Ethylene trimerisation and tetramerisation catalysts with polar-substituted diphosphinoamine ligands†

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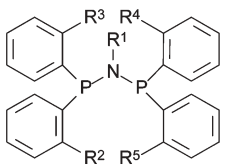
Chromium-based catalyst systems with polar-substituted diphosphinoamine ligands are selective for either trimerisation or tetramerisation of ethylene, depending on the position of the polar groups on the aryl rings.

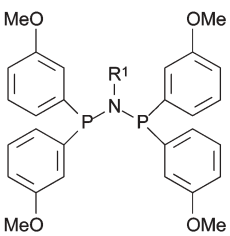
New technologies for the selective oligomerisation of ethylene to valuable 1-alkenes such as 1-hexene and 1-octene remain an imperative in the co-monomer industry.[1] To this end, we have previously reported several new chromium-based catalysts for the selective trimerisation of ethylene to 1-hexene.[2]

Recently, a highly active ethylene trimerisation system, generated *in situ* using a chromium source, a diphosphinoamine ligand of the type $Ar_2PN(Me)PAr_2$ (Ar = *ortho*-methoxyaryl) and an alkyl aluminoxane activator, was reported.[3] It was claimed that the *ortho*-methoxy groups act as pendant donors to the metal centre,[4] and are essential for catalytic activity. We subsequently reported the use of related chromium–diphosphinoamine systems for the trimerisation of ethylene to 1-hexene[5] and the unprecedented selective tetramerisation of ethylene to 1-octene.[6] *ortho*-Substitution of the diphosphinoamine ligand $Ar_2PN(R)PAr_2$ with non-coordinating groups (Ar = *ortho*-alkylaryl) surprisingly resulted in a highly selective ethylene trimerisation system, while using an unsubstituted ligand (Ar = Ph) gave tetramerisation of ethylene to 1-octene with selectivities of up to 71%. The nature and position of substituents on the ligands' aryl groups were thus found to be crucial to the selectivity of these oligomerisation reactions, and it is clear that pendant coordination through aryl donor-substituents is not alone essential for catalytic activity. We report here the results of a study into the role of polar aryl-substitution in chromium–diphosphinoamine ethylene trimerisation and tetramerisation systems.

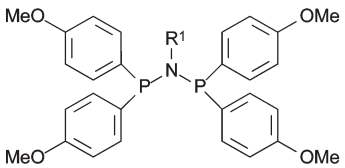
The active catalyst was obtained by introducing a mixture of a chromium(III) source, typically $Cr(acac)_3$, and the ligand to an autoclave containing solvent and methylaluminoxane (MAO). The autoclave was then pressurised with ethylene and maintained at pressure and temperature throughout the course of the reaction. Ligands **1–9** were prepared and tested under two sets of conditions, and the results are shown in Table 1.



1: R^1 = Me, R^2 = R^3 = R^4 = R^5 = OMe
4: R^1 = Me, R^2 = R^3 = R^4 = R^5 = H
6: R^1 = iPr, R^2 = R^3 = R^4 = R^5 = H
7: R^1 = iPr, R^2 = R^5 = OMe, R^3 = R^4 = H
8: R^1 = iPr, R^2 = OMe, R^3 = R^4 = R^5 = H
9: R^1 = iPr, R^2 = Et, R^3 = R^4 = R^5 = H



2: R^1 = Me



3: R^1 = Me
5: R^1 = iPr

Changing the pattern of aryl substitution progressively from *ortho* (**1**, runs 1 and 2) to *meta* (**2**, runs 3 and 4) to *para* (**3**, runs 5 and 6) changes the selectivity of the catalyst from selective trimerisation to predominantly tetramerisation (50% C_8 in run 5). The selectivities obtained with ligand **3** were thus closer to those obtained with the unsubstituted analogue **4**[6] (runs 7 and 8) than with the electronically similar **1**. *meta*-Substituted ligand **2** gave poor activity and higher PE formation, but C_6 and C_8 selectivities obeyed the trend described above.

As reported for the $Ph_2PN(R)PPh_2$ tetramerisation systems,[6] replacement of the *N*-methyl by the bulkier isopropyl group improves both catalytic activity and selectivity to C_6 and C_8. The best tetramerisation results were thus obtained with **5**, which gave a C_8 selectivity of 68% with activity of 112700 g/g Cr.h in one example (run 10). Compared with the unsubstituted analogue **6**[6] (runs 11 and 12), *para*-methoxy substituted ligand **5** results in similar C_8 and higher C_6 selectivities, although at lower activity. Other significant product components include cyclic compounds, particularly methylcyclopentane and methylenecyclopentane in the C_6 fraction, and a complex array of C_{10} to C_{14} oligomers resulting from co-trimerisation and co-tetramerisation reactions of ethylene with 1-hexene or 1-octene.

In general, higher activities are observed at 45 bar, 45 °C than at 30 bar, 65 °C. This can be attributed to both the higher ethylene pressure and reduced catalyst deactivation at lower temperatures. With some of the ligands (**2–7**), higher PE formation occurs at 45 bar, 45 °C, and, in general, higher C_8 at the expense of C_6 is observed at 45 bar, 45 °C compared with 30 bar, 65 °C.

† Electronic supplementary information (ESI) available: experimental details of the new ligand syntheses and catalyst screening runs. See http://www.rsc.org/suppdata/cc/b4/b412432d/

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Table 1 Ethylene oligomerisation results

Run[a]	Ligand	Pressure (bar)	Temperature (°C)	Activity (g/g Cr.h)	PE (wt %)	C6 (wt %)	1-hexene in C6 fraction (%)	C8 (wt %)	1-octene in C8 fraction (%)	C10–C14 (wt %)
1	**1**	30	65	25000	< 1	91	> 99	7	> 99	< 1
2[b]	**1**	45	45	159600	< 1	82	> 99	13	> 99	5
3	**2**	30	65	12800	11	30	67	33	92	9
4	**2**	45	45	25400	19	16	55	22	90	10
5	**3**	30	65	45200	< 1	26	47	50	94	11
6	**3**	45	45	54600	12	17	35	38	91	14
7[c]	**4**	30	65	26500	1	25	39	59	94	10
8	**4**	45	45	44000	40	4	23	22	92	11
9	**5**	30	65	72300	1	39	88	51	99	8
10[d]	**5**	45	45	112700	3	24	74	68	99	4
11[c]	**6**	30	65	11700	< 1	33	87	61	> 99	6
12[e]	**6**	45	45	272400	1	17	70	68	99	7
13	**7**	30	65	154000	1	70	> 99	2	> 99	26
14	**7**	45	45	45600	7	48	> 99	6	> 99	33
15	**8**	30	65	76300	< 1	74	98	6	99	20
16	**8**	45	45	243900	< 1	63	98	17	98	19
17	**9**	30	65	15800	< 1	47	89	47	94	3
18	**9**	45	45	159300	< 1	27	72	63	98	5

[a] Standard conditions unless otherwise stated: 0.033 mmol $Cr(acac)_3$, 2 eq. ligand, 300 eq. activator, 100 ml toluene solvent, 30 minutes (or time taken to fill the reactor if less). [b] 0.02 mmol $Cr(THF)_3Cl_3$. [c] 0.033 mmol $Cr(THF)_3Cl_3$. [d] 0.015 mmol $Cr(THF)_3Cl_3$, 1.2 eq. ligand. [e] 0.022 mmol $Cr(acac)_3$.

We have shown that the selectivity of *ortho*-alkyl substituted diphosphinoamine oligomerisation systems can be shifted from trimerisation to tetramerisation by reducing the number of such substituents stepwise from four to zero.[5] The selectivity in these systems is thus clearly mediated by a steric effect. To establish whether the selectivity of the *ortho*-methoxy substituted diphosphinoamine systems is determined by a similar steric effect or by pendant coordination as proposed,[3] ligands with two (**7**) and one (**8**) *ortho*-methoxy groups were prepared and evaluated. Interestingly, only a small shift in selectivity towards C_8 is observed on reducing the number of *ortho*-methoxy substituents (runs 13–16). Ligand **8** (runs 15 and 16) remains predominantly selective for trimerisation, with a maximum of 17% C_8 observed. By comparison, the sterically similar *ortho*-ethyl substituted ligand **9**[5] resulted in a C_8 selectivity of 63% under the same conditions (run 18).

From these results it is clear that two separate effects can mediate the switch from tetramerisation to trimerisation. Firstly, steric bulk in the immediate vicinity of the metal centre favours trimerisation, and a direct relationship between the extent of crowding (number of *ortho* substituents) and the preference for trimerisation may be observed.[5] Secondly, however, a coordination effect may also be deduced from the predominantly trimerisation behaviour of **8**. Only a single *ortho*-methoxy group is required to interact with the metal centre, possibly as a hemilabile donor. This explains why reduction in the number of potentially coordinating substituents does not significantly affect the preference of the system for trimerisation.

It seems reasonable to assume that 1-hexene and 1-octene are formed *via* a common metallacycloheptane intermediate.[7] Thus it may be postulated that the selectivity towards these products is determined by the relative rates of β-hydride transfer[8] (1-hexene) *vs.* further ethylene insertion to form a metallacyclononane (1-octene) from this species. In the case of *ortho*-alkyl substituted ligands, steric bulk around the catalytic centre may constrain the ring into a more favourable conformation for metal-mediated β-hydride transfer. In the case of *ortho*-methoxy substituents, competitive coordination by the pendant donors may retard the coordination and insertion of ethylene into the metallacycle. In this way, the trimerisation behaviour of these two groups of catalysts may be rationalised. Further experimental and theoretical investigations into the mechanism and selectivity of these selective oligomerisation reactions and the nature of the catalytic species are ongoing.

In conclusion, we have shown that the nature, position and number of aryl-substituents on diphosphinoamine ligands play an important role in determining the selectivity of chromium catalysed oligomerisation reactions. *ortho*-Substitution at the diphosphinoamine aryl rings is key to the switch between tetramerisation and trimerisation selectivity, which may be mediated by either steric crowding around the catalytic centre (non-polar substitution) or by pendant coordination of a donor substituent.

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