The Effect of Aromatic Ethers on the Trimerisation of Ethylene using a Chromium Catalyst and Aryloxy Ligands

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Abstract: A catalyst system consisting of a chromium source, a 2,6-disubstituted phenol and an aromatic ether solvent, on activation with triethylaluminium, is active and selective for the trimerisation of ethylene to form 1-hexene. The aromatic ether appears to play a role as both solvent and reagent and is pivotal in ensuring both the good activity of the system as well as selectivity to the desired product, 1-hexene.

Keywords: anisole; chromium; ethylene trimerisation; 1-hexene; homogeneous catalysis; O ligands; phenols

Chromium catalysts have been shown to be useful for both the oligomerisation and polymerisation of ethylene. 1-Hexene is used commercially as a comonomer for the production of, amongst others, linear low-density polyethylene (LLDPE) and the production of low cost, high purity 1-hexene *via* the selective trimerisation of ethylene is thus of value. A variety of different homogeneous catalyst systems consisting mainly of coordination complexes of chromium activated by aluminium alkyls and/or partially hydrolysed aluminium alkyls have been developed for this purpose. Perhaps the best known of these systems is that developed by the Phillips Petroleum Company which consists of a chromium source, 2,5-dimethylpyrrole and an alkylaluminium as activator.[1] A number of catalyst systems containing multidentate phosphine ligands have also shown great promise in this regard.[2,3,4] The Institut Francais du Petrole (IFP) has developed a catalyst system comprising an aryloxyaluminium complex together with a chromium source and an alkylalumium activator for the oligomerisation of ethylene to mainly 1-butene and 1-hexene.[5] We have now shown that the combination of a 2,6-disubstituted phenol with a chromium source and an alkylaluminium activator also yields a catalyst for the selective trimerisation of ethylene. An aromatic solvent, and in particular an aromatic ether, such as anisole, has been found to substantially increase both the activity and the selectivity of this system while also leading to a decrease in the amount of polymeric side product formed during the trimerisation reaction.

As part of our investigation, a variety of aryloxy compounds were synthesised and tested as ligands for chromium and it was established that 2,6-diphenylphenol (**1**) produced the most active and selective ethylene trimerisation system. The best activity achieved with this system, was around 23000 g/g Cr/h, although 13.6 mass % polyethylene was produced as by-product (run 1, Table 1). Through manipulation of reaction conditions, the polymer content could be reduced to 8.6 mass %, albeit at the expense of catalyst activity (run 2, Table 1). 2-Phenylphenol (**6**) as ligand for the catalyst system failed to produce 1-hexene, suggesting that both pendent phenyl groups are essential for catalytic activity. None of the modifications to the pendent phenyl groups yielded a more active catalyst system than that obtained with 2,6-diphenylphenol (runs 10, 11, 15 and 17, Table 1). *ortho*-Methoxy substitution on the pendent phenyl groups failed to produce an active catalyst, possibly due to steric crowding around the metal centre. In contrast to this, *para*-methoxy substitution on the pendent phenyl groups produced an active catalyst (compare runs 10 and 15, Table 1).

In addition to the above studies, a number of different aromatic and aromatic ether solvents were evaluated and anisole proved to be the best solvent for the trimerisation reaction. The catalyst system was inactive using 4-bromoanisole as solvent (run 9, Table 1), suggesting that halogenated solvents act as catalyst poisons. It was further demonstrated that while anisole itself may also, to a limited extent, act as a ligand for the trimerisation of ethylene (compare runs 5 and 7, Table 1) its use as a solvent dramatically improves the activity and selectivity of the system (compare runs 1 and 6, Table 1).

The system was also found to be sensitive to temperature especially with respect to the product distribution obtained. At $100\,°C$, the only product formed is polyethylene while at temperatures between $115\,°C$ and $130\,°C$, substantially less polyethylene is produced, with the main products being 1-hexene, a small amount of higher oligomers and polyethylene. At temperatures higher than $130\,°C$, the amount of higher oligomers in the product distribution increases significantly.

Based on a GC-MS analysis of the liquid products obtained, it would appear that there are two competing mechanisms taking place: a linear chain growth mechanism producing a range of higher oligomers, as well as the generally accepted metallacycle mechanism,[6] producing primarily 1-hexene (see Figure 1). The metallacycle mechanism involves the oxidative addition of two ethylene molecules to form a five-membered metallacycle. The subsequent insertion of a third ethylene molecule gives a seven-membered metallacycle which can then undergo reductive elimination to give 1-hexene. A side reaction is the reaction, *via* the same mechanism, of a 1-hexene molecule with two ethylene molecules to give a number of linear and branched decene isomers. The GC-MS analysis also revealed the presence of small amounts of a wide range of even-carbon number oligomers, which are seen as evidence for the linear chain growth mechanism. The presence of the aromatic ether in the catalyst system seems to produce a catalyst that favours the metallacycle mechanism and as such improves the selectivity to 1-hexene. It would also appear that the selection of the correct temperature appears to be important in producing a catalyst which favours a metallacycle mechanism.

Included in the investigation were compounds that may mimic the aryloxy compounds in their role as ligands for the reaction. In the presence of a suitable base, a ketone may enolise and in the case of 1,3-diphenylacetone (**5**), form a conjugated system with one of the phenyl groups. The oxygen anion of the enolate could then co-ordinate to the chromium in the same way as the aryloxy anion. The use of 1,3-diphenylacetone as ligand (run 13, Table 1) produced a reaction showing good selectivity to 1-hexene within the C_6 fraction, but a large amount of polymer was formed.
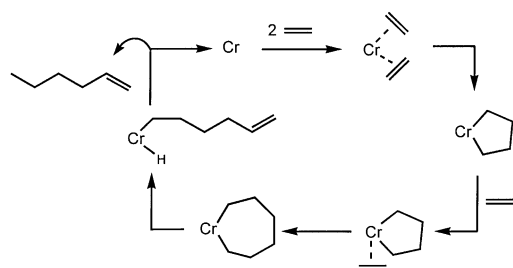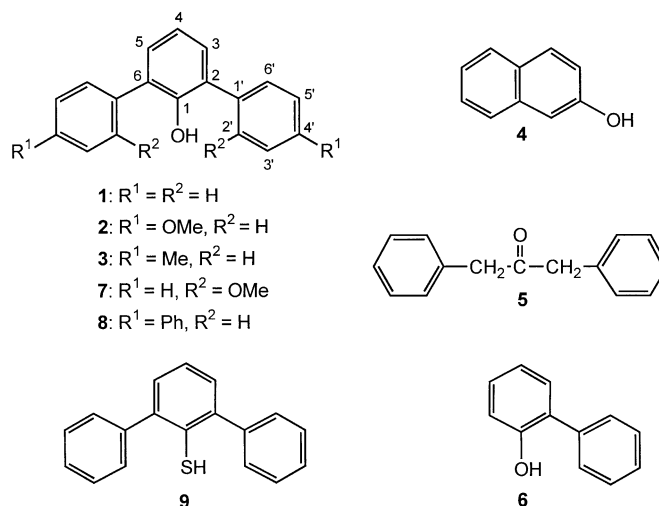

Scheme 1. Ligand structures.

In addition to the above studies, it was reasoned that thiophenols having pendent phenyl groups in the *ortho*-positions could also act as suitable ligands for chromium and hence 2,6-diphenylthiophenol (**9**) was synthesised and evaluated in a catalytic run (run 18, Table 1). This system was neither active nor selective for the trimerisation of ethylene to 1-hexene.

The magnetic susceptibility of the catalyst system consisting of chromium(III) tris-2-ethylhexanoate, 2,6-diphenylphenol and triethylaluminium (TEA) in firstly xylene and secondly anisole was measured using the Evans' method.[7] The system in xylene gave a μ_{eff} value of 5.17 BM and in anisole a μ_{eff} value of 3.61 BM. This would suggest that the oxidation state of the chromium with xylene as solvent was high-spin chromium(II), while the oxidation state of the chromium with anisole as solvent was low-spin chromium(II) or possibly a mixture of chromium(III) and chromium(II). From these results we conclude that the anisole does fundamentally affect the nature of the chromium species formed in the catalytic mixture.

The optimum conditions for this catalyst system, as reported in run 1 (Table 1), result in an active and selective catalyst system for the production of 1-hexene. The major by-products produced by this system are polyethylene and higher oligomers. The system is sensitive to temperature and solvent properties, requiring temperatures from 115 to $130\,°C$ and a co-ordinating, aromatic ether solvent, such as anisole, for good activity and selectivity toward 1-hexene.

Experimental Section

General Remarks

All reactions were carried out under a nitrogen atmosphere using standard Schlenk-line techniques. Solvents were dried

Figure 1. Metallacycle mechanism for ethylene trimerisation.

Table 1. Ethylene trimerisation results.

Run[a]	Ligand (equiv.)	Activator (equiv.)	Solvent	Pressure (C₂/barg)	Temperature (°C)	Productivity (g/g Cr/h)	Selectivity[b]	C₆ (wt %)[c]	Polymer (wt %)
1	1 (14.5)	TEA (20)	anisole	37.5	130	22 769	98.9	89.7	13.6
2	1(14.5)	TEA(20)	anisole	25	123	7653	98.7	91.2	8.6
3	1 (5)	TEA (10)	anisole	50	130	13 033	97.8	87.6	21.5
4	1 (5)	TEA (10)	anisole	25	130	2330	97.5	85.1	11.4
5	–	TEA (20)	anisole	37.5	130	1365	90.7	53.8	33.0
6	1 (14.5)	TEA (20)	xylene	37.5	130	7691	94.3	86.3	29.0
7	–	TEA (20)	xylene	37.5	130	–	–	–	–
8	1 (14.5)	TEA (20)	4-methylanisole	37.5	130	9413	98.7	88.9	22.8
9	1 (14.5)	TEA (20)	4-bromoanisole	37.5	130	–	–	–	–
10	2 (24)	TEA (20)	anisole	35	120	3490	98.1	78.6	59.0
11	3 (14.5)	TEA (20)	anisole	37.5	130	–	–	–	–
12	4 (14.5)	TEA (20)	anisole	37.5	130	2487	96.2	53.8	55.8
13	5 (30)	TEA (30)	anisole	35	115	3566	91.3	29.4	63.0
14	6 (24)	TEA (21)	xylene	35	120	–	–	–	–
15	7 (24)	TEA (20)	anisole	35	120	–	–	–	–
16	1 (14.5)	TEA (20)	ethoxybenzene	37.5	130	7600	94.6	60.4	70.5
17	8 (5)	TEA (10)	anisole	37.5	120	6492	96.2	70.0	45.2
18	9 (14.5)	TEA (20)	anisole	37.5	120	–	–	–	–

[a] Standard conditions: 0.06 mmol of chromium per 100 mL of solution, 30 minute reaction.
[b] Selectivity to 1-hexene in C₆ fraction.
[c] Weight % C₆ in liquid fraction.

and deoxygenated by conventional methods prior to use. All catalytic runs were carried out in a 300-mL Parr autoclave at pressures from 25 to 50 barg and temperatures from 115 to 130 °C. In each case the chromium source used was chromium(III) tris-2-ethylhexanoate. The amount of ligand and activator used was calculated relative to the amount of chromium used and the amounts are included in brackets in Table 1, expressed as molar equivalents relative to chromium. The chromium source, ligand and activator were combined in a Schlenk tube in 20 mL of the solvent of choice for the reaction. The mixture was then immediately transferred to the autoclave containing 80 mL of solvent at the required reaction temperature and the reactor was then pressurised with ethylene which was fed on demand. After a period of 30 minutes, the reaction was quenched by the addition of ethanol and the reactor depressurised. The polymer was filtered, dried and weighed and the liquid fraction was analysed by GC.

2,6-Diphenylphenol, β-naphthol, 1,3-diphenylacetone and 2-phenylphenol were purchased from Sigma-Aldrich and used without further purification. A general synthetic procedure for the substituted *m*-terphenyl ligands is described below.

Synthesis of *m*-Terphenyl Ligands

Compounds **2**, **3** and **7** were prepared in good yields by reaction of the MOM-protected 2,6-dibromophenol with two equivalents of the respective arylboronic acids under Suzuki conditions[8] and subsequent acid hydrolysis (4 M HCl, 1,4-dioxane) of the MOM ether. For the synthesis of **8**, Suzuki coupling[8] of 2,6-dibromoanisole and two equivalents of 1-benzyloxyphenyl-4-boronic acid followed by hydrogenolysis (H₂/Pd-C) of the benzyl ether afforded the 2,6-bis(4-hydroxyphenyl)phenyl methyl ether. This intermediate was converted

to its triflate derivative (triflic anhydride, pyridine, DMAP) and coupled to two equivalents of phenyl boronic acid under Suzuki conditions affording **8** after demethylation with boron tribromide. The *O*-aryl to *S*-aryl conversion was invoked in 2,6-diphenylphenol **1** *via* the Newman–Kwart strategy leading to thiol **9**.[9,10]

2,6-Bis(*p*-methoxyphenyl)phenol 2: Mp 98–100 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.50 (4H, d, *J* = 8 Hz, 2 × H-3′/H-5′), 7.24 (2H, d, *J* = 8 Hz, H-3/H-5), 7.03 (1H, t, *J* = 8.4 Hz, H-4), 7.02 (4H, d, *J* = 8.3 Hz, 2 × H-2′/H-6′), 5.40 (1H, bs, OH), 3.87 (6H, s, 2 × OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 159.1 (2 s), 149.4 (s), 130.5 (4d), 129.8 (2 s), 129.5 (2d), 128.3 (2 s), 120.6 (d), 114.3 (4d), 55.3 (2q); MS (70 eV): *m/z* = 306 (100%, [M]⁺); anal. calcd. for C₂₀H₁₈O₃: C 78.43, H 5.88; found: C 78.11, H 5.54.

2,6-Bis(*p*-tolyl)phenol 3: ¹H NMR (400 MHz, CDCl₃): δ = 7.47 (4H, d, *J* = 8.2 Hz, 2 × H-3′/H-5′), 7.30 (2H, d, *J* = 8.3 Hz, H-3/H-5), 7.26 (4H, d, *J* = 8.4 Hz, 2 × H-2′/H-6′), 6.88 (1H, t, *J* = 8.1 Hz, H-4), 5.68 (1H, s, OH), 2.43 (6H, s, 2 × CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 149.8 (s), 137.8 (2 s), 135.0 (2 s), 131.4 (4d), 130.2 (4d), 121.8 (2d), 120.7 (d), 21.3 (2q); MS (70 eV): *m/z* = 274 (100%, [M]⁺).

2,6-Bis(*o*-methoxyphenyl)phenol 7. Mp 124–126 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.42 (2H, d, *J* = 8.1 Hz, 2 × H-3′), 7.40 (2H, t, *J* = 8 Hz, 2 × H-5′), 7.32 (2H, d, *J* = 8 Hz, H-3/H-5), 7.12 (2H, t, *J* = 8 Hz, 2 × H-4′), 7.09 (2H, d, *J* = 8 Hz, 2 × H-6′), 7.05 (1H, t, *J* = 8 Hz, H-4), 3.87 (6H, s, 2 × OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 156.3 (2 s), 151.2 (s), 132.2 (2d), 130.9 (2d), 128.9 (2d), 127.8 (2x), 127.1 (2 s), 121.2 (2d), 120.5 (d), 111.3 (2d), 55.9 (2q); MS (70 eV): *m/z* = 306 (100%, [M]⁺); anal. calcd. for C₂₀H₁₈O₃: C 78.43, H 5.88; found: C 78.25, H 5.68.

2,6-Bis(*p*-biphenyl)phenol 8. Mp 120–125 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.73 (4H, t, *J* = 8.4 Hz, 2 × H-3″/H-

5″), 7.66 (4H, d, $J = 8.2$ Hz, 2 × H-3′/H-5′), 7.59 (4H, d, $J = 8.5$ Hz, 2 × H-2″/H-6″), 7.48 (2H, t, $J = 8.2$ Hz, 2 × H-4″), 7.38 (2H, d, $J = 8.5$ Hz, H-3/H-5), 7.31 (4H, d, $J = 8.4$ Hz, 2 × H-2′/H-6′), 7.10 (1H, t, $J = 8.2$ Hz, H-4), 5.42 (1H, s, OH); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 149.4$ (s), 141.1 (2 s), 140.4 (2 s), 138.5 (2 s), 135.7 (2 s), 131.3 (4d), 130.3 (2d), 130.0 (4d), 128.9 (2d), 128.1 (4d), 127.1 (4d), 121.3 (d); MS (70 eV): $m/z = 398$ (100%, [M]$^+$); anal. calcd. for C$_{30}$H$_{22}$O: C 90.45, H 5.53; found: C 90.08, H 5.19.

2,6-Diphenylthiophenol 9. Mp 185–190 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.34$ (1H, t, $J = 8$ Hz, H-4), 7.23 (6H, m, 2 × H-3′/H-4′/H-5′), 7.10 (2H, d, $J = 8.2$ Hz, H-3/H-5), 6.75 (4H, d, $J = 8.3$ Hz, 2 × H-2′/H-6′); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 147.9$ (2 s), 141.5 (2 s), 132.9 (s), 129.9 (2d), 129.8 (4d), 128.2 (d), 127.4 (4d), 126.5 (2d); MS (70 eV): $m/z = 262$ (100%, [M]$^+$); anal. calcd. for C$_{18}$H$_{14}$S: C 82.44, H 5.34; found: C 82.25, H 5.09.

Acknowledgements

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