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Selective Cotrimerization of Ethene and Styrenic Comonomers

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Summary: Chromium catalysts supported by bis(diarylphosphino)amine ligands, on activation with methylaluminoxane (MAO), selectively cotrimerize ethene and styrenic comonomers to give predominantly linear products via 2,1-insertion of comonomer.

In recent years, catalysts have emerged capable of the selective trimerization of ethene to 1-hexene via a distinctive metallacyclic mechanism.[1] In 2002, we reported catalysts based on chromium complexes of ligands of the type $Ar_2PN(Me)PAr_2$ (Ar = *o*-methoxy-substituted aryl group) with productivity figures over an order of magnitude better than those of previous systems.[2] This unprecedented performance led to interest both from a mechanistic viewpoint and in ligand structural modification,[3] the most significant subsequent development being the report from Bollmann and co-workers that relatively minor changes to ligand structure and reaction conditions can lead to ethene tetramerization rather than trimerization.[4]

The codimerization of ethene and styrene is known for a variety of nickel and palladium catalysts. This reaction proceeds via an insertion/elimination mechanism and has been extended to asymmetric variants with the correct ligand choice.[5] In contrast, the scope of chromium trimerization catalysts with substrates beyond ethene has not been explored, even though cotrimerization of ethene with other comonomers such as styrene is a potentially simple catalytic route to ω-substituted alkenes. We show here that our chromium trimerization catalysts are effective for the cotrimerization of ethene and styrenic comonomers via a metallacyclic mechanism to give predominantly linear products and that the structure of the ligand used controls the product distribution obtained.

The catalytic protocol employed is based on that which gave the best results for ethene homotrimerization, using $Ar_2PN(Me)PAr_2$ (**I**; Ar = 2-(MeO)C_6H_4), $CrCl_3(THF)_3$, and 300 equiv of MAO (Figure 1).[2] Results are presented in Table 1. A low ethene pressure of 1 bar is used throughout to maximize the potential yield of cotrimer vs 1-hexene. As the styrene concentration is increased, the yield of cotrimer increases as expected (runs 2−6), up to greater than 95% of the total mass of product at high comonomer concentration. Turnover frequencies are approximately half that of ethene homotrimerization and are similar at various low concentrations of comonomer. As the amount of styrene is increased further, a steady dropoff in activity is observed. Although this could be due to an increasing concentration of catalytically dormant species with increasing styrene,

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Table 1. Cotrimerization Data

run no.[a]	comonomer	ligand	comonomer concn[b]/mol dm^{-3}	total yield of products[c]/g	TOF/h	product distribn (wt %)[d]							
						cotrimers							
						total cotrimer	wt% within cotrimer fraction						
							1	**2**	**3**	**4** and **5**[f]	**6** and **7**	1-hexene	C10 alkenes[e]
1	none	I		9.0	8654							73.0	25.0
2	styrene	I	0.04	7.8	4430	10.6	49.2	13.3	20.9	0.0	16.6	67.2	21.4
3	styrene	I	0.38	9.8	4660	42.7	53.3	9.9	20.6	0.0	16.2	38.4	18.1
4	styrene	I	1.0	8.8	3630	64.8	51.1	9.6	20.7	0.0	18.6	21.5	13.8
5	styrene	I	1.6	8.6	3245	76.7	52.1	12.1	19.1	0.0	16.7	10.5	5.3
6	styrene	I	6.0	8.2	2674	95.8	54.5	8.6	22.2	0.0	14.7	4.2	0.0
7[g]	styrene	I	6.0	4.8	1720	82.7	52.8	9.4	22.0	0.0	15.8	16.0	1.3
8[h]	styrene	I	6.0	20.6	1120	95.3	56.3	8.8	21.5	0.0	13.4	3.9	0.7
9	styrene	II	6.0	8.6	2724	98.3	24.3	10.3	7.3	0.0	58.1	1.7	0.0
10	styrene	III	6.0	4.0	1288	98.0	13.3[i]			0.0	86.7	2.0	0.0
11[g]	styrene	III	6.0	3.9	1232	100.0	4.8[i]			0.0	95.2	0.0	0.0
12	4-methoxystyrene	I	1.0	0.3	127	35.0	48.7	9.5	25.0	0.0	16.8	59.8	5.2
13	4-chlorostyrene	I	1.0	2.1	713	72.3	74.2	8.1	12.6	0.0	5.1	19.1	8.6
14	2-chlorostyrene	I	1.0	0.2	143	0.0						100.0	0.0

[a] Conditions unless stated otherwise: 0.02 mmol of $Ar_2PN(Me)PAr_2$, 0.02 mmol $CrCl_3(THF)_3$, 300 equiv of MAO, toluene diluent, 44 mL total volume; 1 bar of ethene; 25 °C moderated by external bath; 1 h run time. [b] Ethene concentration is approximately 0.15 mol dm^{-3} for a typical run, as determined by NMR. [c] Calculated from mass gain during run and product distribution, verified by GC vs internal standard (mesitylene). [d] Determined by GC and GCMS; see Scheme 1 for numbering of products. [e] C14 alkenes are also detected is some cases (2% for run 1); this has been observed previously.[3] [f] Hydrogenation of a typical product (run 8) to yield the parent alkane skeletal isomers reveals trace amounts (0.4 wt %) of 2-phenylhexanes. [g] Run at 70 °C. [h] Run for 6 h. [i] Total linear isomers: ratio of isomers could not be determined at this concentration.

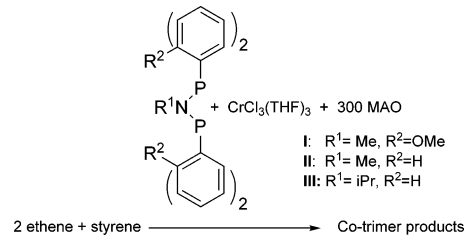


Figure 1. Styrene/ethene cotrimerization.

the presence of low levels of catalyst poisons in this comonomer, despite our purification methods (see the Supporting Information), cannot be ruled out. Increasing the reaction temperature from 25 to 70 °C (runs 6 and 7) has little effect on turnover frequency but leads to a small decrease in the amount of cotrimer materials obtained. An extended run time (run 8) leads to a lower overall TOF value, indicating some catalyst deactivation with time.

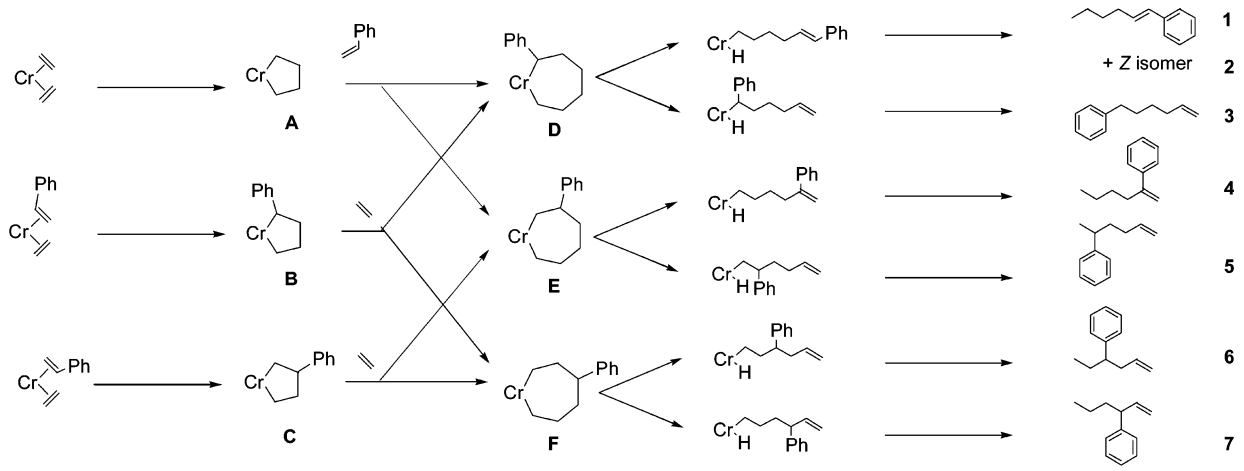
Changing the ligand used to **II**, in which methoxy substituents have been removed, gives the same activity within error (compare runs 6 and 9), whereas ligand **III**, the most successful of those reported by Blann and co-workers for ethene tetramerization,[4] gives a TOF approximately half that of **I** (runs 10 and 11). It is noteworthy that **II** and **III** are essentially inactive for ethene homotrimerization under these conditions[2] and, consistent with this, only trace amounts of 1-hexene byproducts are detected for these ligands. The distributions of cotrimer isomers are significantly different for **II** and **III** compared to that for **I** (vide infra); however, only products arising from cotrimerization (rather than cotetramerization) are observed. This is consistent with the hypothesis that the balance between ligand and metallacyclic steric bulk is important in the number of monomers that are oligomerized.[3b,c]

Product distribution analysis for all runs reveals that C12 cotrimers formed from two ethene units and a single styrene are the exclusive cotrimer products in all cases: C18 cotrimers formed from one ethene unit and two styrenes or styrene homotrimers are not detected. In line with this result, attempted homotrimerization of styrene (no ethene) with the same catalysts was unsuccessful.[6] The major byproducts observed are the expected 1-hexene, together with C10 alkenes formed via cotrimerization of ethene and 1-hexene; these same products are observed in the absence of styrene (run 1).

Closer examination of the cotrimer product distribution for **I** reveals that this is largely invariant with respect to temperature, styrene concentration, and run time (compare runs 2−7). Three skeletal isomers are observed, linear phenylhexenes **1**−**3** being the major products (>80%). Within these linear products there is a mixture of 6-phenylhex-1-ene (**3**) and (*E*/*Z*)-1-phenylhex-1-ene (**1**/**2**). These products are entirely consistent with a metallacyclic mechanism (Scheme 1). This mechanism is complicated compared to that for ethene homotrimerization because of the possibility for 1,2- or 2,1-regiochemistry of styrene insertion. Three metallacyclopentane intermediates are possible via oxidative coupling of two ethene units (**A**) or one ethene and one styrene unit with 1,2- (**B**) or 2,1-regiochemistry (**C**). Styrene insertion into **A** can again be 1,2 or 2,1 to yield the metallacycloheptanes **E** or **D**. These can β-eliminate from either side of the metallacycle, which, after reductive elimination, gives the illustrated possible final products. Similarly for **B** and **C**, ethene insertion can occur into either side of the metallacycle to give seven-membered rings. In total, these various possibilities give the three possible skeletal isomers (**1**−**3**, **4** and **5**, and **6** and **7**) that are observed experimentally. The fact that isomers **1**−**3** account for over 80% of the total product, with the remainder being **6** and **7** and only trace amounts of **4** and **5**, indicates that **E** is not a significant intermediate. **E** can only be obtained via 1,2-insertion, suggesting that there is a strong preference for 2,1-styrene insertion in these systems. It is possible to obtain all of the observed products from the common metallacyclopentane **B**; it is also noteworthy that ethene insertion into the least hindered side of this ring leads to the major products. However, at this stage it is not possible to rule out significant involvement for **A**, especially considering the presence of 1-hexene byproducts. The distribution of **1**−**3** observed is more difficult to rationalize, and we note that the internal isomers **1** and **2**, which are the major products, are

(6) Similar results are obtained with attempted 1-hexene homotrimerization.[3]

Scheme 1. Cotrimerization Mechanism and Possible Products



predicted to arise from β-elimination from the more hindered side of intermediate **D**.

Ligand **II** also shows a strong preference for 2,1-insertion, products **4** and **5** again being absent. However, a significant change in product distribution is observed, with the branched isomers **6** and **7** now accounting for 58.1% of the cotrimer product. A possible explanation for this is that the less sterically encumbered ligand **II** makes ethene insertion into the bulkier phenyl-substituted side of metallacycle **B** more facile. This change is even more dramatic on moving to **III**, with **6** and **7** now accounting for over 95% of the total products. The role of the isopropyl group on this ligand leading to such a large change in selectivity is difficult to rationalize, especially since this ligand is bulkier than **II**, although we note that this same subtle substituent effect proves to be crucial in achieving high selectivity for ethene tetramerization.[4]

Analysis of the C10 alkenes formed as a byproduct via ethene/1-hexene cotrimerization reveals over 95% selectivity to methylnonenes (analogous to **4** and **5**).[7] These products can only arise from 1,2-insertion of 1-hexene (cf. intermediate **E**), indicating a dramatic change in preferred regiochemistry compared to that for styrene.[8,9]

We have extended this reaction to a limited number of substituted styrene comonomers (runs 12−14). The productivity observed for 4-chlorostyrene is lower than that for styrene, although the amounts of cotrimer produced are similar (compare runs 4 and 13). A larger effect is seen for 4-methoxystyrene, with both productivity and selectivity being significantly reduced (runs 4 and 12). It is tempting to invoke an electronic rationale for this observation, but we suggest poisoning of the electrophilic catalyst center by the potentially ligating methoxy group is more likely. Our hypothesis was that ortho substitution of the substrate may promote a change to 1,2-regiochemistry because of the steric congestion of 2,1-inserted products. In fact, cotrimerization activity is completely switched off with 2-chlorostyrene under our conditions (run 14) and only 1-hexene is observed.

In conclusion, the catalysts described are efficient in selectively cotrimerizing ethene and one styrenic comonomer via a metallacyclic mechanism. Predominantly linear materials are obtained for the methoxy-substituted ligand **I**, although changes to ligand structure allow control over the product distribution to yield branched isomers. All of the products obtained indicate a strong preference for 2,1-styrene insertion. We are currently exploring a broader range of ligand structures, with the goal of increasing selectivity to terminal alkene isomers, as well as the utility of the ω-substituted alkene products as functionalized comonomers for polyolefinic materials.[10]

Acknowledgment. We thank Dr. Hazel Mottram for assistance with the GCMS measurements and the Royal Society and the Univeristy of Bristol for funding.

Supporting Information Available: Text giving experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Analysis of C10 product from run 1; 95.2% methylnonenes by GC.

(8) This is consistent with the different regiochemistries of insertion observed for styrene compared to 1-hexene polymerization with metallocene catalysts: (a) Caporaso, L.; Izzo, L.; Zappile, S.; Oliva, L. *Macromolecules* **2000**, *33*, 7275. (b) Zambelli, A.; Longo, P.; Pellecchia, C.; Grassi, A. *Macromolecules* **1987**, *20*, 2035. (c) Murray, M. C.; Baird, M. C. *J. Mol. Catal. A: Chem.* **1998**, *128*(1−3), 6542.

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