

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 system³ and the Sasol mixed heteroatomic systems,^{4,5} although catalysts based on Ta⁶ and Ti⁷ 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 Ar₂PN(R)PAr₂ (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, R¹–R⁴ = OMe and R⁵ = 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

The diphosphinoamine ligands **1–3** were synthesised using literature procedures¹¹ 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 C₆ fraction of 90% of which 99.5% was 1-hexene. An encouraging feature was the distinctly lower C₁₀ 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. CrCl₃(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

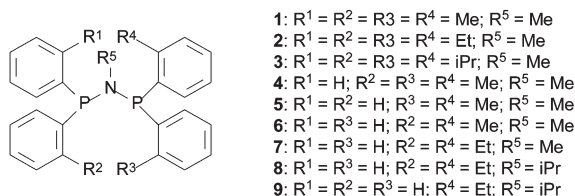


Fig. 1

† Electronic supplementary information (ESI) available: experimental details of the new ligand syntheses and catalyst screening runs. See <http://www.rsc.org/suppdata/cc/b412431f>
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Table 1 Ethylene oligomerisation results^a

Entry (Ligand)	Pressure C ₂ (bar)	Temperature (°C)	Time (min)	Productivity ^b (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 CrCl₃(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 C₈ selectivity increasing to 42% and the C₆ fraction decreasing to 42%. The selectivity to 1-hexene in the C₆ fraction was concomitantly reduced to 82%. The other major C₆ components were methylcyclopentane and methylene-cyclopentane, 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 C₆ 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 C₈-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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