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Evaluation of mid-to-late transition metal imine catalysts for acetylene oligomerisation: A high activity bis(imino)pyridine iron(**II**) catalyst

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ABSTRACT

Bis(imino)pyridine complexes of Co and Fe, and diimine complexes of Ni and Pd, have been tested as catalysts for acetylene oligomerisation and polymerisation. While Co, Ni and Pd complexes displayed low activity, an Fe complex led to an extremely active system for acetylene polymerisation after activation with methylaluminoxane (MAO). The product output could be shifted towards short-chain oligomers by addition of the chain transfer reagent $ZnEt_2$, leading to polyene oligomeric chains bound to Zn. Complex branched and cyclic higher oligomers were partially identified, and some possible mechanisms for their formation proposed. The Fe system did not successfully catalyse copolymerisation of acetylene and ethylene, although there was evidence of limited acetylene incorporation into ethylene oligomers.

1. Introduction

Given our current high dependence on petroleum-based fuels, there is an increasing need to make more effective use of all available feedstocks. The pyrolysis of natural gas can be employed to produce acetylene and hydrogen, hence acetylene conversion reactions are of interest as a means of upgrading abundant gas reserves into liquid fuels [1–3]. While Hall and coworkers have explored acetylene hydrogenation to ethylene, followed by oligomerisation [1,2], we became interested in the alternative of direct oligomerisation of acetylene. For this reason, we have recently been exploring the metal-catalysed oligomerisation of acetylene to liquid products [4–6]. This represents a potential alternative to the more mature gas-to-liquid technologies such as syngas based Fischer–Tropsch or methanol synthesis. As such, the potential of an acetylene based technology seems worthy of investigation. In a broader context, the oligomerisation or polymerisation of alkynes is also of interest due to the high electrical conductivities achievable with conjugated polymers [7], and the use of alkyne oligomerisation for organic synthesis [8,9].

While a range of techniques for alkyne oligomerisation are possible (for instance ionic and radical processes) [10,11], we reasoned that a metal-catalysed route may offer better molecular weight control, in analogy to metal-catalysed olefin oligomerisation [12–14]. Any process aimed at the production of fuels would necessitate very high catalyst productivities and good chain length control. Our initial work in this area has shown that a range of early transition metal- and lanthanide-based complexes were ineffective in this regard [5]. Furthermore, while others have demonstrated that excellent chain length control is achievable with lanthanide and actinide metallocenes, catalyst activities are generally very low (TOFs ca. $<20\,h^{-1}$) [15–22]. Our findings of low activity for early transition metals are in accord with these earlier studies and, additionally, we unexpectedly discovered that chain growth preferentially occurs at the co-catalyst, $AlEt_3$ [4–6].

Over the last 15 years the development of mid to late transition metal catalysts for olefin oligomerisation and polymerisation has provided significant advances in these areas [23,24]. The most notable examples are probably the chelate imine complexes of Fe, Co, Ni and Pd, structures **I** and **II** [25–27]. It therefore occurred to us that these systems may be useful as catalysts for acetylene oligomerisation. Heterogeneous nickel-based catalysts have previously been employed for acetylene linear oligomerisation with some success [3], while all of the metals Fe, Co, Ni and Pd are known to catalyse cyclooligomerisations of alkynes [8]. A further attraction of Fe catalysts of structure **I** is the high degree of chain length

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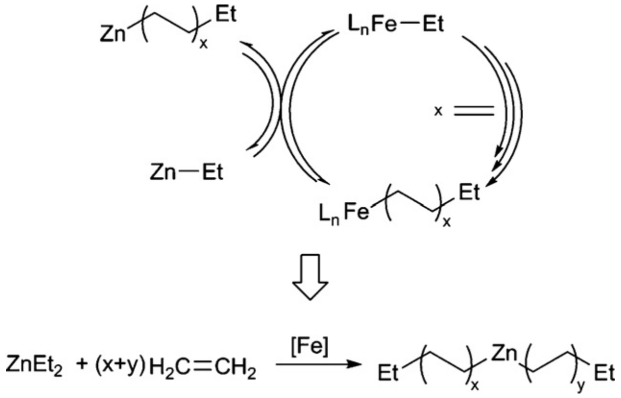
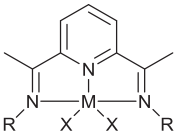
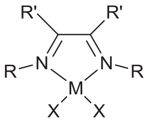


Scheme 1. Fe-catalysed chain growth at Zn.

control available in ethylene oligomerisation, through the addition of diethylzinc as a chain transfer reagent [28–30]. While ethylene chain growth occurs at Fe, rapid and reversible chain transfer with $ZnEt_2$ leads to a Poisson distribution of oligomeric chains at Zn (Scheme 1, catalysed chain growth at Zn). The average chain length can be controlled by altering the concentrations of Fe and Zn and the reaction time.



I, M = Co, Fe



II, M = Ni, Pd

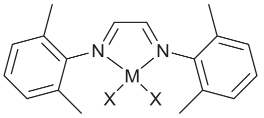
Herein we report the first account of acetylene oligomerisation and polymerisation testing with catalyst systems **I** and **II**. It is shown that the Fe catalyst leads to a highly active catalyst for acetylene polymerisation, and the use of diethylzinc as a chain transfer agent to shift the output towards oligomers is explored. Some aspects of this work have recently been communicated [31].

2. Results and discussion

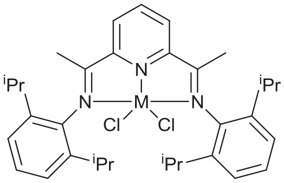
2.1. Initial trials and polymerisation with Fe/MAO

The catalyst systems investigated during this work comprise Ni(II) dibromide and Pd(II) dichloride complexes of an α-diimine ligand, **1** and **2** [32], and Co(II) and Fe(II) dichloride complexes of a bis(imino)pyridine ligand, **3** and **4** [33,34]. These systems, in combination with the activator methylaluminoxane (MAO), form highly active catalysts for ethylene polymerisation. In addition, the iron catalyst **4** has been shown to afford excellent oligomer molecular weight control through chain transfer with $ZnEt_2$ (Scheme 1) [28,29].

Activation of toluene solutions of pre-catalysts **1**–**3** with MAO and exposure to acetylene (1 bar gauge) led to disappointing results. No oligomers or polymer were formed with **1** or **2**, while **3** led to a small amount of precipitated polyacetylene (corresponding to a TON in acetylene of 550 after 30 min). In stark contrast, exposure of the activated Fe catalyst **4** ([Fe] = 0.1 mM, 100 equiv. MAO) to acetylene effected an almost instantaneous evolution of a dark purple gel (indicative of mixed *cis*/*trans* polyacetylene) [35] and significant heating of the solution. Over a 30 min run, the entire reactor contents form a solid mass of gel, with very little free toluene remaining. Evaporation of the solvent leaves a dark purple to black, film-like polymer with a metallic sheen. The IR spectrum displays bands at 1327, 1016 and 734 cm^{-1}, again characteristic of both *cis* and *trans* polyacetylene [7]. The formation of polyacetylene/toluene gels is well known [35].



M = Ni, X = Br (**1**)
M = Pd, X = Cl (**2**)



M = Co (**3**)
M = Fe (**4**)

We have recently communicated the results of acetylene polymerisation with this catalyst [31]. It was found that the morphology of the polymer depends upon the reaction conditions, as has been observed previously [36]. When the reaction was carried out at lower concentrations of catalyst (with stirring), a fine powder of polyacetylene precipitates. Under these conditions, it was shown that rapid catalyst deactivation is a result of catalyst encapsulation by the insoluble polymer. In the absence of stirring, a polyacetylene film forms at the surface of the solution, even at very low catalyst concentrations. We have been able to prepare polyacetylene films at concentrations of **4** as low as 4 μM. This is in contrast to typical catalysts for acetylene polymerisation, for which a high (mM) concentration is normally a prerequisite for film formation [37]. The ability to form films at such low concentrations presumably relates to the extremely high intrinsic activity of this catalyst system. At the microscopic scale, the films are composed of intertwined fibrils of diameter around 50 nm, as has been shown previously [7].

The highest yields of polymer are formed under gel-forming conditions in a mechanically stirred reactor. After 30 min under these conditions, TONs in acetylene up to ca. 9000 can be achieved, although the rate of polymerisation slows markedly over the run, particularly so at the start. This is due to mass transport limitations as a result of catalyst incorporation within the polymer and slow diffusion of acetylene through the gel, similar to observations made by others [35,38]. In order to gauge the intrinsic activity of the catalyst before diffusion limitations, a run was stopped after 2 min and the polymer yield determined. This run revealed an activity over this time period of 62,500 h^{-1} (TOF), or ca. 29,000 g(PA) $g(Fe)^{-1}$ h^{-1}. To the best of our knowledge, this is the most active catalyst system for acetylene polymerisation reported to date [39,40]. Remarkably, the activity of this system towards acetylene, initially at least, appears comparable to that with ethylene as the monomer [33,34].

2.2. Oligomerisation with 4/MAO/$ZnEt_2$

Given the extremely high activity of the catalyst system composed of the iron catalyst **4** and MAO, we were interested to shift the product distribution towards oligomers, with the ultimate aim of producing a liquid product in the fuel range. The effect of diethylzinc on this system has been demonstrated to control the chain length in ethylene polymerisation, through rapid and reversible chain transfer (Scheme 1) [28–30]. We thus reasoned that $ZnEt_2$ may have a similar effect on polyacetylene chain growth.[2]

Initial reactions under standard conditions ([Fe] = 0.1 mM, 100 equiv. MAO) with 500 equivalents of $ZnEt_2$ (relative to the Fe catalyst) showed that the reaction with acetylene (1 bar gauge) was again very rapid (exotherm to ca. 50 °C in the absence of external cooling), but the formation of large amounts of purple polyacetylene gel was not observed under these conditions. Instead a bright

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[2] We have also trialled an analogous iron catalyst with *ortho*-tolyl *N*-substitution, which is known to lead to ethylene oligomerisation. With acetylene, this catalyst led only to benzene however, and will be reported separately.

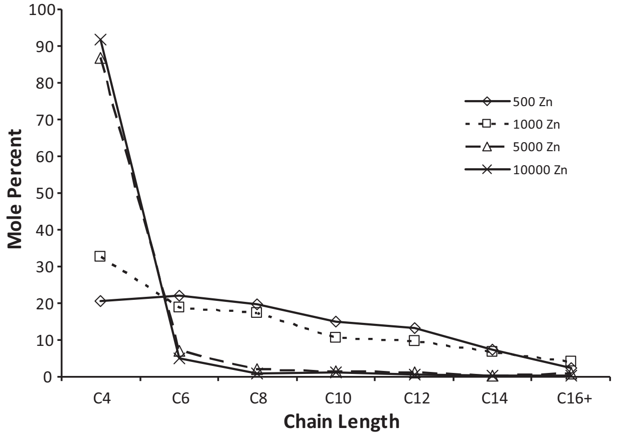


Fig. 1. Oligomer distribution as a function of $ZnEt_2$ loading (equiv. vs. Fe) for the system **4**/MAO/$ZnEt_2$. Toluene, RT, 30 min. [**4**] = 0.1 mM, 100 equiv. MAO.

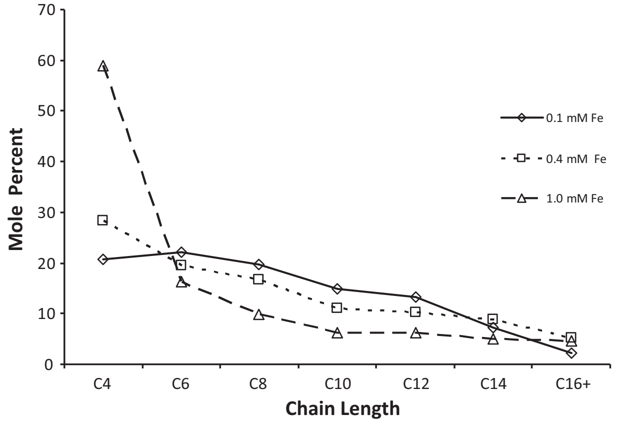
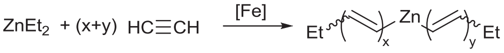


Fig. 2. Oligomer distribution as a function of [**4**] for the system **4**/MAO/$ZnEt_2$. Toluene, RT, 30 min, 100 equiv. MAO, 500 equiv. $ZnEt_2$.

red solution quickly formed, which thickened noticeably after ca. 10 min. This thickening was accompanied by a slowing of the rate of acetylene uptake and a milder exotherm. Work up yielded over 2 g of bright red polymer, which darkened to black over time when exposed to air. GC–MS analysis of the liquid phase (following hydrolysis) revealed the presence of 1-butene, 1,3-hexadiene and several isomers of octatriene, as well as higher oligomers. These short polyene oligomers are consistent with multiple acetylene insertions into a metal-ethyl group. Full oligomer identification is considered separately below in Section 2.3. A small amount of benzene (acetylene cyclotrimer) was also detected along with the acyclic products, which was also found to be present in polymerisation runs in the absence of $ZnEt_2$.

The effects of varying the ratios of iron catalyst **4** and $ZnEt_2$ are displayed in Table 1. An increase in diethylzinc concentration leads to a greater proportion of oligomeric product (entries 1–4), with a concomitant decrease in the amount of polymer formed. This is consistent with a process of chain transfer to zinc taking place, which lowers the overall molecular weight of the product [29,30]. An increase in $ZnEt_2$ concentration is expected to accelerate the chain transfer process and lead to a greater abundance of shorter chain length products. This is illustrated in Fig. 1, which displays the distribution of oligomer chain lengths as a function of $ZnEt_2$ loading. Indeed, at very high loadings of $ZnEt_2$ (>5000 equiv.), the main product is 1-butene. With 10,000 equivalents of $ZnEt_2$ present, only 5% polymer is formed (Table 1, entry 4).

As expected, the absence of chain termination provides that the oligomeric chains remain bound to Zn prior to quenching. This is illustrated by quenching the reaction solution with D_2O, which results primarily in the formation of [D_1]-oligomers (GC–MS analysis). As such, the overall reaction represents a catalysed chain growth process on zinc (Eq. (1)), in direct analogy to that which occurs with ethylene (Scheme 1). It is worth noting that acetylene chain growth at $ZnEt_2$ does not occur in the absence of **4**/MAO.



(1)

An increase in the iron catalyst concentration from 0.1 to 0.4 and 1.0 mM (entries 1, 5 and 6) at constant acetylene pressure and keeping the iron to zinc ratio constant at 500 equiv. results in a lowering of the overall productivity. This does not seem to be due to mass transfer limitations, but rather a noticeable deactivation of the catalyst at high $ZnEt_2$ loadings. The reason for this is unclear. The increased amount of $ZnEt_2$ relative to acetylene will result in a faster rate of chain transfer relative to propagation and consequently to lower molecular weight products. The effect of this on the oligomer distribution is illustrated in Fig. 2.

The results presented above show that $ZnEt_2$ as a chain transfer agent is capable of shifting the product distribution to short-chain oligomers. Nontheless, in the absence of chain termination reactions the production of oligomers is stoichiometric with respect to zinc. We therefore evaluated the effect of hydrogen on the process, hopeful that hydrogenative chain termination (Eq. (2)) might occur. This would produce M-hydrides (Zn or Fe) in the system, thus making initiation of a new chain possible. Oligomerisation with a mixed gas system comprising 10 bar H_2 and 2 bar acetylene did in each case lead to reduced polymer formation (Table 1, entries 7 and 8) relative to comparative tests in the absence of hydrogen. However, this seems only to be due to an inhibitory effect of hydrogen on the growth reaction; a quench with D_2O exclusively produces [D_1]-oligomers, showing that chain termination according to Eq. (2) is not occurring. This poisoning effect of hydrogen is also reflected in the productivities of the catalyst with H_2 present and seems to be more pronounced at higher catalyst concentrations. The reason for this effect is unclear, but it can be clearly seen that this strategy is unsuccessful with regards to rendering the process catalytic in $ZnEt_2$.

(2)

2.3. Identification of higher oligomers

While lower soluble oligomers (butene, hexadiene, octatriene) were relatively straightforward to identify, and are as expected for 1,2-insertions of acetylene into a M-Et group, higher products are more complicated and feature a number of overlapping peaks for each molecular weight (for example, Fig. 3). Quantification (GC–FID) of each carbon-number fraction was based upon group of peaks with the same molecular weights according to GC–MS analysis. An interesting observation made during this analysis was related to product molecular weights above the C_{10} products. After hexadiene (C_6H_{10}, MW 82), sequential addition of acetylene should increase each mass by 26, leading to a distribution of C_8H_{12} (MW 108), $C_{10}H_{14}$ (MW 134), $C_{12}H_{16}$ (MW 160) and so on. This pattern of oligomers is indeed observed until C_{12}, at which point products of both MW 160 and 164 are detected (with 164 seemingly more prominent). This pattern is also repeated in the C_{14} and C_{16} oligomers, although becomes less clear due to the low abundance of these products. Given these observations, we were interested to gain further information on the structures of the higher oligomers, which may provide clues as to the underlying mechanisms.

Table 1
Effect of $ZnEt_2$ on oligomerisation with **4**/MAO.[a]

Entry	[**6**] (mM)	$ZnEt_2$ (equiv.)	Productivity[b]	Mass of products (g)	Polymer (wt%)	Oligomer (wt%)
1	0.1	500	18,670	2.45	95	5
2	0.1	1000	22,330	2.93	91	9
3	0.1	5000	12,880	1.69	23	77
4	0.1	10,000	14,020	1.84	5	95
5	0.4	500	10,190	5.35	84	16
6	1.0	500	2510	3.30	59	41
7[c]	0.1	500	9680	1.27	83	17
8[c]	1.0	500	1090	1.43	Trace	100

[a] Conditions: toluene (50 mL), RT, 30 min, 100 equiv. MAO, 1 bar gauge C_2H_2.
[b] TON of acetylene relative to **4**.
[c] Reaction performed under acetylene/H_2 (2 bar:10 bar).

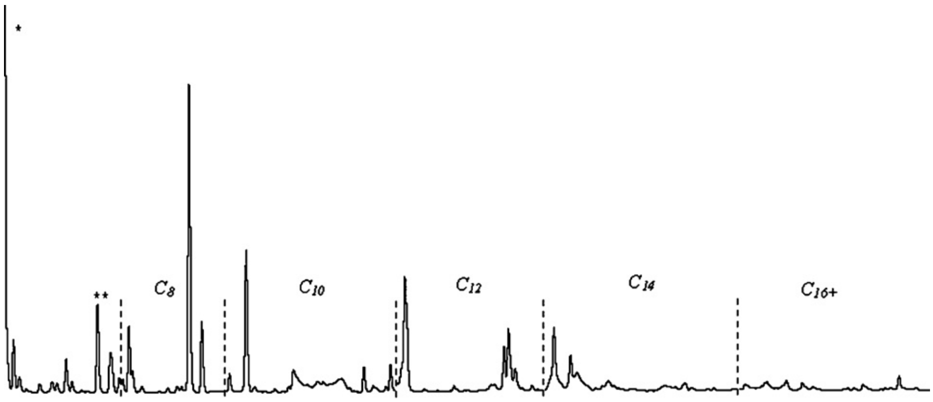


Fig. 3. Representative GC trace of C_8 and higher products formed from acetylene oligomerisation with the system **4**/MAO/$ZnEt_2$. *Toluene (solvent), **xylene impurities within toluene.

Hydrogenation of a sample was undertaken to simplify the chromatogram and yield saturated oligomers which are more easily identified (see Fig. 4). The first observations are that only a fraction of the C_{10} oligomers are converted to *n*-decane and that the non-linear isomers a and b are most abundant. The earliest eluting C_{10} compound (peak a) was confirmed as 3-ethyloctane by mass spectral library comparison and co-elution of a genuine sample. The other isomer b was found to be ethylcyclooctane by a combination of library spectral comparison, Kovats' indices and co-elution. Clearly, the mode of chain growth for higher oligomers is more complicated than simple acetylene insertion into a linearly growing chain. Addition of a M-Et group across a double bond in the growing polyene is one possible way that an ethyl branch could be introduced (Eq. (3)). However, such a process cannot be responsible for branching in the C_{10} fraction, as the molecular weight of all C_{10} compounds (134, pre hydrogenation) is inconsistent with the addition of an ethyl group (138). Furthermore, as shown below, the presence of two points of metal attachment which result from this addition are expected to lead to a [D_2]-oligomer after quenching with D_2O. Only [D_1]-oligomers are formed in the C_{10} fraction from a D_2O quench. We have previously made similar observations of ethyl branching during acetylene chain growth at $AlEt_3$ [4,5], and proposed that this could be due to an intramolecular σ-bond metathesis reaction involving the chain end. This is shown in Scheme 2, whereby the metal effectively jumps to the opposite end of the triene chain. A further acetylene insertion at this point can lead to both 3-ethyloctane and ethylcyclooctane through the sequences shown in Scheme 2. Ethylcyclooctane could also be formed through back-biting insertion of the linear C_{10} chain, which is also shown in Scheme 2.

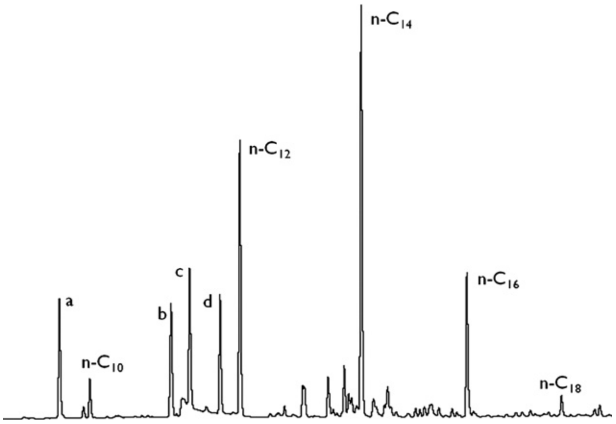
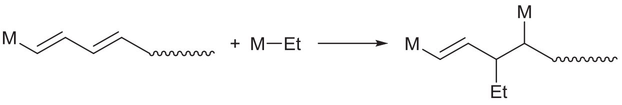
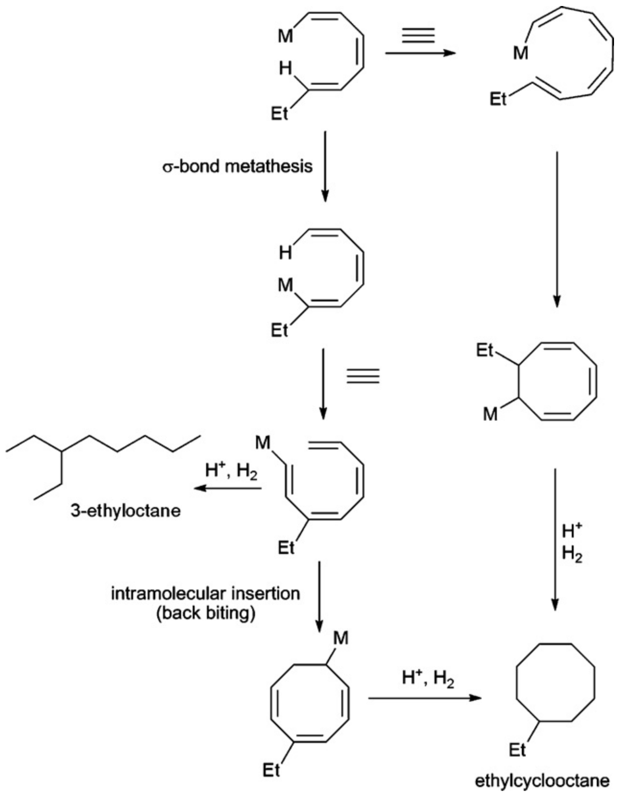


Fig. 4. GC trace of higher oligomers after hydrogenation, formed by the acetylene oligomerisation system **4**/MAO/$ZnEt_2$.

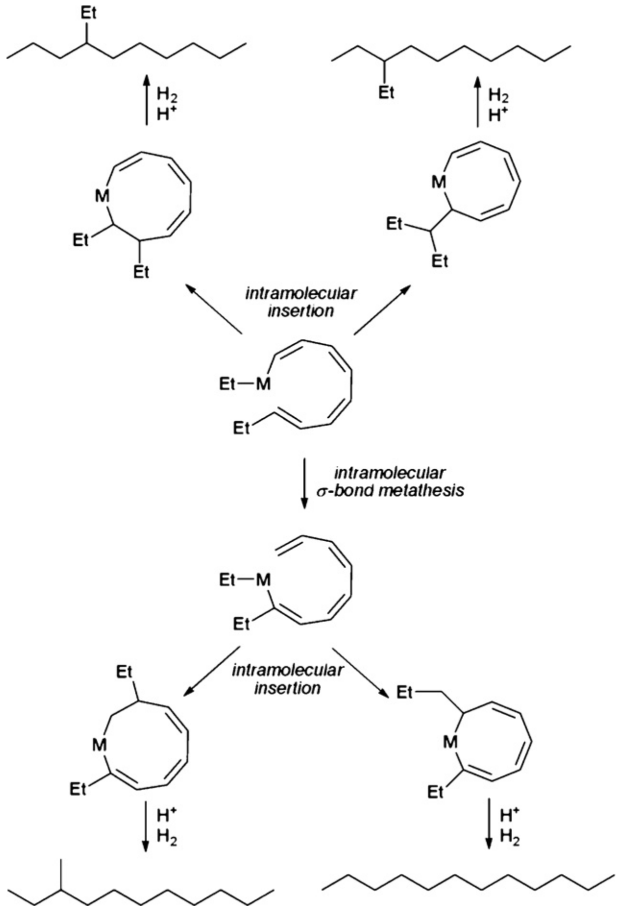


(3)

The major product after hydrogenation in the C_{12} fraction is *n*-dodecane, along with two significant branched products (c and d in Fig. 4). We were unable to definitively identify these two products, but their earlier elution times together with fragmentation patterns suggest branched structures. In this case it seems that branching probably occurs through the process shown in Eq. (3), as the molecular weight of 164 (pre hydrogenation) is consistent with addition of an ethyl group. Furthermore, the major isotopomers formed in the C_{12} fraction after a D_2O quench are [D_2]-oligomers, consistent with two points of metal attachment. Possible pathways leading to the formation of branched and linear C_{12} isomers by these processes are shown in Scheme 3. Only intramolecular insertion of chain-end unsaturation is illustrated here, however intermolecular insertion into a M-Et moiety is also possible. As such, a large number



Scheme 2. Possible mechanistic routes to 3-ethyloctane and ethylcyclooctane (M = Fe or Zn).



Scheme 3. Possible mechanistic routes to branched and linear C_{12} products which involve M-Et addition across chain-end unsaturation (M = Fe, Zn).

of structural isomers are possible through addition of a M-Et group across unsaturation in the oligomer chain. Evidently, the formation of higher oligomers is not as straightforward as a simple stepwise insertion reaction of acetylene. The mechanisms proposed here remain speculative; however they do offer an explanation for the formation of the products that have been identified so far.

2.4. Co-oligomerisation and co-polymerisation of acetylene and ethylene

Given the known reactivity of the system **4**/MAO with ethylene and now acetylene, it was of interest to investigate the possible formation of co-oligomers and co-polymers of the two monomers. There are several reasons for this. Firstly, insertion of ethylene would yield saturation adjacent to the metal centre, from which β-hydride elimination is possible. In that case, the possibility exists that ethylene incorporation could increase the likelihood of chain termination and thereby reduce the molecular weight. Secondly, in the context of polyethylene, the incorporation of double bonds into the polymer structure may help to facilitate biodegradation. Such copolymers featuring longer conjugated sections have potential as conductive polymers without the stability and handling issues of polyacetylene, while the presence of double bonds might also allow further functionalisation and tuning of polymer properties. Some reports of the production of such polymers have been presented [41–43].

A number of experiments were conducted with various premixed ratios of acetylene in ethylene (5%, 1%, 0.1%), whereby the gas mixtures were prepared in a separate ballast vessel, which was subsequently used to pressurise the reactor. The first trials were conducted in the absence of $ZnEt_2$. The results obtained initially seemed promising, with the colour of the resulting polymers ranging from dark purple (5% C_2H_2) through light purple (1% C_2H_2) to off-white (0.1% C_2H_2), indicative of reducing levels of polyconjugation with reduced acetylene concentration (Table 2 and Fig. 5). However, at higher pressure (4 bar gauge) with 5% acetylene (Table 2, entry 1), it was evident that the polymer was not homogeneous in colour, but featured white streaks running though dark purple regions. This hinted at a mixture of polymers, rather than a true copolymer, which was confirmed by NMR spectroscopy. Most of the light purple polymer formed with 1% acetylene (Table 2,

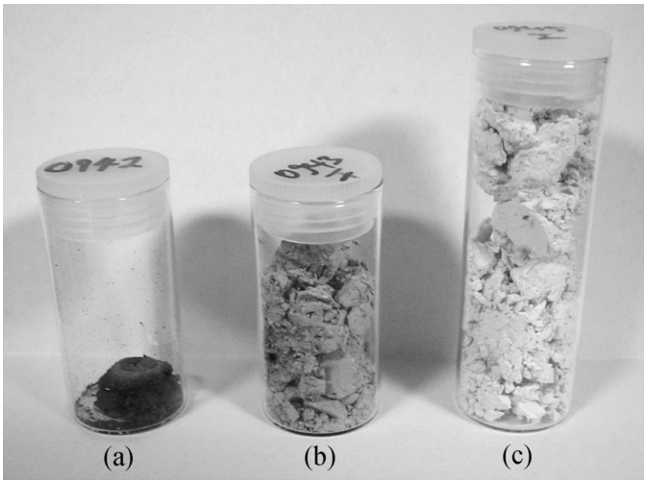


Fig. 5. Polymers produced through the use of different ethylene/acetylene mixtures with **4**/MAO: (a) 5% C_2H_2; (b) 1% C_2H_2; and (c) 0.1% C_2H_2.

Table 2
Acetylene/ethylene co-oligomerisation and co-polymerisation with **4**/MAO.[a]

Entry	% C_2H_2	$ZnEt_2$ (equiv.)	Oligomers (g)	Polymer (g)	Polymer appearance
1[b]	5	–	–	0.225	Purple with white regions
2	5	–	–	0.045	Purple
3	1	–	–	1.905	Light purple
4	0.1	–	–	3.809	Off-white
5	5	500	0.312	0.060	Light red
6	1	500	0.522	2.364	Pink
7	0.1	500	0.210	6.292	White

[a] Conditions: toluene (50 mL), RT, 30 min, [**4**]= 0.1 mM, 100 equiv. MAO, 1 bar gauge mixed gas.
[b] 4 bar gauge mixed gas.

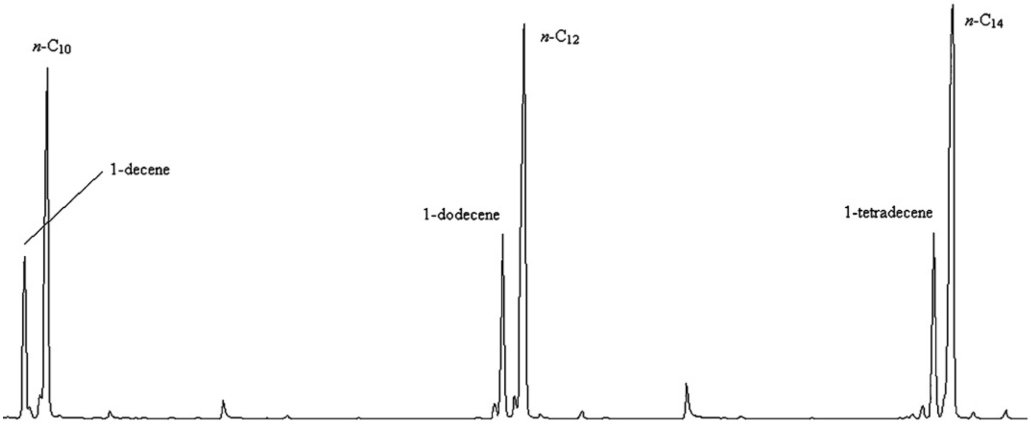


Fig. 6. GC trace of C_{10}–C_{14} products formed by oligomerisation of ethylene/acetylene (5% acetylene) with **4**/MAO/$ZnEt_2$.

entry 3) could be dissolved in 1,2,4-trichlorobenzene at 145 °C, but a small amount of dark insoluble polyacetylene remained behind. The ^1H NMR spectrum showed no sign of olefinic signals, instead displaying only methylene backbone and methyl end-group signals characteristic of polyethylene. We conclude that the catalyst produces a mixture of homo-polymers, rather than an ethylene/acetylene co-polymer.

It is interesting to note that the yield of polymer increases as the concentration of acetylene is reduced (Table 2, entries 2–4). This presumably results from reduced catalyst encapsulation in polyacetylene and precipitation from solution (Section 2.1). It is also noteworthy that the major product formed is polyacetylene even at only 5% acetylene concentration, demonstrating the higher affinity and polymerisation rate of acetylene relative to ethylene with this catalyst system. At lower concentrations of acetylene (1%, 0.1%) however, polyethylene formation seems to dominate.

When the mixed gas reactions were repeated with 500 equivalents of $ZnEt_2$ present, both mixed polymer and oligomers were formed (entries 5–7). In this case, analysis of the oligomers reveals some evidence for limited acetylene incorporation into growing polyethylene chains. The main products (after hydrolytic workup) are even-numbered *n*-alkanes, as expected from chain transfer of growing ethylene oligomers to zinc (according to Scheme 1). However, a significant amount of α-olefin is also observed, particularly with gas composed of 5% acetylene (see Fig. 6). When the reaction was quenched with D_2O, more than 90% of the oligomers formed were [D_1]-isotopomers, indicating that the α-olefins are bound to Zn and that β-hydride elimination from a M-alkyl is not a significant route to these. Instead, acetylene insertion into an Fe-alkyl is the most likely route. The observation that the alkenes produced in this case are primarily α-olefins (a minor amount of an internal olefin can also be detected) might suggest that the inclusion of an acetylene unit is the final stage in the formation of these oligomers. The reason for this is unclear at this stage.

3. Summary and conclusions

Mid to late transition metal chelate imine complexes have proven to be efficient catalysts for ethylene polymerisation, and herein we have investigated their extension to acetylene polymerisation and oligomerisation. While Co, Ni and Pd complexes led to disappointing results, the Fe complex **4** led to an extremely active system for acetylene polymerisation following activation with MAO. To the best of our knowledge, complex **4** leads to the most active acetylene polymerisation catalyst reported to date, and can be used to produce polyacetylene films at extremely low concentrations [31]. Unfortunately, attempts to copolymerise acetylene and ethylene with this system led to mixtures of polyacetylene and polyethylene, rather than a true co-polymer.

The product distribution from the polymerisation of acetylene with the catalyst system **4**/MAO can be shifted to lower molecular weight products through the use of fast chain transfer agents such as $ZnEt_2$. At high loadings of $ZnEt_2$ the formation of predominantly short chain oligomers is observed after hydrolysis. Both branched and cyclic oligomers have been identified and their formation can be explained by a mechanism involving sigma-bond metathesis. Due to the absence of any chain termination reactions, the formation of oligomers is stoichiometric in zinc. Attempts to use hydrogen as a chain termination reagent have been unsuccessful so far. Further work is required before this catalyst could be used for efficient conversion of acetylene to fuel range oligomers. Nonetheless, herein we have demonstrated the excellent potential of Fe-based catalysts for high activity acetylene conversions.

4. Experimental

4.1. General details

Unless noted otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk techniques, or in a nitrogen glovebox. Solvents were purified by passage through an innovative technologies solvent purification system and, where appropriate, stored over a sodium mirror. Acetylene (99.0%) was purified by passage through a column of activated molecular sieves (3 Å) and alumina. GC analysis showed that no acetone was present in the purified acetylene. The precatalysts, **1** and **2** [32], and **3** and **4** [34] were prepared according to literature procedures. Methylaluminoxane (MAO), 10 wt% in toluene, was supplied by Albemarle.

4.2. GC–FID and GC–MS analysis

Oligomer quantification was carried out by GC–FID on an HP 5890 chromatograph fitted with an HP1 column (25 m × 0.32 mm internal diameter and 0.52 μm film). The carrier gas was nitrogen with a flow rate of 3.0 mL per min. The column oven was held at 40 °C for 4 min then ramped to 300 °C at 20 °C per min. Identification of the oligomers, both before and after hydrogenation, was carried out by GC–MS. Analyses were carried out on a Varian 3800 GC coupled to a Varian 1200 triple quadrupole mass spectrometer in single quadrupole mode. The column was a Varian 'Factor Four' VF-5ms (30 m × 0.25 mm internal diameter and 0.25 micron film). Injections of 1 microlitre of diluted samples were made using a Varian CP-8400 autosampler and a Varian 1177 split/splitless injector at 240 °C with a split ratio of 25:1. The ion source was at 220 °C, and the transfer line at 290 °C. The carrier gas was helium at 1.2 mL/min using constant flow mode. For separation of C_4 and C_6 components the column oven was held at −30 °C for 2 min then ramped to 250 °C at 15 °C per min. For all other separations the column oven was held at 50 °C for 2 min then ramped to 290 °C at 8 °C per min. The range from *m/z* 35 to 450 was scanned 4 times per second. Oligomers were identified by their characteristic electron ionisation spectra, supported by Kovats' retention indices relative to published data. 3-Ethyloctane and ethylcyclooctane were further identified by comparison of GC retention times and mass spectra with authentic samples.

4.3. Acetylene polymerisation

In a typical run, polymerisation was conducted in a 400 mL Lab-Crest glass pressure reactor. The oven dried reaction vessel was purged with argon for 30 min followed by acetylene. Solvent (toluene) was then introduced such that a final volume of 50 mL would be obtained. The Fe catalyst **4** was dissolved/suspended in toluene in a Schlenk flask under argon, and activated with 100 equivalents of MAO. An aliquot (5 μmol of Fe) of the activated catalyst was then added to the reactor before pressurising to 1 bar gauge with acetylene, with rapid stirring. External cooling was applied early in the run to maintain the temperature at 20–23 °C. After the desired run time, acetylene was bled and the gel collected and washed with toluene. Evaporation of the solvent afforded dry polyacetylene, which was weighed to determine the yield. Polyacetylene films could be prepared according to the procedure of reference [31].

4.4. Acetylene oligomerisation

The general procedure described above (Section 4.3) was followed, except that the desired quantity of $ZnEt_2$ was added to the reactor prior to the catalyst/MAO solution. After the desired reaction time, the acetylene flow was stopped and the solution cooled with an ice bath to around 5 °C, after which excess gas pressure was released. A weighed internal standard (*n*-nonane or *n*-heptane) was injected before the solution was carefully quenched with 10% HCl, keeping the solution cool to avoid the loss of low molecular weight oligomers. A sample of the organic phase was filtered through celite and Na_2CO_3, and analysed by GC–FID and GC–MS as described above. The bulk solution was vacuum filtered through a glass frit; any solid polymer was collected, dried and weighed. Particularly fine polymer was separated from the solution by centrifuging the solution for 15 min.

4.5. Hydrogenation of oligomers

The sample for hydrogenation was added to a glass autoclave liner, along with a stirrer bar and the catalyst (ca. 100 mg of 5% Pd/C or ca. 10 mg of PtO_2). The solution was degassed with argon for several minutes and the flask placed inside the autoclave which had been flushed with argon. Upon sealing, the autoclave was purged with H_2 then filled to a pressure of 10 bar. The reactor was heated in a sand or oil bath at 80 °C and the mixture stirred for 24 h. The H_2 cylinder was then detached and the mixture allowed to cool; any remaining pressure was then released. A sample could be taken for GC analysis using a needle with a positive argon pressure flowing through the autoclave. If further reaction was needed the process could be resumed, otherwise the solution was removed and filtered for storage. Where only a small amount of sample was available, the procedure was performed in a Schlenk flask. In this case, the reaction flask was purged with hydrogen, and then stirred for 48 h under 1 bar gauge of hydrogen without heating.

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