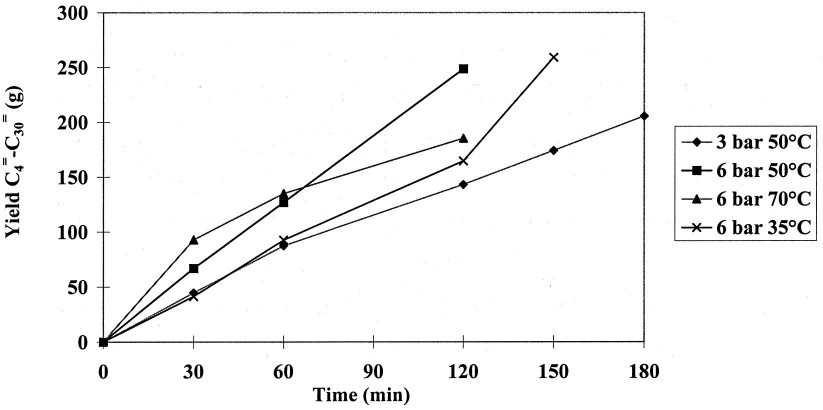


Fig.7: Effect of temperature and pressure on ethylene oligomerization (4.9 μmol **1**/DAN-FABA, ca. 0.55 mmol TIBA; 400 mL toluene; yield determined by GC analysis of reaction mixture samples)

Alkane or olefin (product) solvent might be preferable to aromatic solvents for industrial ethylene oligomerization processes. Whereas the **1**/DAN-FABA system exhibited no significant decay in toluene (1 h, 50 °C, 6 bar), a comparable experiment in *iso*-octane (2,4,4-trimethylpentane) showed both lower initial activity and high decay (Fig.8). The K factor and product quality were effectively identical in the two solvents. A study of the effect of activator and scavenger on catalysis in *iso*-octane solvent was initiated, with the emphasis on preventing catalyst decay.

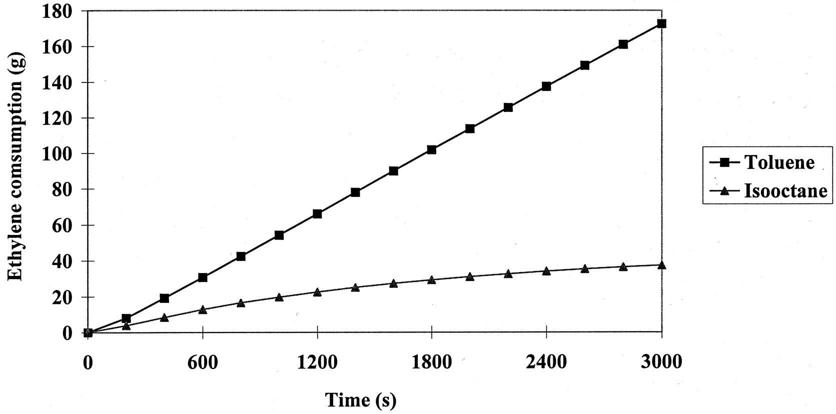


Fig.8: Effect of solvent on ethylene consumption (5 μmol **1**/DAN-FABA, 3 bar, 50 °C, ca. 0.55 mmol TIBA, 400 mL solvent; ethylene consumption from mass-flow measurements)

The effect of activator and activator/Zr ratio on catalysis in *iso*-octane solvent is illustrated in Fig.9. DAN-FABA, TRI-FABA and $B(C_6F_5)_3$ were compared in 1:1 molar ratio with **1**. With $B(C_6F_5)_3$, negligible activity was found under these conditions. The two borate activators showed similar initial activity but catalyst decay was somewhat more rapid with TRI-FABA. A two-fold excess of DAN-FABA resulted in similar initial activity but much higher catalyst decay, perhaps due to formation of dicationic mono-zirconium species.[18] With a half equivalent of DAN-FABA a similar decay *profile* was observed as with equimolar reagents, but with half the total activity.

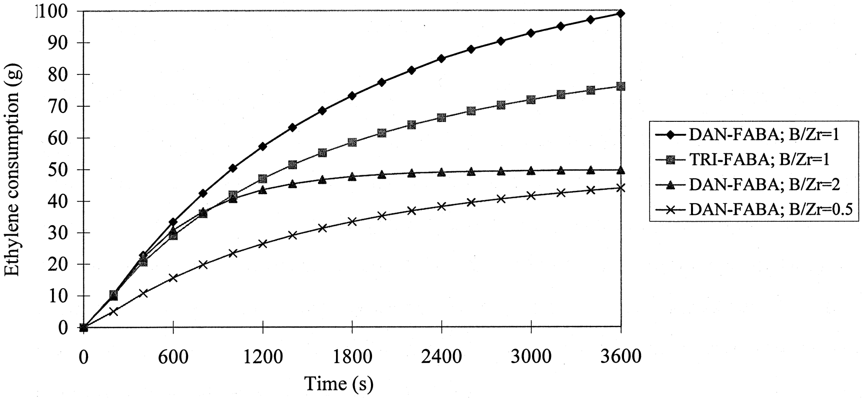


Fig.9: Effect of activator and molar ratio of complex **1** and activator on ethylene consumption (15 μmol **1**, 3 bar, 50 °C, ca. 0.55 mmol TIBA, 275 mL *iso*-octane)

The effect of the amount of TIBA scavenger on catalysis is illustrated in Fig.10. The decay rate increases with TIBA concentration, whereas the initial activity is invariant, suggesting that catalyst decay involves slow reaction of the active species with TIBA. From this data it is clear that a low aluminium concentration (ca. 0.5 mM) is sufficient for scavenging purposes, at least under these experimental conditions.

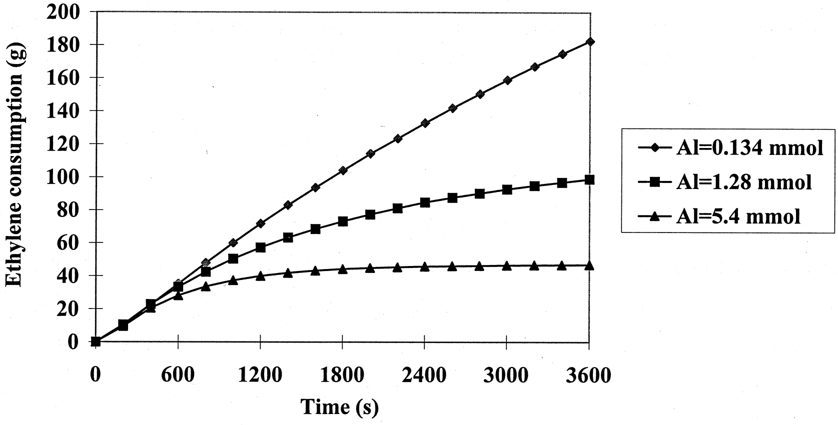
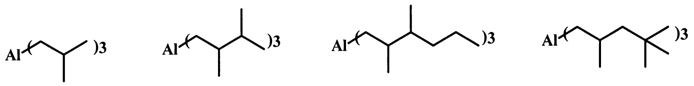


Fig.10: Effect of amount of TIBA scavenger on ethylene consumption (15 μmol **1**/DAN-FABA, 6 bar, 50 °C, 275 mL *iso*-octane)

Alternative Scavengers to TIBA

We hypothesized that reaction between the active centre and scavenger might be suppressed with bulkier alkylaluminium reagents. In unrelated studies we have shown that alkylaluminoxanes (Fig.11), formed on hydrolysis of alkylaluminiums (water/Al ratio 1:2), with *beta,gamma-* or *beta,delta*-branched alkyl groups, are excellent cocatalysts (often superior to MAO) in metallocene-based olefin polymerization catalysis.[19,20)



TIBA **I** **II** **TIOA**

$$2\ AlR_3 + H_2O \xrightarrow[4\text{-}10\ ^oC]{Toluene} AlR_3 + 1/n\ \{Al(R)O\}_n$$

Fig.11: Branched alkylaluminiums and alkylaluminoxanes used as scavengers (NMR of hydrolysis products consistent with equimolar trialkylaluminium and alkylaluminoxane)

These alkylaluminoxanes are not (in their own right) *activators* in this oligomerization system. However, we decided to investigate these and the bulky alkylaluminiums as *scavengers* with DAN-FABA as activator.

Use of alkylaluminiums I, II and tri-*iso*-octylaluminium (TIOA) as scavenger resulted in an approximate doubling of the oligomerization activity (over 1 h) relative to TIBA, primarily due to lower catalyst decay (Fig.12).[21)]

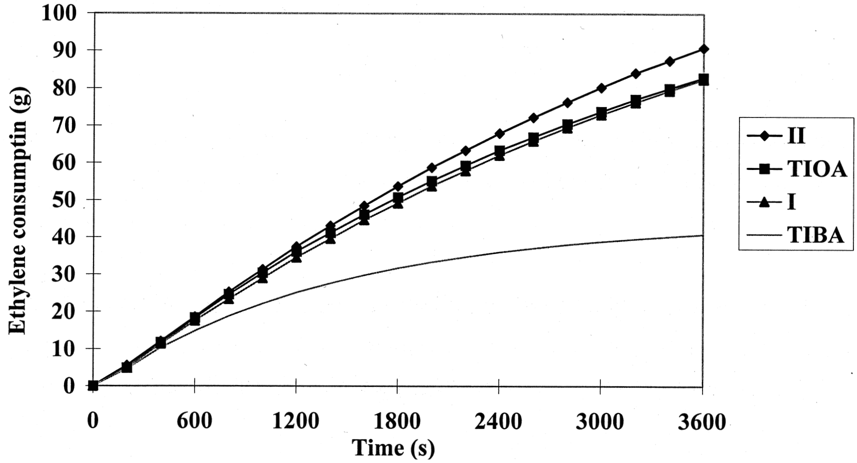


Fig.12: Influence of branched *trialkylaluminium* scavenger on ethylene consumption (7.5 μmol **1**/DAN-FABA, 0.6 mmol Al, 6 bar, 50 °C, 275 mL *iso*-octane)

Branched alkylaluminoxanes were found to be even more effective scavengers than the branched trialkylaluminiums, with virtually no decay observed over 1 h (50 °C, 6 bar).[21)] TIBAO, and the three aluminoxanes with doubly branched alkyl groups, exhibited similar kinetic profiles with activities in the range 100-110 Kg/g Zr.h (Fig.13). In contrast MAO as *scavenger* afforded even lower activity than with TIBA. In other studies (in *toluene* solvent in the absence of a borate activator) MAO was found to activate $\{Me_2SiNCMe_3\}_2ZrCl_2(THF)_n$ (n = 0,1), but the ethylene oligomerization activity was rather low. The poor scavenging ability of MAO may be related to the low solubility in the *alkane* solvent used. Information on the influence of scavenger on ethylene oligomerization is summarized in Table 3. No significant effect on the K factor or product quality of scavenger variation was detected.

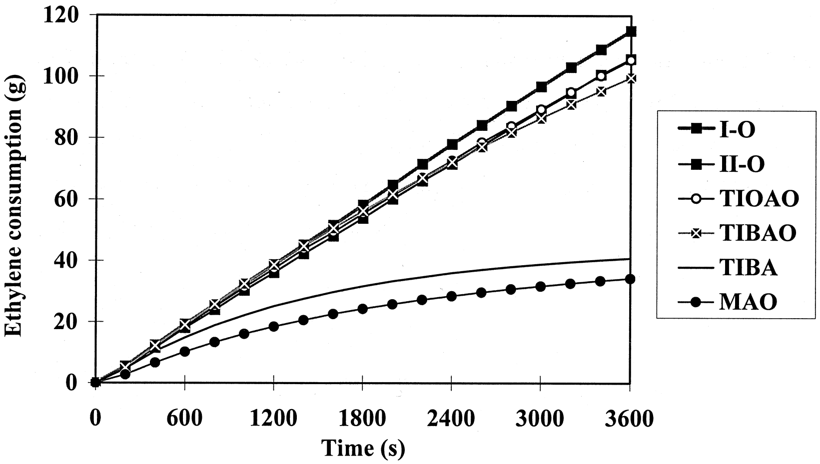


Fig.13: Comparison of branched *alkylaluminoxane* scavengers with MAO and TIBA (7.5 μmol **1**/DAN-FABA, 0.6 mmol Al, 6 bar, 50 °C, 275 mL *iso*-octane)

Table 3. Effect of scavenger on ethylene oligomerization activity and product quality (7.5 μmol **1**/DAN-FABA, 0.6 mmol Al, 6 bar, 50 °C, 60 min, 275 mL *iso*-octane)

Scavenger	Activity $C_4^=$-$C_{30}^=$ (Kg/g Zr.h)	K factor	Purity $C_6^=$ fraction (% 1-hexene)
TIBA	43.0	0.73	99.7
TIBAO	105.4	0.70	99.7
I	83.2	0.73	99.7
I-O	100.6	0.69	99.7
II	90.0	0.73	99.7
II-O	112.5	0.70	99.7
TIOA	85.0	0.71	99.7
TIOAO	105.8	0.73	99.7
MAO	38.7	0.72	99.7

Nature of alpha-Olefin Product of Oligomerization

It has already been noted that the only significant $C_6^=$ by-product was 2-ethyl-1-butene. GC analysis of *higher* olefins indicated that linear alpha-olefins (LAO) always represented the major product, although the proportion of other products increased with carbon-number (e.g. for $C_{18}^=$ fraction, Table 4, 6.1-13.7 % are non-LAO by GC). However, ^{1}H NMR analysis of the non-volatile oligomer fraction ($C_{10}^=$ and higher) revealed that > 98 % of the product (depending on the temperature, pressure and total product yield, see Table 4) contained a vinyl end group (CH_2=CHR) and vinylidene products (CH_2=C(R')R) accounted for < 1 %. This apparent discrepancy was resolved using ^{13}C NMR spectroscopy, which revealed the presence of alkyl branching remote from the end group. Two kinds of branches were distinguished, namely ethyl and butyl (or longer), in amounts (5.9 - 14.0 %) consistent with the proportion of non-LAO products observed by GC methods (Fig.14).

Table 4. Constituency of non-volatile olefin product obtained in toluene as determined by NMR and GC analysis (4.9 μmol **1**/DAN-FABA, ca. 0.55 mmol TIBA, 400 mL toluene)

Temp.	**Pressure**	**Yld.**	**Olefins (^{1}H NMR)**			**Olefins with branching (^{13}C NMR)**			**Non-LAO content**
		$C_4^=$-$C_{30}^=$	vinyl	cis/trans	vinylidene	Ethyl	Butyl+	**Sum**	**of $C_{18}^=$ fraction (GC)**
(°C)	(bar)	(g)		mol %			mol %		**mol %**
50	3	205	98.2	1.1	0.7	6.3	7.7	**14.0**	**13.7**
35	6	260	99.2	0.5	0.3	2.8	3.1	**5.9**	**6.1**
50	6	249	98.7	0.7	0.6	4.7	4.9	**9.6**	**8.5**
70	6	185	98.4	1.0	0.6	3.6	5.9	**9.5**	**10.3**

It may therefore be concluded that the major non-LAO products of ethylene oligomerization are remote-branched AO's, formed by insertion of 1-butene, 1-hexene or higher AO's in a growing chain, followed by one or more ethylene insertions and termination by *beta*-hydrogen transfer. As detailed in Table 4, higher reaction temperatures or lower pressures result in a reduction in the product quality (LAO content) reflecting a large increase in remote branching and a much smaller increase in vinylidene and internal olefin formation.$^{16,17)}$

Terminal vinylidenes < 1 mol %

Remote-branched alpha-olefins 6-14 mol %

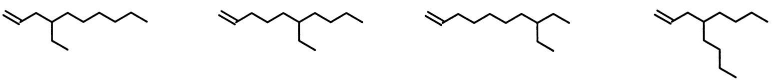


Fig.14: Postulated structures of branched AO products of oligomerization ($C_{12}^=$ fraction)

Conclusions

Electrophilic Group 4 complexes of the diamide ligand, $[Me_3CN(SiMe_2)_2NCMe_3]^{2-}$, are not susceptible to the metallation found for the Si-C-Si analogue, and are sufficiently crowded to weaken the blocking (anion, solvent, base) coordination *proposed* to be responsible for the low olefin polymerization activity of the more open (Si-bridged) diamide system. Well-characterized neutral and cationic alkyl compounds have been prepared, although in the absence of anion ($[BzB(C_6F_5)_3]^-$) or Lewis base (NMe_2Ph, olefin ?) coordination to zirconium, simple mono-zirconium alkyl cations are cleanly converted to other species.

These electrophilic species catalyze ethylene *oligomerization,* affording highly linear AO's under mild conditions ($C_6^=$ fraction > 99.5 % 1-hexene at 50 °C, 6 bar). Use of TIBA as scavenger allows a 20-fold reduction in catalyst intake giving high activities (290 Kg/g Zr.h) in toluene solvent. Lower *initial* activities and high catalyst *decay* are observed in *alkane* solvent. The former may be due to poorer anion-cation separation than in toluene, whereas reaction of TIBA with the active species is implicated in catalyst decay. Decay was countered by replacement of TIBA with more crowded trialkylaluminium scavengers or, even more effectively, branched alkylaluminoxane scavengers. The composition of the product, consisting of LAO's (major) and remote-branched AO's (minor), is consistent with occasional insertion of higher AO product into the growing chain and predominant chain transfer after ethylene (rather than AO) insertion.

The diamide systems represent some of the most active and selective early transition metal ethylene oligomerization catalysts,15,22,23) and compare favourably in selectivity to very recently reported highly active iron- and cobalt-based ethylene oligomerization catalysts.16,17)

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