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Zirconium complexes as catalysts for the oligomerisation of ethylene: the role of chelate ligands and the Lewis acid cocatalyst in the generation of the active species

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Abstract

Highly effective catalysts for the conversion of ethylene into linear α-olefins may be generated in situ from zirconium tetrachloride, a β-aminoketone or β-aminothioketone ligand and an alkylaluminium chloride Lewis acid cocatalyst. Catalysts may also be generated from $ZrCl_4 \cdot 2HL$ adducts (where HL = monodentate, oxygen-bound β-aminoketones), and from bis-ligand complexes of the type $ZrCl_2L_2$ (where L = monovalent, bidentate β-aminoketones or β-aminothioketones) on treatment with an alkylaluminium chloride cocatalyst. Product distribution and catalyst activity can be adjusted by ligand substituent variation and/or by the method of catalyst formation. Catalyst systems generated from preformed complexes, $ZrCl_2L_2$, were in general significantly more active than those formed in situ or from the bis-ligand adducts, $ZrCl_4 \cdot 2HL$. Activities of up to 60,000 turnovers/h were obtained with selected complexes. However, in situ mixtures and bis-ligand adducts generally gave a much narrower oligomer distribution, with up to 95% of the oligomers occurring in the C_4–C_{10} range for a number of the systems tested. In situ NMR (nuclear magnetic resonance) tests indicate that complex ligand/cocatalyst interactions are present and that these new oligomerisation systems are active even under very mild conditions, 30°C and 1 atm ethylene.

Keywords: Zirconium; Oligomerisation; Ethylene; Catalyst; Alpha-olefins; β-Aminoketones

1. Introduction

Although zirconium-based oligomerisation systems have been industrialised by Idemitsu, the active species and mechanistic aspects of these zirconium oligomerisation systems are not well-understood. An examination of the patent and general literature reveals a number of conflicting viewpoints. There is little agreement on the role of the added ligands, the active species, metal oxidation state [1,2] or even the active metal [1–4]. Recently however, it has been generally assumed that active species similar to those found in polymerisation systems are present. The control of catalyst activity through variations in ligand substituents has only recently been demonstrated [5]. No evidence exists to show that product distribution could be varied in a similar manner.

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Except for the initial work by Attridge and coworkers [6,7], in which an ion pair or polar binuclear complex was postulated as the active species for an oligomerisation system containing no cocatalyst, there has been no detailed discussion of reaction mechanisms or of active species. Most oligomerisation systems are ternary systems containing a zirconium source, an added ligand and an alkylaluminium (chloride) cocatalyst. A vast number of ligands have been used in oligomerisation systems but without mention [8–12], except by Young, of their role. According to Young [13], the ligands act primarily as solubilising agents allowing rapid interaction of $ZrCl_4$ with the added cocatalyst, a proposal based on the similar reactivities of $ZrCl_4$:ester adducts and $Zr(O\text{–}i\text{Pr})_4$ with Attridge's $ZrBz_4$ systems. Young discussed the relevant role of titanium(IV) in titanium-based oligomerisation chemistry (only soluble, unreduced titanium(IV) species oligomerise olefins) and generally agreed with Attridge's proposed active species [14,15]. Although soluble zirconium alkoxides or diketonates had previously been used in catalyst systems, the role of the alkoxide, diketonate or other deprotonated ligands had not been examined until recently [12,16–22]. This is surprising when considering, for example, the effect of ligand substituents on catalytic activity in nickel-based oligomerisation systems containing β-diketones [12,16–19, 23,24].

A number of zirconocene-based polymerisation systems were also shown to have oligomerisation behaviour [25,26]. For many of these examples, unfavourable steric factors appeared to induce oligomerisation, e.g., propylene or higher 1-olefins were oligomerised while ethylene was polymerised. More recently, a number of zirconocene-based systems have been used to oligomerise ethylene [27,28], including cationic species formed in situ in the absence of a cocatalyst [29–31]. An active cationic species similar to that suggested for polymerisation and that originally proposed by Attridge for oligomerisation is therefore highly likely.

Theoretical studies into β-hydride elimination with Ziegler–Natta type polymerisation systems using permethylscandocenes have indicated a four-centre transition state with a positive charge build-up on the β-carbon (Fig. 1) and a positive activation energy for the reaction [32]. Bercaw states that steric interactions are important in this hindered system, i.e., the *n*-butyl group eliminates more slowly than *n*-propyl, due to greater interaction of the β-alkyl substituent with the Cp methyls in the transition state. Electron-releasing groups on the β-carbon increase rates while electron-withdrawing groups have the opposite effect. Jordan [33,34], working with methyl-substituted zirconocenes, observed similar effects on β-hydride elimination rates for zirconium complexes.

For Cp-based polymerisation systems, increasing the Lewis basicity of the Cp ring decreases the rate of β-hydride elimination. Where the Lewis acidity of the metal centre is sufficiently reduced by increasing the number of Lewis basic Cp groups attached to the metal [35], e.g., for Cp_3ZrH/Et_3Al systems, living polymerisation catalysts are generated in which the rate of β-hydride elimination is negligible. It is believed therefore, that an increase in the Lewis acidity of the metal centre decreases insertion rates relative to elimination, thereby increasing the tendency to oligomerisation [28].

Few studies have examined the complex interactions between ligands and alkylaluminium cocatalysts. Alkylaluminiums react rapidly at low temperature with ligands having acidic protons [36–40], e.g., acetylacetones, quinols, pyridine carboxylic acids or alcohols, whereas reactions with amines, amides, Schiff's bases or α-aminoketones depend on the alkylaluminium

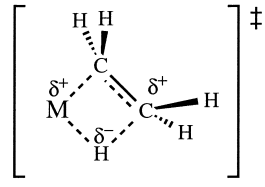


Fig. 1. Proposed β-hydride elimination transition state.

used and the proton basicity. Adduct formation often occurs initially and elevated temperatures are required to promote further reaction [41]. The reaction of alkylaluminiums with α-aminoketones depends on ligand substitution patterns and coordination mode can be difficult to determine by NMR (nuclear magnetic resonance) [42]. There is only one reported reaction of an alkylaluminium with a β-aminoketone; the tetradentate, divalent bis-β-aminoketone, Et(-HNacac)$_2$, formed from the reaction of ethylene diamine with two equivalents of acetylacetone [43]. In this case, the ligand reacts on contact with TEA at room temperature to release two equivalents of ethane. On heating for several hours at 70°C, further reaction occurs, releasing another two equivalents of ethane.

We have investigated a range of chelating ligand systems that may be employed to generate and stabilise a metal centre with high Lewis acidity and have previously reported the synthesis of a range of bis-ligand adducts and complexes of zirconium [44,45]. Of interest is the role the ligand plays in the oligomerisation process. If, in contrast to the proposal of Young [13], the ligand remains associated with the metal centre during catalysis, then catalytic activity may be modified through ligand variations. It would be expected that electron-withdrawing groups on the ligand would then help to increase metal centre Lewis acidity and increase ligand hemi-lability. Herein, we present for the first time a detailed examination of zirconium catalysts containing the β-aminoketone ligand system where the catalyst activity and product distribution can be controlled by variations to the substituents on the backbone carbons and on the amino nitrogen.

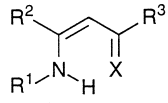
2. Experimental

All syntheses and catalytic reactions were carried out under purified nitrogen using normal Schlenk techniques. Solvents were dried and purified using standard techniques. Infrared spectra were recorded on a Hitachi 270-30 spectrometer, ^{1}H- and ^{13}C-NMR spectra were recorded with a Varian EM390, Bruker CXP 200 or a Bruker AM300. The gas chromatography (GC) analyses were carried out using a HP 5890A with a 50-m BP-1 column using the following conditions: temperature program, 50–260°C; iso, 10°C/min; injection temperature, 300°C; sample, 0.5 μl; carrier gas pressure, 150 KPa nitrogen; FID (flame ionization detector).

The β-aminoketone ligands (Fig. 2) were prepared using known methods either in the presence of a drying agent [46], in refluxing toluene using a Dean–Stark apparatus [47] or by reaction with the TMS–ether of the appropriate β-diketone [48]. The β-aminoketones have been shown to exist in predominantly the aminoketone form [46,49] and will be described as such throughout this paper especially in catalytic solutions where the actual species is often unknown.

The β-aminothioketones are readily obtained from the respective β-aminoketone by treatment with Et_3OBF_4, followed by reaction with NaSH in DCM [50] or by thiolation with Lawesson's Reagent [51]. They are also accessible from dithiolium salts by reaction with a primary amine [52–55]. The synthesis and characterisation of the β-aminoketone bis-ligand adducts Fig. 3 and complexes Fig. 4 is described elsewhere [44].

Catalysis was carried out following the method described by Shiraki et al. [10] and all reactions and transfers were completed using inert gas techniques. The autoclave used in most



X=O;	R^1-HNR^2acR^3ac	(R^1-HNacac where R^2=R^3=Me)
		(R^1-HNtfac where R^2=Me, R^3=CF_3)
		(R^1-HNbzac where R^2=Me, R^3=Ph)
		(R^1-HNbzbz where R^2=R^3=Ph)
X=S;	R^1-HNR^2acSR^3ac	(R^1-HNacSac where R^2=R^3=Me)

Fig. 2. The β-aminoketone ligand nomenclature.

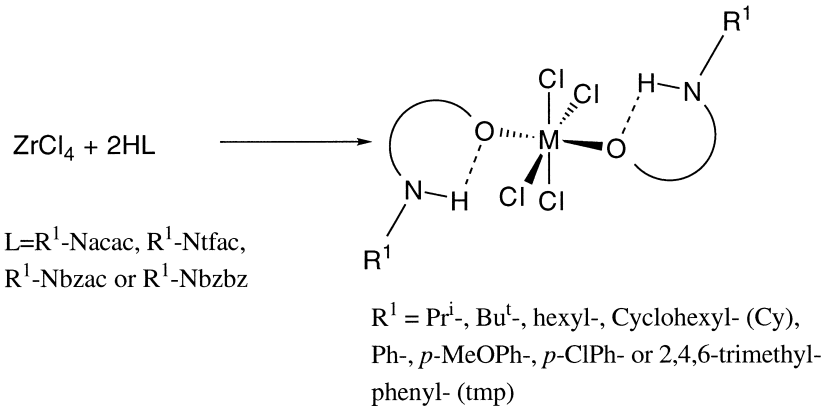


Fig. 3. Synthesis of β-aminoketone adducts of zirconium.

tests has an internal volume of 75 ml and is made from stainless steel, material 1.4571, working pressure and temperature 100 bar and 300°C. A glass liner for the autoclave was used in all reactions and the contents were mixed using a magnetic stirrer. Larger autoclaves (up to 350 ml) were used when required.

2.1. In situ catalytic testing with added free ligands

In a typical run, in a 100-ml Schlenk flask, $ZrCl_4$ (0.1227 g, 0.5265 mmol) was suspended in 20 ml of toluene and stirred for 20 min. Cocatalyst (EASC 2.632 mmol) was added to give an Al:Zr ratio of 10:1 and the suspension stirred at 60°C for 20 min. The suspension was cooled to 25°C and Pr^i–HNacac (0.1487 g, 1.053 mmol) added. A clear, pale yellow solution formed which was stirred for 20 min. An aliquot of the above solution (0.76 ml, 0.02 mmol of zirconium) was transferred to an autoclave containing 19 ml of toluene at 50°C (When thiophene was used as the added ligand, a clear solution did not form, in which case an aliquot of the slurry was transferred to the autoclave.). The autoclave was transferred to a silicon oil bath preheated to 100°C and pressurised with ethylene to 35 bar. The pressure was manually held at 30–35 bar for 1 h. After 1 h, the autoclave was placed in an ice bath to cool, slowly depressurised, 1 ml of 1 M NaOH solution and 0.50 ml of nonane (internal standard for GC analysis) added. The deactivated catalyst solution was filtered through a pre-weighed No. 4 filter paper, the solids rinsed twice with 2 ml of toluene, and the filtrates dried over Na_2SO_4. The filter paper was air-dried and then weighed to give a wax recovery.

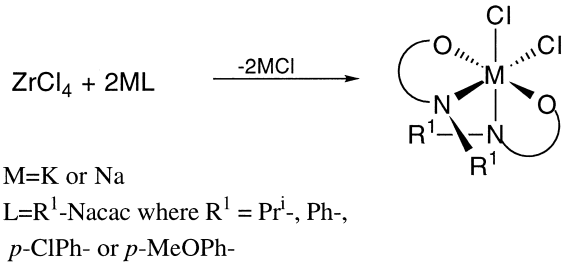


Fig. 4. Synthesis of bis-ligand β-aminoketone complexes of zirconium.

The dried filtrates were analysed by GC and the oligomer distribution calculated relative to the area of the standard nonane peak. A sensitivity of 1:1 was used between nonane and the produced linear α-olefins. The weight of oligomer produced in the C_{10}–C_{30} range was analysed and a Schultz–Flory plot drawn. A line of best fit was calculated by linear regression analysis and a theoretical product distribution was calculated up to C_{40} (an arbitrary cut-off point). A weight distribution of oligomers

was recovered and the weight of recovered waxes was calculated.

2.2. Catalytic testing of bis-ligand adducts and complexes

In a typical experiment, in a 100-ml Schlenk flask approximately 0.5 mmol of $ZrCl_4 \cdot 2Pr^i$–HNacac (1) was suspended in 20 ml of toluene and stirred for 10 min. Cocatalyst was added to give an Al:Zr ratio of 10:1 and the solution stirred at 60°C for 20 min. A clear, pale yellow solution formed. The suspension was cooled to 25°C and an appropriate aliquot was taken to give 0.020 mmol of zirconium in a total of 20 ml of toluene in the autoclave. Catalysis and product workup is as described above for the in situ catalytic testing of free ligands.

When bis-β-aminoketone complexes were tested, the solution was kept at 20°C after adding EASC to avoid catalyst decomposition.

2.3. In situ NMR reactions and catalysis

Reactions between free ligands, adducts and complexes in the presence of ethylene have been monitored by in situ NMR tests. The general procedure was the same for all experiments and is described in detail below for the reaction of $(MeOPh–Nacac)_2ZrCl_2$ with EASC in the presence of ethylene. All reactions were conducted using standard Schlenk techniques.

Into an NMR tube fitted with a screw cap and septa was placed $(MeOPh–Nacac)_2ZrCl_2$ (0.0320 mg, 0.056 mmol) and dry toluene-d_8 (0.28 ml) added to give a solution concentration of 0.2 M. To this suspension was added EASC (0.56 ml of a 1 M solution) to give a final solution concentration of 0.1 M zirconium with a Zr:Al ratio of 1:10. The solution was mixed with a gentle stream of nitrogen and NMR spectra acquired. A gentle-stream of ethylene was passed through the solution at room temperature using a stainless steel needle (or teflon canula) while venting the NMR tube to atmosphere. Further NMR spectra were collected as more ethylene was added or as the temperature was increased.

3. Results and discussion

3.1. In situ testing and adduct formation

Catalyst systems formed in situ by mixing $ZrCl_4$ and a β-aminoketone in the presence of a

Table 1
Effect of Al:Zr ratio and cocatalyst on catalytic activity

Test	Ligand	Al:Zr ratio	Alkylaluminium[a]	TOF[b] (m/m Zr/h)	C_4–C_{10}^c (%)	Wax (%)	α-Olefin (%)
1.1	Pr^i–HNacac	5	EASC	< 500			
1.2	Pr^i–HNacac	10	EASC	8106	92.2	1.5	96.9
1.3	Pr^i–HNacac	20	EASC	11,481	92.5	1.1	87.1
1.4	Pr^i–HNacac	10	EASC[d]	3970	–	–	
1.5	Pr^i–HNacac	10	MAO	–		0.59[e]	
1.6	Pr^i–HNacac	10	DEAC	< 500			

Reaction conditions for all tables (unless otherwise stated): 50 ml autoclave, Zr 0.020 mmol, Zr:Al 1:10, L:Zr 2:1, $T = 100$°C, ethylene 30–35 bar, $t = 60$ min, solvent = 20 ml toluene.
[a]Alkylaluminium = EASC 97%, diethylaluminiumchloride (DEAC) 97%, triethylaluminium (TEA) 1.9 M in toluene, methylalumoxane (MAO) 10.4% in toluene.
[b]TOF: turn over frequency; moles ethylene consumed per mole zirconium per hour.
[c]C_4–C_{10} (%): weight percent of product with 4–10 carbons.
[d]L:Zr 1:1; significant solvent alkylation.
[e]Polymerisation: autoclave filled within 1 min.

Table 2
Effect of β-aminoketone substituent variation on in situ catalytic activity

Test	Ligand	TOF (m/m Zr/h)	α	C_4–C_{10} (%)	Wax (%)	α-Olefin (%)
4.1	Pr^i–HNtfac	2580	0.702	84.9	1.4	91.3
4.2	Cy–HNacac	3956	0.624	93.4	0.9	94.0
4.3	tmp–HNacac	5315	0.676	88.3	1.3	99.5
4.4	hex-HNacac	7527	0.660	89.7	1.7	95.9
1.2	Pr^i–HNacac	8106	0.632	92.2	1.5	96.9
4.5	Bu^t–HNacac	8345	0.692	86.7	0.9	99.0
4.6	Ph–HNacac	15,959	0.720	82.2	1.4	95.0
4.7	*p*-ClPh–HNacac	16,203	0.713	83.5	1.1	97.6
4.8	*p*-MeOPh–HNacac	29,455	0.738	79.4	1.0	98.4
4.4.1	hex-HNacac	7527	0.660	89.7	1.7	95.9
4.4.2	hex-HNbzac	5442	0.641	91.1	2.0	> 95.0
4.4.3	hex-HNbzbz	< 500				
4.6.1	Ph–HNacac	15,959	0.720	82.2	1.4	> 95.0
4.6.2	Ph–HNbzac	12,212	0.734	79.9	1.5	93.3
4.6.3	Ph–HNbzbz	< 500				

Variation of both the amino (4.1–4.8) and ligand backbone substituents (4.4.1–4.6.3).
tmp = 2,4,6-trimethylphenyl.
p-ClPh = *para*-chlorophenyl.
p-MeOPh = *para*-methoxyphenyl.
Cy = cyclohexyl.

cocatalyst are active for the oligomerisation of ethylene (Table 1). An Al:Zr ratio of > 10:1 was required for catalysis. Lower ratios did not lead to effective formation of the active catalytic species and addition of a large excess of EASC did not significantly improve performance. The presence of a potentially reactive amine proton may lead to the consumption of some of the added cocatalyst and therefore, an excess may be needed to achieve optimum activities, as indicated by Young when $Zr(OPr^i)_4 \cdot HOPr^i$ was used.

The EASC proved to be the most effective cocatalyst for catalyst solutions containing Pr^i–HNacac under the conditions tested and was used in all subsequent tests (Table 1). Activities and TOFs of around 8000 were obtained. In general, a relatively short average oligomer weight was produced and the reproducibility with these homogeneous systems was excellent.

Variation of substituents on the β-aminoketones led to large modifications in catalytic activity (Table 2) especially for phenyl-substituted β-aminoketones. This work demonstrates the consequence of systematic variation of ligand substituents in these zirconium-based oligomerisation systems, thereby indicating the importance of the ligand in the active species. Results indicate that electron-withdrawing groups (Ph, ClPh, MeOPh [1] [56]) on the amine increase catalyst activity (Tests 4.6–4.8) while bulky substituents lead to lower activities (Cy, Bu^t and tmp, Tests 4.2, 4.5 and 4.3). This is consistent with the prediction that electron-withdrawing groups lead to more active catalysts by increasing the Lewis acidity of the metal centre. Increased phenyl substitution on the β-aminoketone backbone decreased catalyst activity (Tests 4.4.1–4.4.3 and 4.6.1–4.6.3).

While it was evident that in situ addition of β-aminoketones effectively promotes zirconium-based oligomerisation of ethylene, and that activities and product distributions can be altered through ligand substituent variations, the role of the ligand was not manifest. An impor-

[1] Interaction of the methoxy group with the added cocatalyst effectively makes this an electron-withdrawing group.

Table 3
Comparison of catalytic activity between systems formed in situ and from $ZrCl_4$–bis-β-aminoketone adducts

Test	Ligand/adduct	TOF (m/m Zr/h)	α	C_4–C_{10} (%)	Wax (%)	α-Olefin (%)
1.3	Pr^i–HNacac[a]	8106	0.632	92.2	1.5	96.9
3.1	$ZrCl_4 \cdot 2Pr^i$–HNacac (1)	5301	0.607	92.5	2.7	90.9
3.2	Ph–HNacac[a]	17,245	0.778	70.7	0.8	98.6
3.3	$ZrCl_4 \cdot 2$Ph–HNacac (2)	18,863	0.772	72.6	0.4	99.4

[a] Free ligand added in situ in the same proportion as for the adduct.

tant first step in understanding the catalytic process was to isolate possible intermediates in the catalytic process and test these for catalytic activity. Addition of β-aminoketones to $ZrCl_4$ gave rise to the bis-ligand adducts [$ZrCl_4 \cdot 2$R-HNacac], the isolation and characterisation of which has been previously described [44]. A comparison of catalytic behaviour for catalysts formed in situ and for catalysts formed from the bis-ligand adducts revealed no significant difference (Table 3), suggesting that adducts may initially be formed during the in situ experiments. Both catalyst activities and product distributions were very similar for systems with common ligands. As both catalyst systems seem to give rise to the same catalyst species, screening of new ligands was performed in situ.

Recent work has indicated that catalytic activity for β-diketone-containing zirconium catalyst systems may be correlated to the backbone methine proton NMR shift [5], with a shift to higher field indicating a higher metal centre Lewis acidity, leading to higher catalyst activities. In this study, a comparison of the methine proton shifts of the free ligands indicates that those ligands with the largest methine shifts, which contain phenyl substituents on the ligand backbone, have the lower in situ catalytic activities (Table 4). It is possible that this lower activity is due to steric causes, but as no isolable complexes of these particular ligands have yet been synthesised, it is not known whether there is a problem in forming the zirconium complex or a problem forming the insertion transition state.

Excluding systems where the ligand has phenyl substituents on the backbone, one significant observation was that the use of *N*-phenyl-substituted ligands resulted in high activities with an increase in the average oligomer weight of the products (see Table 3). The reason for this behaviour is discussed later.

Substitution of the hard donor atom, oxygen, by the soft donor, sulfur, could be expected to increase ligand lability and has previously been shown to be very effective in promoting catalysis, especially in nickel-based oligomerisation chemistry [57,58]. As there appears to be an advantage in using soft donor atoms in zirconium-based oligomerisation systems [10], a number of monothio-β-diketones have been tested catalytically in situ (Table 5). Results indicated very effective catalysis but without

Table 4
Characteristic ligand ^{1}H-NMR shifts related to in situ catalytic activity

Ligands	Methine (ppm)	Amine (ppm)	TOF (m/m Zr/h)
Ph–HNacPhac	5.86	13.07	12,212
Ph–HNbzbz	6.095	12.91	< 500
Ph–HNacac	5.15	12.40	15,959
p-ClPh–HNacac	5.153	12.39	16,203
p-MeOPh–HNacac	5.119	12.27	29,455
tmp–HNacac	5.170	11.83	5315
hex-HNbzbz	≈ 7.3[a]	11.5	< 500
hex-HNacPhac	5.63	11.4	5442
Bu^t–HNacac	4.898	11.37	8345
Pr^i–HNtfac	5.214	11.1	2580
Cy–HNacac	4.912	11.0	3956
hex-HNacac	4.92	10.85	7527
Pr^i–HNacac	4.88	10.80	8106

[a] Methine resonance situated under phenyl resonances.

Table 5
Catalytic activity of β-aminothioketone-containing systems

Test	Ligand	Alkylaluminium[a]	TOF (m/m Zr/h)	α	C_4–C_{10} (%)	Wax (%)	α-Olefin (%)
1.2	Pr^i–HNacac	EASC	8106	0.632	92.2	1.5	96.9
5.1	Pr^i–HNacSac	EASC	8374	0.600	83.5	1.5	92.3
5.2	Ph–HNacSac	EASC	11,780	0.829	56.0	0.9	89.3
5.3	Ph–HNacSac	EASC	7252	0.837	47.5	11.8	97.8
5.4	Hex-HNacSac	EASC	1919	0.796	59.8	10.2	94.0
5.5	Pr^i–HNacSac	EADC	5392	0.616		2.3	> 95.0
5.6	Pr^i–HNacSac	DEAC	< 500				
5.7	Pr^i–HNacSac	MAO[b]				0.6 g	

[a] The EASC 97%, DEAC 97%, TEA 1.9 M in toluene, MAO 10.4% in toluene.
[b] Polymerisation occurred; autoclave filled within 1 min.

noticeable improvements over the β-aminoketone systems.

4. Catalytic activity of bis-ligand complexes, $(R\text{-}Nacac)_2ZrCl_2$

Apart from several specific examples, it was apparent that deprotonation of the β-aminoketone ligands was not occurring under catalytic conditions. This was reflected in the catalytic behaviour of the bis-ligand complexes, [$(R\text{-}Nacac)_2ZrCl_2$]. A comparison of the catalytic behaviour of the catalysts formed from the bis-ligand complexes and catalysts generated from the in situ addition of free ligand is shown in Table 6. The catalytic activity differences, especially for the initial tests where $R^1 = Pr^i$, were considerable with systems containing bis-ligand complexes being up to three times as active as the in situ tests, e.g., TOFs of 29,510 as compared to 8106 for the Pr^i–Nacac-containing systems. These oligomerisation rates are among the highest reported for zirconium complex catalysts [5]. Associated with this dramatic increase in activity was a significant change in product distribution with oligomers of higher average molecular weight being formed (higher α-value). It is apparent that the catalytic species formed from the bis-ligand complexes is different from those generated from the in situ mixtures or based on the adduct compounds.

It was also observed that there was a greatly reduced induction time before ethylene consumption started when preformed complexes were used in comparison to in situ testing or testing of adducts, possibly indicating that species formed from the preformed complexes

Table 6
Activity of bis-ligand complexes of zirconium in comparison with in situ testing of the free ligand and bis-ligand adducts

Test	Ligand/complex	TOF (m/m Zr/h)	α	C_4–C_{10} (%)	Wax (%)	α-Olefin (%)
1.3	Pr^i–HNacac[a]	8106	0.631	92.2	1.5	96.9
2.1	$ZrCl_4 \cdot 2Pr^i$–HNacac	5301	0.607	92.5	2.7	90.9
6.1	$(Pr^i\text{–}Nacac)_2ZrCl_2$ (4)	29,510	0.815	60.1	1.4	99.4
3.6	Ph–HNacac[a]	17,245	0.778	70.7	0.8	98.6
6.2	$(Ph\text{–}Nacac)_2ZrCl_2$ (5)	33,726	0.813	60.0	2.4	99.1
3.7	ClPh–HNacac[a]	16,203	0.713	83.5	1.1	97.6
6.3	$(ClPh\text{–}Nacac)_2ZrCl_2$ (6)	32,078	0.858	41.5	1.1	94.5
3.8	MeOPh–HNacac[a]	29,455	0.737	79.4	1.0	98.4
6.4	$(MeOPh\text{–}Nacac)_2ZrCl_2$ (7)	54,420	0.858	46.0	1.0	95.3

[a] Free ligand added in situ in the same L:Zr ratio as for the complex.

may be active at a much lower temperature, i.e., catalysis occurred at or near 50°C, the initial temperature of the autoclave.

The high activities of bis-ligand complex systems is thought therefore to be due to the formation of a more favourable environment around the metal centre which is not possible without ligand deprotonation or apparently through in situ catalyst generation. The complexes have a favourable *cis*-chloride configuration [44] which is also thought to be important for active catalyst formation where a Cossee mechanism is proposed [41]. To further evaluate these reactions, $(R^1\text{-Nacac})_2ZrCl_2$/EASC systems were examined by NMR.

4.1. In situ NMR studies of free ligand / EASC systems

The large variation in catalytic activity between systems containing *N*-phenyl- and the *N*-alkyl-substituted β-aminoketones in this study requires rationalisation. An explanation is that for the *N*-phenyl-substituted ligands, deprotonation occurs in the presence of the added cocatalyst, EASC. Evidence for this is provided by NMR. Reaction of EASC with Pr^i–HNacac in the absence of zirconium leads to adduct formation but not to ligand deprotonation even at elevated temperature (no significant ethane evolution or loss of amine proton resonance up to 75°C). This contrasts directly with the reaction of EASC and Ph–HNacac where the ligand is deprotonated at or below 40°C.

On reacting free Pr^i–HNacac with EASC (Al:ligand 10:1), the expected two sets of cocatalyst resonances (shifted downfield) are observed at 25°C, indicating a rapid exchange of free and coordinated cocatalyst on the NMR time scale (Fig. 5a). The two β-aminoketone ligand environments reflect two EASC aluminium environments. The process of adduct

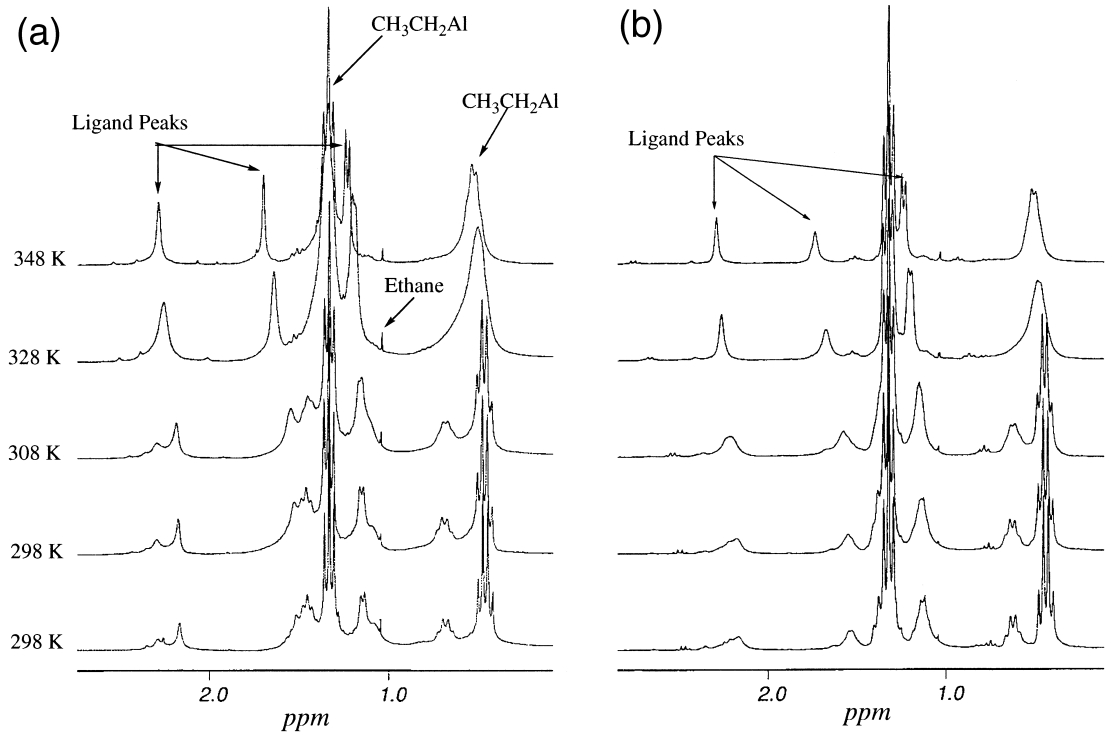


Fig. 5. The VT ^{1}H-NMR of mixtures of (a) Pr^i–HNacac and (b) $ZrCl_4 \cdot 2Pr^i$–HNacac with EASC showing the major ligand and EASC peaks with trace ethane evolution.

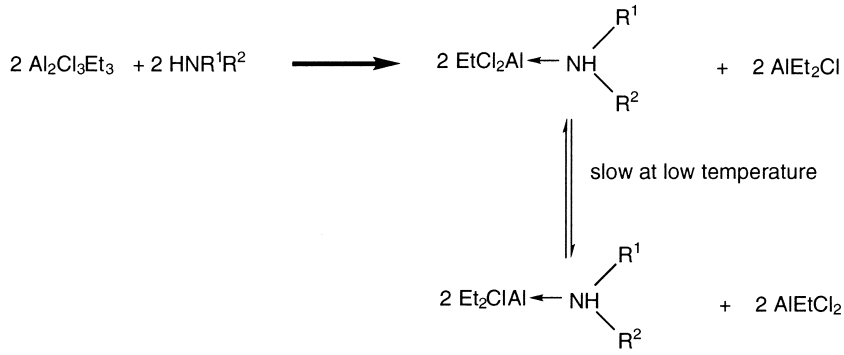


Fig. 6. Schematic representation of proposed free ligand/cocatalyst interactions.

formation can best be envisaged as shown in Fig. 6. On warming to 75°C, peaks coalesce, giving only one ligand and one clear EASC–ethyl environment similar to that for EASC under the same conditions. The ligand is not deprotonated and the proton is most likely associated with the amine, as indicated by secondary splitting of the isopropyl methine peak at 75°C (δ 3.56 ppm, not shown).

In a similar reaction between free Ph–HNacac and EASC, the ligand is immediately deprotonated, with formation of ethane leading to two distinct ligand environments which remain even at 100°C. This facile ligand deprotonation is the same for all *N*-phenyl-substituted β-aminoketones studied to date. Although difficult to confirm, it is thought that the appearance of the second set of ligand resonances on ligand deprotonation may reflect the formation of a dimeric species with a four-membered Al–O ring (Fig. 7). Such a species has been proposed previously [43].

4.2. In situ NMR studies of $ZrCl_4 \cdot 2R$-HNacac / EASC systems

The presence of $ZrCl_4$ could be expected to complicate the system with the possibility of ligand exchange reactions and competition for oxygen adduct formation by two oxyphilic metals (Al and Zr). The VT ^{1}H-NMR spectra for the in situ reaction of EASC with $ZrCl_4 \cdot 2Pr^i$–HNacac are shown in Fig. 5b and selected data are presented in Table 7. The spectra are

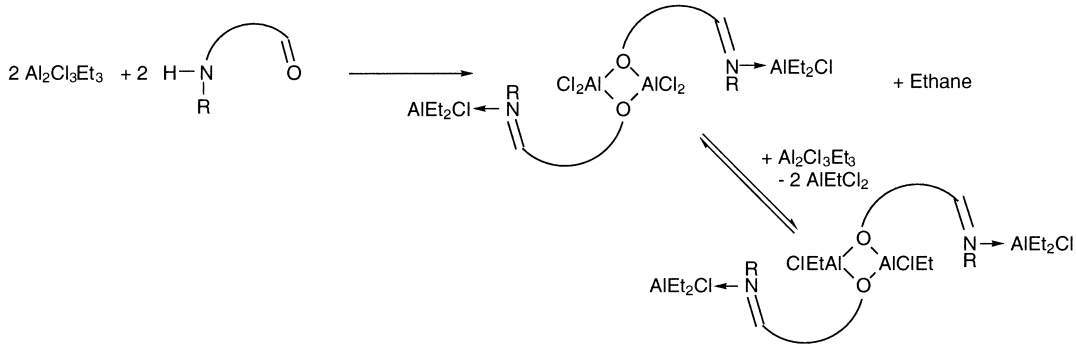


Fig. 7. Simplified scheme showing the proposed reaction of EASC with *N*-aryl-substituted β-aminoketones.

Table 7
Selected ^{1}H-NMR data for in situ VT-NMR experiments containing Pr^i–HNacac in C_6D_6 at 75°C

System	β-Aminoketone ligand shifts					EASC shifts		
	Me C(O)	H	Me C(N)	N–H	CH Pr^i	Me Pr^i	EASC CH_2	EASC CH_3
EASC							0.49	1.27
Pr^i–HNacac (free)	2.24	5.10	1.77	11.32	3.49	1.11	–	–
Pr^i–HNacac + EASC	2.30	4.90	1.72	10.39	3.54	1.24	0.53	1.35
$ZrCl_4 \cdot 2Pr^i$–HNacac + EASC	2.29	4.91	1.74	10.27	3.56	1.24	0.51	1.33

remarkably similar to those for the free ligand/EASC interaction (Fig. 5a). There is no indication of significant ethane production up to 75°C. The EASC resonances, especially the minor peaks, are again shifted downfield. A single environment is indicated for the β-aminoketone ligand with the peaks broad at low temperature. The amine resonances show the largest shift. The spectra have been interpreted as indicating an O-bonded zirconium–ligand adduct with amine–EASC adduct formation. Ligand peak broadening at low temperature is probably due to amine–EASC adduct formation and reflects changes to EASC resonances on warming. The broadening of the carbonyl methyl resonance (δ 2.17 ppm) at low temperatures indicates some possible continued interaction between oxygen and the cocatalyst.

Bubbling ethylene through the EASC/$ZrCl_4 \cdot 2Pr^i$–HNacac system solution described above and heating to 75°C result in the loss of the ethylene resonance at approximately 5.4 ppm

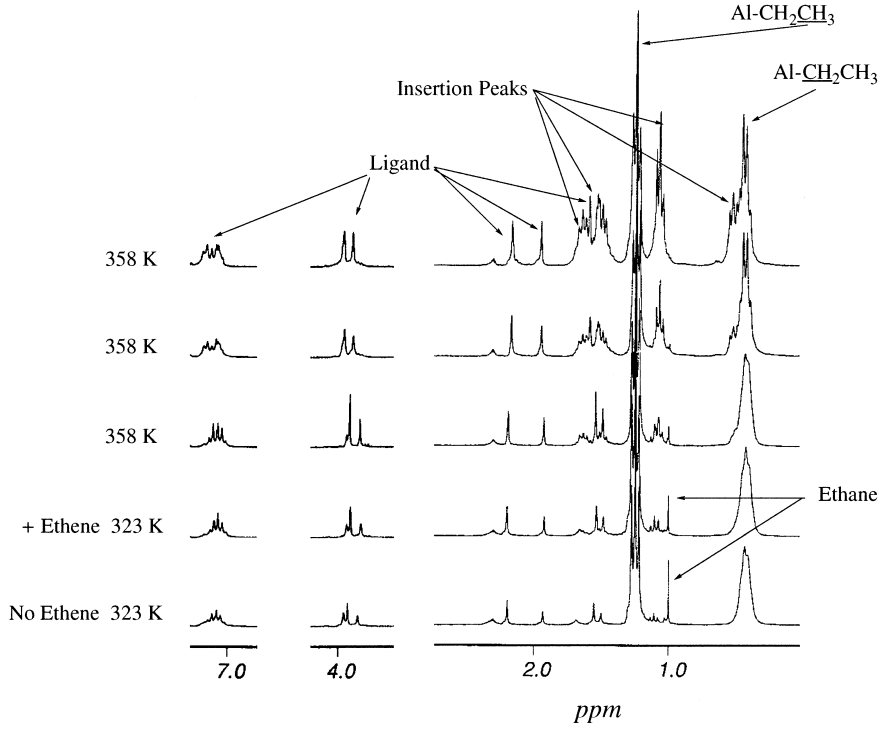


Fig. 8. Ethylene insertion into the active complex formed on reacting $ZrCl_4 \cdot 2$MeOPh–HNacac with EASC.

Table 8
Typical ^{1}H-NMR and ^{13}C-NMR shifts for Zr–R groups reported in the literature

	^{1}H-NMR		^{13}C-NMR		References
	CH_2	CH_3	CH_2	CH_3	
$(MeOPh–Nacac)_2ZrCl_2$ + EASC	≈ 0.50	1.11	58.69	17.98 (weak)	this work
$(MeOPh–Nacac)_2ZrCl_2$ + EASC + ethylene	0.50, 1.50, 1.63	1.11	64.86, 29.18, 27.60, 14.83	12.32	this work
$[Cp'_2Zr(Et)(THF)]^+$	1.17	1.41	60.61	17.52	[59]
$[Cp'_2Zr(Et)(NCMe)_n]^+$	0.77	1.21	40.5	17.1	[33]
$Cp'_2Zr(Et)Cl$	0.88	1.29	45.5	17.9	[33]
$[Cp'_2Zr(n\text{Pr})(THF)]^+$	1.19, 1.63	0.95	72.76, 27.37	20.76	[59]
$[Cp'_2Zr(n\text{Bu})(THF)]^+$	1.57, 1.26, 1.19	0.89	69.62, 36.20, 29.43	13.66	[59]

and the appearance of new sets of peaks at δ 1.13 and 1.55 ppm. Other peaks around 0.6 ppm may be obscured. This is clear and direct evidence for the insertion of ethylene at low pressure (1 atm ethylene). The ligand–Pr^i resonances are found at around 1.1 ppm at 25°C and it therefore remains uncertain as to whether insertion occurs at lower temperatures (near RT). If insertion does occur at the lower temperatures, then it is slow. Surprisingly, even under conditions where ethylene insertion occurs and therefore in the likely presence of a Zr–R bond, the β-aminoketone ligand is not deprotonated, suggesting in these examples that there is little or no zirconium/amine interaction.

In contrast, EASC reacts immediately with $ZrCl_4 \cdot 2$Ph–HNacac, resulting in ligand deprotonation. Heating results in further irreversible changes as indicated by the appearance of a third set of ligand resonances and loss of minor peaks. Bubbling ethylene through the solution at RT results in no noticeable reaction. Similar behaviour has been observed for all *N*-phenyl-substituted β-aminoketone systems examined to date. However, to generate stable, active catalytic systems with *N*-phenyl-substituted ligands, the reaction temperature must be held below 50°C before ethylene addition.

The $ZrCl_4 \cdot 2$(MeOPh–HNacac) reacts completely with the added cocatalyst by 50°C. Two distinct ligand environments are seen (bottom spectrum, Fig. 8). The triplet at δ 1.11 ppm (50°C) is thought to indicate partial zirconium alkylation by the cocatalyst. On addition of ethylene, this peak, along with the other new peaks at 1.50, 1.63 and 0.50 ppm, increase in intensity. As no significant change is observed for the EASC peaks on ethylene insertion in terms of area or position, it is believed that the insertion is occurring at the zirconium metal centre rather than aluminium, although longer reaction times may be required to indicate if significant changes to the EASC peak areas do occur. At 50°C, the insertion rate remains slow

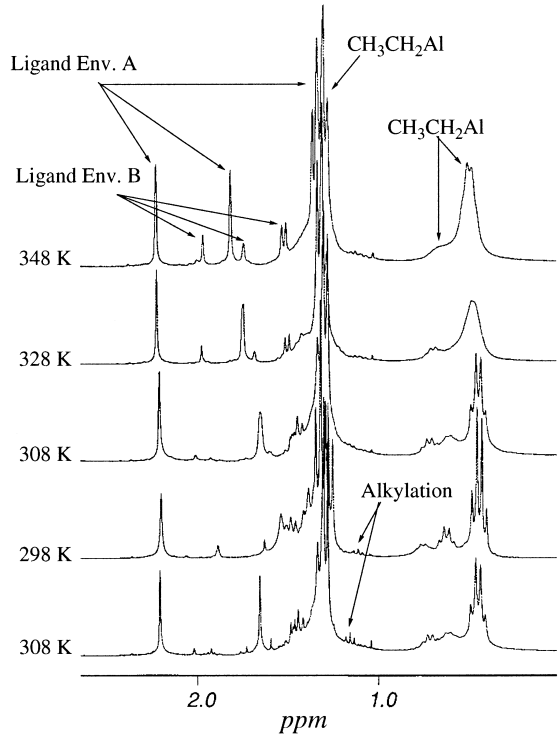


Fig. 9. Reaction of $(Pr^i–Nacac)_2ZrCl_2$ with EASC monitored by VT ^{1}H-NMR.

as indicated by monitoring the ethylene proton resonance at 5.45 ppm. The insertion rate increases on increasing the reaction temperature to 85°C. As more ethylene is repeatedly bubbled through the NMR tube, the new peaks grow in intensity and the ethane formed initially is flushed from the solution. The peaks assigned to the Zr–alkyl species compare favourably with known values reported for other alkyl zirconium systems (Table 8).

In this experiment, the slow appearance of peaks at 5 ppm (three sets of multiplets) and 6 ppm (a broad multiplet) indicate the formation of linear α-olefins. Therefore, the species formed under these mild conditions is an active oligomerisation catalyst.

4.3. In situ NMR studies of (R-Nacac)$_2$ZrCl$_2$ / EASC systems

On reacting bis-ligand complexes with EASC at room temperature, a number of general observations are noted: generally, two ligand environments are seen which are significantly different from those previously observed for adducts; amine/cocatalyst interactions are reduced; alkylation of the metal centre is clearly evident and catalyst systems insert ethylene under very mild conditions.

Reacting (Pr^i–Nacac)$_2$ZrCl$_2$ with EASC results in the formation of what appears to be three distinct sets of EASC resonances which do not completely coalesce even at 75°C (Fig. 9). Ligand resonances remain surprisingly sharp and the *N*-alkyl resonances are in general shifted significantly downfield, as would be expected for strong electron withdrawal from the delocalised chelate system. A second set of ligand resonances (environment B) intensifies as the temperature is increased, suggesting a temperature-dependant ligand exchange reaction or a ligand/EASC dissociative reaction (the latter appears to be likely on considering the strong upfield shift of the backbone methyl and me-

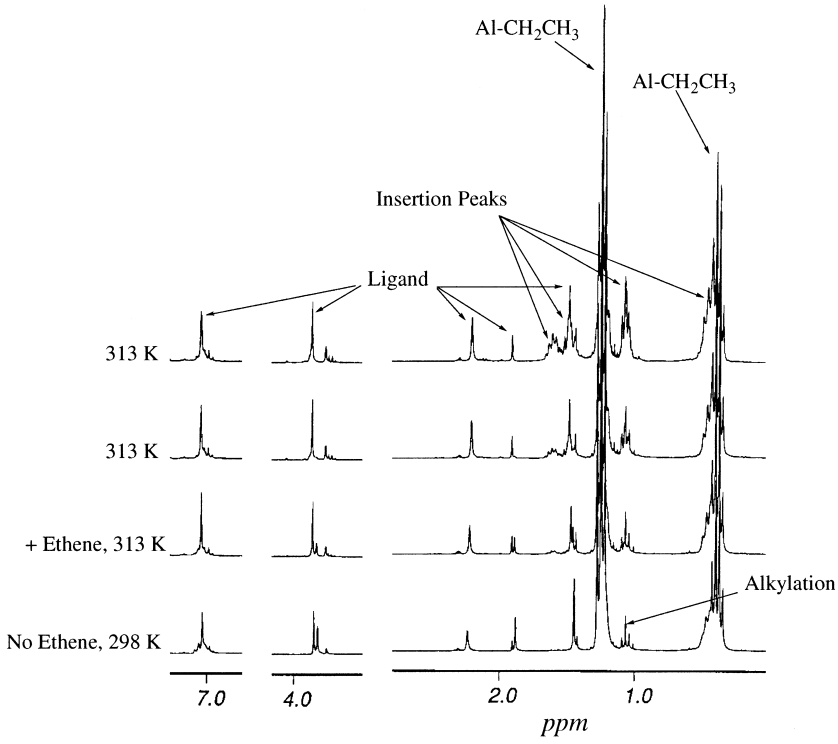


Fig. 10. Reaction of (MeOPh–Nacac)$_2$ZrCl$_2$ with EASC monitored by VT-^{1}H-NMR.

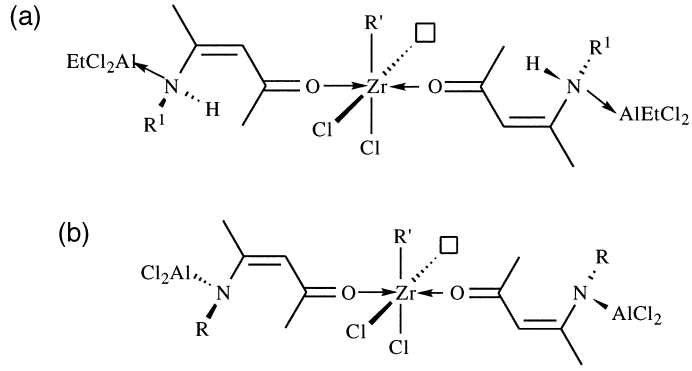


Fig. 11. (a) Proposed active species in the $ZrCl_4 \cdot 2R\text{-}HNacac/EASC$ systems. Possible EASC–oxygen or EASC–metal centre interactions have been omitted for clarity. (b) Proposed intermediates derived from the $ZrCl_4 \cdot 2R\text{-}HNacac/EASC$ system. Possible cocatalyst–oxygen or metal centre interactions have been omitted for clarity.

thine resonances and by comparison to the positions in free *N*-phenyl *β*-aminoketones/EASC systems). A triplet is observed at δ 1.11 ppm and is probably due to alkylation of the zirconium. The associated quartet is probably obscured by the upfield EASC resonances. There is no indication of decomposition on heating the system to 75°C. As on cooling the system back to 35°C (bottom spectrum), there are no permanent changes in the spectrum. On bubbling ethylene through the system, ethylene is inserted at 35°C (not shown).

Reacting $(MeOPh\text{–}Nacac)_2ZrCl_2$ with EASC at 25°C (the solution was not heated—to avoid decomposition) and bubbling ethylene through the mixture led immediately to ethylene insertion (Fig. 10). Two major ligand environments are apparent and a clear triplet at δ 1.07 ppm is present before the solution is contacted with ethylene (bottom spectrum). In this case, insertion is rapid at 30°C and 1 atm pressure of ethylene. Peaks were observed at 5 and 6 ppm, indicating that *β*-hydride elimination is occurring even under these mild conditions (not shown).

The peak positions for the insertion product are similar to those for the *n*-propyl group in $[Cp'_2Zr(Pr^n)(THF)]^+$ and the *n*-butyl group in $[Cp'_2Zr(Bu^n)(THF)]^+$ (Table 8). The changes observed in the proton spectra are also reflected in the ^{13}C-NMR spectra of this system. Before ethylene addition, trace peaks thought to be associated with alkylation of the metal by the cocatalyst are found at δ 17.9 (weak) and 58.69 ppm. These are similar to those previously observed for other alkyl zirconium complexes (Table 8). On addition of ethylene, new peaks are observed at 12.34, 14.83, 29.18 and 64.68 ppm.

5. Conclusions

Zirconium-based oligomerisation systems containing *β*-aminoketone ligands have been

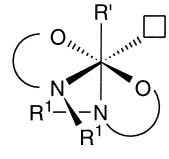


Fig. 12. Proposed active species in the $(R\text{-}Nacac)_2ZrCl_2/EASC$ system. Possible EASC–oxygen or metal centre interactions have been omitted for clarity.

shown to be remarkably active with many having activities significantly higher than many of those previously reported. The catalysts are very selective to linear α-olefins with low wax formation. The oligomer distribution can be controlled by the choice of adducts or complexes and by the method of catalyst formation. Selected catalysts are active even under very mild conditions showing, in in situ NMR experiments, the ability to form α-olefins at 30°C and 1 atm of ethylene. Evidence of metal centre alkylation and ethylene insertion is provided.

The ability to influence product distributions through ligand variations indicates that the ligand plays a major role in the active catalyst. Bulky substituents tend to reduce catalytic activity presumably due to steric interference. Catalyst systems containing backbone phenyl-substituted ligands have lower oligomerisation activities than methyl-substituted systems. The use of *N*-phenyl-substituted β-aminoketones, especially those with electron-withdrawing functional groups on the phenyl substituent, leads to the most active catalyst systems. As discussed previously, the *N*-phenyl group appears to facilitate deprotonation of the ligands and hence, generation of an active species of the type observed for the bis-ligand catalysts. The NMR evidence tends to indicate that if a chelated metal complex is formed prior to cocatalyst addition, it remains intact during catalysis. However, it does not form or is slow to form if the catalyst is generated in situ. This is particularly evident for alkyl-substituted β-aminoketones where during oligomerisation, and therefore in the presence of highly reactive metal alkyl bonds, the ligand is not deprotonated.

Although the systems are very complex with a number of possible ligand/cocatalyst interactions occurring, it is believed that a catalyst precursor is formed through a process in which the cocatalyst alkylates the zirconium and concurrently abstracts a halide atom to form a polar binuclear species or a tight ion pair consistent with that proposed in other studies. From the evidence presented, we would propose that the active species shown in Figs. 11 and 12 may be formed during catalysis.

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