Highly selective chromium-based ethylene trimerisation catalysts with bulky diphosphinoamine ligands†

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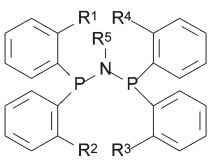
***In situ* prepared chromium catalysts containing bulky diphosphinoamine (PNP) ligands, upon activation with MAO, are extremely efficient catalysts for the trimerisation of ethylene to 1-hexene.**

While conventional ethylene oligomerisation reactions generally produce a mathematical distribution of LAO's (linear alpha olefins),[1] there has been considerable interest in the selective oligomerisation of ethylene to specific carbon chain length olefins. In particular, the selective trimerisation of ethylene to 1-hexene has received a great deal of attention from the academic and industrial community alike.[2] The major use for 1-hexene is as a comonomer in the production of linear low density polyethylene (LLDPE). The majority of the known trimerisation catalysts are chromium-based, including the Phillips pyrrolide system[3] and the Sasol mixed heteroatomic systems,[4,5] although catalysts based on Ta[6] and Ti[7] have also been described. We have recently reported the unprecedented tetramerisation of ethylene to 1-octene catalysed by an aluminoxane activated chromium–diphosphine catalyst system.[8] We report herein a similar catalyst system with ligands of the type $Ar_2PN(R)PAr_2$ (Fig. 1) containing alkyl substituents in the *ortho* position. Upon activation with an aluminoxane, these catalysts are both highly active and selective for the trimerisation of ethylene.[9]

The first account of the use of diphosphinoamine ligands (with *ortho*-methoxy substituents, Fig. 1, R^1–R^4 = OMe and R^5 = Me) and Cr as catalysts for trimerisation was published by Carter *et al.*[10] It was proposed that the *ortho*-methoxy groups act as pendant donors to the chromium metal center and are a prerequisite for catalytic activity. This was postulated by the authors after ligand **2** proved to be completely inactive towards catalysis under the conditions employed.

After the successful application of unsubstituted diphosphinoamine ligands for the tetramerisation of ethylene,[8] we turned our attention towards the sterically encumbered *ortho*-alkyl substituted derivatives **1–9** as ligands for chromium-based oligomerisation catalysts. To our surprise, a number of these catalysts proved to be highly active and selective towards ethylene trimerisation, despite the above report to the contrary.[10]



1: $R^1 = R^2 = R3 = R^4 = Me$; $R^5 = Me$
2: $R^1 = R^2 = R3 = R^4 = Et$; $R^5 = Me$
3: $R^1 = R^2 = R3 = R^4 = iPr$; $R^5 = Me$
4: $R^1 = H$; $R^2 = R^3 = R^4 = Me$; $R^5 = Me$
5: $R^1 = R^2 = H$; $R^3 = R^4 = Me$; $R^5 = Me$
6: $R^1 = R^3 = H$; $R^2 = R^4 = Me$; $R^5 = Me$
7: $R^1 = R^3 = H$; $R^2 = R^4 = Et$; $R^5 = Me$
8: $R^1 = R^3 = H$; $R^2 = R^4 = Et$; $R^5 = iPr$
9: $R^1 = R^2 = R^3 = H$; $R^4 = Et$; $R^5 = iPr$

Fig. 1

The diphosphinoamine ligands **1–3** were synthesised using literature procedures[11] while the novel ligands **4–9** were prepared *via* a similar two step route. The catalysts were prepared by stirring the chromium precursor and ligand briefly in a solvent before adding the mixture to a 300 ml Parr reactor containing solvent and the aluminoxane. The oligomerisation reactions were subsequently conducted isothermally with ethylene fed on demand. Ligand **1** was evaluated under two sets of conditions, namely 30 bar, 65 °C and 45 bar, 45 °C. Our initial results with ligand **1** were immediately promising (Table 1, entry 1) with a selectivity towards the C_6 fraction of 90% of which 99.5% was 1-hexene. An encouraging feature was the distinctly lower C_{10} fraction (0.5%) as compared with that reported by BP with the *ortho*-methoxy equivalent (7–29%). This implies a reduction in the amount of secondary trimerisation (ethylene 1-hexene co-trimerisation) and is of importance for the process economics. Increasing the ethylene pressure to 45 bar and reducing the temperature (entry 2) gave a marked improvement in the activity of the catalyst (298800 g/g Cr.h), but also an increase in the 1-octene selectivity (10.5%) at the expense of 1-hexene (86%). The higher catalyst productivity under these conditions corresponds with results obtained for the related diphosphinoamine-based tetramerisation catalysts,[8] and consequently all subsequent catalytic runs were conducted under these conditions.

Since the unsubstituted diphosphinoamine derived catalysts yielded predominantly 1-octene,[8] it was postulated that steric bulk around the metal centre caused by the *ortho*-methyl substituents was responsible for the increased selectivity towards 1-hexene. In line with this reasoning, the bulkier ligands **2** and **3** with *ortho*-ethyl and *ortho*-isopropyl groups respectively were also evaluated. This premise proved correct, with the catalyst containing ligand **2** producing 93% 1-hexene (entry 4), while there was no further improvement in moving to the even bulkier ligand **3** (entry 9). It is also interesting to note that the choice of chromium precursor [$Cr(acac)_3$ *vs.* $CrCl_3(THF)_3$ *vs.* Cr(III) 2-ethylhexanoate – (entries 3–5)] did not make a substantial difference in the overall selectivities. Similarly, this reaction can be conducted in both aromatic and paraffinic solvents (see entries 3 and 6) using different aluminoxane-based activators (see entries 3, 7 and 8). The best trimerisation result was obtained with ligand **2** at 45 bar and 45 °C (entry 4) with a selectivity towards 1-hexene of 93% and an

† Electronic supplementary information (ESI) available: experimental details of the new ligand syntheses and catalyst screening runs. See http://www.rsc.org/suppdata/cc/b4/b412431f/

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Table 1 Ethylene oligomerisation results[a]

Entry (Ligand)		Pressure C_2 (bar)	Temperature (°C)	Time (min)	Productivity[h] (g/g Cr h)	PE (wt%)	C_6 (wt%)	α-C_6 selectivity (%)	C_8 (wt%)	α-C_8 selectivity (%)	C_{10} (wt%)
1	(**1**)	30	65	30	53 730	2.5	90.4	99.5	5.8	>99	0.5
2[b]	(**1**)	45	45	13	298 800	3.3	86.0	99.1	10.5	>99	0.3
3[b]	(**2**)	45	45	10	324 110	3.4	90.7	99.7	4.2	>99	1.5
4[c]	(**2**)	45	45	15	161 660	0.6	93.0	99.8	3.6	>99	1.1
5[d]	(**2**)	45	45	10	305 720	1.0	92.0	99.8	3.9	>99	3.0
6[e]	(**2**)	45	45	10	131 250	8.5	85.9	99.7	5.3	>99	1.0
7[f]	(**2**)	45	45	30	197 020	5.7	87.0	99.6	5.5	>99	1.0
8[g]	(**2**)	45	45	30	35 170	2.2	89.7	99.6	5.4	>99	1.1
9	(**3**)	45	45	20	100 840	2.4	92.9	99.3	2.7	93.8	1.4
10[b]	(**4**)	45	45	30	96 940	12.0	41.5	81.9	41.9	98.3	1.2
11	(**5**)	45	45	18	37 470	8.3	17.1	55.3	66.0	98.2	1.4
12	(**6**)	45	45	30	26 460	9.0	29.8	26.0	47.6	94.9	2.8
13	(**7**)	45	45	30	52 360	3.9	38.3	39.1	49.1	95.9	2.0
14	(**8**)	45	45	18	110 010	2.8	59.1	94.1	34.1	>99	1.7
15	(**9**)	45	45	14	159 300	0.7	27.1	71.9	63.4	98.0	1.5

[a] Standard reaction conditions unless otherwise stated: 0.033 mmol [$Cr(acac)_3$], 2 eq. ligand, 300 eq. MAO, 100 ml toluene as solvent. [b] 0.02 mmol [$Cr(acac)_3$]. [c] 0.033 mmol $CrCl_3(THF)_3$. [d] 0.033 mmol Cr(III) 2-ethylhexanoate. [e] 100 ml cyclohexane as solvent. [f] 0.01 mmol [$Cr(acac)_3$], 300 eq. MMAO-3A. [g] 1000 eq. EAO and 250 eq. TMA. [h] Calculated according to run times. Standard run time: 30 min or time taken to fill the reactor (10–15 min).

activity approaching 162 000 g/g Cr h. The total quantity of useful liquid products (*i.e.* 1-hexene + 1-octene) was 96.6%!

We were also interested in the effect of changing the number of *ortho*-substituents on the aromatic rings: all indications were that removing steric bulk would lead to a decrease in 1-hexene selectivity and an increase in 1-octene. The partially *ortho*-substituted ligands **4–9** were thus tested. Removal of only one *ortho*-methyl group caused a dramatic shift in product selectivity (ligand **4**, entry 10), with the C_8 selectivity increasing to 42% and the C_6 fraction decreasing to 42%. The selectivity to 1-hexene in the C_6 fraction was concommitantly reduced to 82%. The other major C_6 components were methylcyclopentane and methylenecyclopentane, consistent with our observations of the tetramerisation system.[8] Ligands with only two *ortho*-methyl substituents, the unsymmetrical ligand **5** and its symmetrical counterpart **6**, both afforded catalysts favouring the formation of 1-octene (entries 11 and 12). Ligand **7**, the *ortho*-ethyl substituted analogue of **6**, showed a similar tendency (entry 13). However, on exchanging the *N*-methyl group for an *N*-isopropyl moiety (ligand **8**, entry 14) a change in selectivity back towards 1-hexene was apparent. This can be explained by a translated increase in the steric effect of the ethyl substituents, caused by the greater bulk of the isopropyl group. Interestingly, the 1-hexene selectivity in the C_6 fraction was also significantly improved (entry 13 *vs.* entry 14). An *N*-isopropyl ligand with one *ortho*-ethyl group (ligand **9**, entry 15) gave a C_8-selective catalyst, in line with its reduced steric demand.

In conclusion we have demonstrated that, under the appropriate conditions, pendant coordination is not a prerequisite for selective ethylene trimerisation with diphosphinoamine-based catalyst systems. We have further shown that steric demand plays a crucial role in determining the C6 and C8 selectivities. These new catalyst systems are highly active and may be modified to give various ratios of 1-hexene to 1-octene as required without significant by-product formation.

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