COMMUNICATION

ChemComm
www.rsc.org/chemcomm

High activity ethylene trimerisation catalysts based on diphosphine ligands†

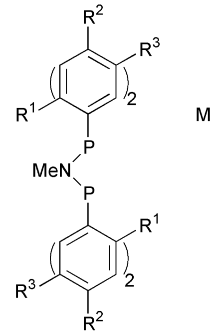
Anthea Carter,[a] Steven A. Cohen,[b] Neil A. Cooley,[a] Aden Murphy,[a] James Scutt[a] and Duncan F. Wass*[a]

[a] *BP, Chemicals Stream, Sunbury on Thames, Middlesex, UK. E-mail: wassdf@bp.com*
[b] *BP, Chemicals Stream, Naperville, Illinois, USA*

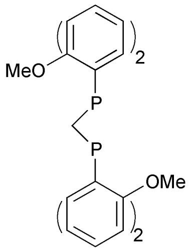
Received (in Cambridge, UK) 8th February 2002, Accepted 11th March 2002
First published as an Advance Article on the web 20th March 2002

Chromium complexes of ligands of the type $Ar_2PN(Me)PAr_2$ (Ar = *ortho*-methoxy-substituted aryl group), on activation with MAO, are extremely active and selective catalysts for the trimerisation of ethylene.

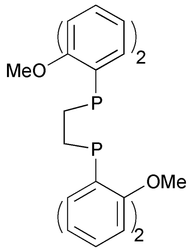
The oligomerisation of ethylene typically gives a broad Schulz–Flory distribution of 1-olefins which must then be separated to give specific carbon number products.[1] The various components of this distribution vary in commercial value, one of the most useful being 1-hexene, a comonomer for linear low-density polyethylene (LLDPE). In recent years, a remarkable family of catalysts has emerged capable of the selective trimerisation of ethylene to 1-hexene by a distinctive mechanism.[2–8] The best known catalysts of this type are those reported by Phillips based on a chromium source, 2,5-dimethylpyrrole ligand and an alkyl aluminium activator.[3] Recently we reported that palladium(II) complexes of ligands of the type $Ar_2PN(Me)PAr_2$ (Ar = *ortho*-substituted aryl group) are efficient catalysts for ethylene/CO copolymerisation and furthermore nickel(II) complexes of these ligands are highly active catalysts for ethylene polymerisation.[9,10] We show here that these same ligands bearing *ortho*-methoxy-substituted aryl groups, together with a chromium source and an alkyl aluminoxane activator, are extremely active and selective ethylene trimerisation catalysts.[11]



1: R^1= MeO, R^2= R^3= H
2: R^1= Et, R^2= R^3= H
3: R^1= R^3= H, R^2= MeO
4: R^1= R^3= MeO, R^2= H
5: R^1= MeO, R^2= H, R^3= F



6



7

The catalyst screening protocol employed reaction of the ligand with a chromium precursor and an alkyl aluminoxane.†‡ The results are given in Table 1. Initial screening of ligand **1** with $[CrCl_3(THF)_3]$ and methyl aluminoxane (MAO) at 1 bar and ambient temperature resulted in a large exotherm, sufficient to cause refluxing of the 1-hexene produced (run 1). Running the catalyst under more controlled pressure and temperature conditions in an autoclave reveals a second order dependence of productivity on ethylene pressure (compare runs 2–4), as is

Table 1 Ethylene trimerisation results

Run[a]	Ligand	Activator	Pressure/bar C_2	Temperature/°C	Yield (g)	Productivity (g/gCr h)	Selectivity (wt%)[b]	Product analysis (wt%) C_6	C_8	C_{10}
1	**1**	MAO	1	[c]	10.3	8 900	99.3	82.2	1.0	14.4
2	**1**	MAO	2	80	5.0	4 610	99.7	91.5	0.6	7.0
3[d]	**1**	MAO	8	80	40	92 250	99.8	85.0	0.4	13.4
4[e]	**1**	MAO	20	80	141	1 033 200	99.9	90.0	1.8	8.5
5[d]	**1**	MAO	8	110	52	95 950	>99.9	86.6	0.5	11.0
6	**1**	MAO	4[f]	80	50	46 130	—	60.0	25.0	11.0
7[g]	**1**	MAO	1	[c]	14.0	8 064	99.8	64.1	0.4	29.0
8	**1**	MAO	0[h]	[c]	0.0	0	—	—	—	—
9[d]	**1**	MAO	8[i]	80	95	175 280	99.7	81.3	0.4	15.4
10[j]	**1**	MAO	1	[c]	11.0	9 500	99.6	80.0	0.8	12.0
11[k]	**1**	MAO	1	[c]	5.6	4 840	99.2	75.0	3.2	15.9
12[d]	**1**	MMAO	8	80	40	92 300	99.7	81.0	0.4	12.7
13[d]	**1**	MAO[l]	8	80	38	90 400	99.8	86.2	0.5	9.0
14	**2**	MMAO	1	[c]	0.0	0	—	—	—	—
15	**3**	MMAO	1	[c]	0.0	0	—	—	—	—
16	**4**	MMAO	1	[c]	7.7	6 650	99.5	84.4	0.7	10.6
17	**5**	MMAO	1	[c]	7.8	6 740	99.4	83.8	1.3	12.5
18	**6**	MMAO	1	[c]	0.0	0	—	—	—	—
19	**7**	MMAO	1	[c]	0.0	0	—	—	—	—

[a] Standard conditions unless otherwise stated: 0.02 mmol ligand, 0.02 mmol $[CrCl_3(THF)_3]$, 300 eq. activator, toluene diluent, 60 min run time; more details may be found in the ESI.† [b] Selectivity to 1-hexene within C_6 fraction. [c] Run start at ambient temperature without control. [d] 0.01 mmol ligand and $[CrCl_3(THF)_3]$. [e] 0.0025 mmol ligand and $[CrCl_3(THF)_3]$. [f] 100 ml 1-butene added. [g] 90 min run time. [h] 50 ml 1-hexene added. [i] 1 bar hydrogen added [j] 0.02 mmol $[CrCl_2(p\text{-tolyl})(THF)_3]$. [k] 0.02 mmol $CrCl_2$. [l] 1.0 g MAO supported on silica (calcined at 200 °C).

---

† Electronic supplementary information (ESI) available: experimental details for catalyst screening runs, together with a typical gas uptake profile. See http://www.rsc.org/suppdata/cc/b2/b201335e/

DOI: 10.1039/b201335e

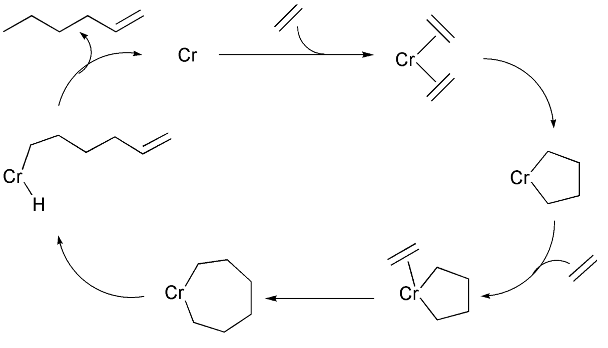
observed for other trimerisation catalysts.[4] At 20 bar ethylene the productivity is over 1 million g/gCr h. This catalytic activity exceeds reported values for the Phillips catalysts by some two orders of magnitude at a given pressure.§ The catalyst is extremely stable and no deactivation was observed over the run time.† The system is also thermally robust (run 5).

Analysis of the product by GCMS reveals good selectivity to 1-hexene, typically > 85% under these conditions, the main by-products being C_{10} olefins. This is consistent with the previously proposed mechanism for trimerisation catalysts (Scheme 1).[2]

Two ethylene molecules coordinate to the chromium centre and oxidatively couple to form a metallacyclopentane. A further ethylene is coordinated and inserts to form a metallacycloheptane. This metallacycle can undergo β-elimination to form an alkyl-hydride species which, after reductive elimination, produces 1-hexene and regenerates the initial chromium species. The C_{10} materials produced are presumably a result of incorporation of one 1-hexene molecule into the growing metallacycles. Consistent with this, addition of 1-butene (Table 1, run 6) increases the yield of C_8 materials. Also, allowing the reaction to procede for a longer run time (Table 1, run 7), *i.e.* a high final concentration of 1-hexene in solution, increases the relative weight percentage of C_{10} to C_6 material. For run 7, small amounts of C_{14} and C_{18} materials (5.0 and 0.6 wt% respectively) are also observed; these may result from the incorporation of two or three 1-hexene molecules respectively or from the re-incorporation of one C_{10} or C_{14} olefin. Attempted trimerisation of 1-hexene alone to produce C_{18} material was unsuccessful (Table 1, run 8), supporting the latter mechanism. In all cases the selectivity to 1-hexene within the total C_6 fraction is extremely high, greater than 99.9% in the case of run 5.

Addition of hydrogen (Table 1, run 9) results in a two-fold increase in productivity but little effect on selectivity; specifically, no hexane is detected. Enhancement of productivity by hydrogen has been previously reported for ethylene trimerisation catalysts.[3]

Other chromium precursors have been investigated, including $[CrCl_2(p\text{-tolyl})(THF)_3]$ which gave identical results to $[CrCl_3(THF)_3]$ (Table 1, runs 1 and 10) but with the advantage of improved precursor solubility. Interestingly, $CrCl_2$ also yielded an active catalyst (Table 1, run 11) albeit with approximately half the productivity of run 1; this suggests that post-activation at least some of the same active species is formed with either Cr(III) or Cr(II) precursors. The structure of this active species is still to be fully elicidated and is the subject of our ongoing study. The range of successful activators was also extended to modified MAO (MMAO) and similar results were again obtained (compare runs 3 and 12).¶ Of significant technological importance, the catalyst was also successfully supported on MAO-silica with no loss in activity or selectivity (Table 1, run 13). It is worth noting that irrespective of the co-catalyst, chromium precursor or conditions used no measurable polymeric by-product is produced in any run.



Scheme 1 Postulated mechanism for ethylene trimerisation.

The exceptional performance of **1** lead us to investigate other related ligand systems. We initially postulated that the steric bulk provided by the *ortho*-substituents on ligand **1** plays a critical role in establishing the catalyst's performance, as is the case for polymerisation catalysis with these ligands.[9,10] However, ligand **2** containing sterically equivalent *ortho*-ethyl substituents was completely inactive under our conditions (Table 1, run 14). Moreover, the electronically related ligand **3**, bearing *para*-methoxy groups was also inactive (Table 1, run 15). However, ligands **4** and **5**, with variations to *para* and *meta* substituents but retaining this *ortho*-methoxy group were active (Table 1, runs 16 and 17). This has lead us to hypothesise that the potential for *ortho*-methoxy groups to act as pendant donors and increase the coordinative saturation of the chromium centre is an important factor. Building on this hypothesis ligands **6** and **7**, which contain the same aryl substitution pattern as **1** but different chelate backbones, were tested but both proved to be inactive. Clearly, the ligand backbone also plays an important role.

In conclusion, this new catalyst has unprecedented performance for ethylene trimerisation to produce 1-hexene. Our results also demonstrate the growing utility of bis(diarylphosphino)-amine ligands in catalysis. The high activity and selectivity of these systems make them very suitable for use in tandem with olefin polymerisation catalysts to produce LLDPE from ethylene alone; results in this area will be reported shortly.

Notes and references

‡ New compounds have been fully characterized.

§ Reference 3 reports productivities up to 66 400 g/gCr h in similar experiments (37.4 bar total pressure, 80 °C). The productivity of the Phillips catalyst also demonstrates a second order ethylene pressure dependence (see ref. 4).

¶ MMAO is similar to MAO; only approximately 20% of methyl groups are replaced by isobutyl substituents.

1 G. V. Schulz, *Z. Phys. Chem. B*, 1935, **30**, 379; P. J. Flory, *J. Am. Chem. Soc.*, 1936, **58**, 1877; J. Skupinska, *Chem. Rev.*, 1991, **91**, 613.

2 J. R. Briggs, *Chem. Commun.*, 1989, **11**, 674.

3 W. K. Reagen, T. M. Pettijohn and J. W. Freeman, *US Pat.*, US 5 523 507, 1996 (to Phillips Petroleum Company).

4 Y. Yang, H. Kim, J. Lee, H. Paik and H. G. Jang, *Appl. Catal. A*, 2000, **193**, 29.

5 F.-J. Wu, *US Pat.*, US 5 744 677, 1998 (to Amoco Corporation).

6 R. D. Köhn, M. Haufe, G. Kociok-Köhn, S. Grimm, P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 4337.

7 S. Liu, S. Elyashiv and A. Sen, *J. Am. Chem. Soc.*, 2001, **123**, 12738.

8 P. J. W. Deckers, B. Hessen and J. H. Teuben, *Angew. Chem., Int. Ed.*, 2001, **40**, 2516.

9 S. J. Dossett, A. Gillon, A. G. Orpen, J. S. Fleming, P. G. Pringle, D. F. Wass and M. D. Jones, *Chem. Commun.*, 2001, 699; S. J. Dossett, *Eur. Pat.*, EP 0850105, 2000 (to BP Chemicals); S. J. Dossett, *Pat. Appl.*, WO 00/06299, 2000 (to BP Chemicals).

10 N. A. Cooley, S. M. Green, D. F. Wass, K. Heslop, A. G. Orpen and P. G. Pringle, *Organometallics*, 2001, **20**, 4769; D. F. Wass, *Pat. Appl.*, WO 01/10876, 2001 (to BP Chemicals).

11 D. F. Wass, *Pat. Appl.*, WO 02/04119, 2002 (to BP Chemicals).