The selective trimerisation of isoprene with chromium *N,N*-bis(diarylphosphino)amine catalysts†

Lucy E. Bowen, Manutsavin Charernsuk and Duncan F. Wass*

Received (in Cambridge, UK) 14th February 2007, Accepted 17th April 2007
First published as an Advance Article on the web 1st May 2007
DOI: 10.1039/b702331f

Chromium catalysts supported by *N,N*-bis(diarylphosphino)-amine ligands, on activation with methyl aluminoxane (MAO), selectively trimerise isoprene with unprecedented activity to predominantly linear materials.

Oligomers of 1,3-dienes are important natural terpenoid compounds and there has been a great deal of interest in the synthesis of such products *via* catalytic oligomerisation.[1] Most studies have focused on dimerisation and a number of catalysts has been reported, in which good selectivities can be achieved by changes to ancillary ligands.[2] Catalytic trimerisation is also known, predominantly for 1,3-butadiene with catalysts often based on 'naked' metal π-allyl complexes.[3] Despite the importance of isoprenoid natural products, reports of catalytic isoprene trimerisation are more rare. The few systems reported are exclusively based on group 10 metal complexes and, in common with 1,3-butadiene studies, often dimerise or give a distribution of oligomeric products.[4] Chromium diphosphine species have been investigated with 1,3-diene substrates but lead exclusively to polymerisation with both 1,3-butadiene and isoprene.[9]

In recent years, catalysts have emerged which are capable of the selective trimerisation of ethene to commercially valuable 1-hexene *via* a distinctive metallacyclic mechanism.[5] In 2002, we reported catalysts based on chromium complexes of ligands of the type $Ar_2PN(Me)PAr_2$ (Ar = *ortho*-methoxy-substituted aryl group) with productivity figures over an order of magnitude better than previous systems.[6] This unprecedented performance led to interest both from a mechanistic viewpoint and in ligand structural modification,[7] the most significant subsequent development being the report from Bollmann *et al*. that relatively minor changes to ligand structure and reaction conditions can lead to ethene tetramerisation rather than trimerisation.[8] We have recently started to explore the utility of these systems with a broader range of substrates[10] and show here that our chromium catalysts are very effective for the trimerisation of 1,3-dienes (Fig. 1).

The catalytic protocol employed is based on that which gave the best results for ethene homo-trimerisation, using $Ar_2PN(Me)PAr_2$ (Ar = 2-$(MeO)C_6H_4$) (**1**), $CrCl_3(THF)_3$ and 300 equivalents of MAO at 70 °C.[6] Results are presented in Table 1.

With 1,3-butadiene, polymerisation is observed, no oligomers below *ca*. C_{30} being detected by GC. ^{13}C NMR spectroscopy reveals the polymer to have a predominantly 1,2- monomer microstructure (60% 1,2-, 33% *cis* 1,4- and 7% *trans* 1,4-), in line with reports for other systems.[9]

Surprisingly, with isoprene (2-methylbut-1,3-diene) selectivity to trimeric products is observed. Turnover frequencies for ligand **1** are up to 660 h^{-1}, over two orders of magnitude more productive than previously reported isoprene trimerisation catalysts.‡ Good selectivity to C_{15} products is observed, typically up to 79.9 wt% with the remaining products consisting largely of higher isoprene oligomers (typically *ca*. 80% tetramer). Within the C_{15} fraction, there are four isomers, three corresponding to linear isomers and one cyclic, the linear trimers being the dominant products in all cases. Hydrogenation of the C_{15} fraction reduces this to two structural isomers, the linear isomer 2,6,11-trimethyldodecane and the cyclic product 1,4,8-trimethylcyclododecane The close similarity of double bond isomers of the unhydrogenated 2,6,11-trimethyldodecatriene products has precluded further characterisation of these species.

Decreasing the concentration of substrate (runs 2 and 3) leads to a modest decrease in both TOF and wt% trimeric material. Decreasing the run temperature to 45 °C (runs 2 and 4) leads to a decrease in both TOF and wt% trimeric material; however, the relative yield of linear material within the C_{15} fraction is significantly increased. Decreasing the temperature further to 25 °C (run 5) gives a more dramatic reduction in productivity. There is no change to TOF or selectivity within error when the run time is increased (runs 4 and 6), indicating good catalyst stability within this timescale.

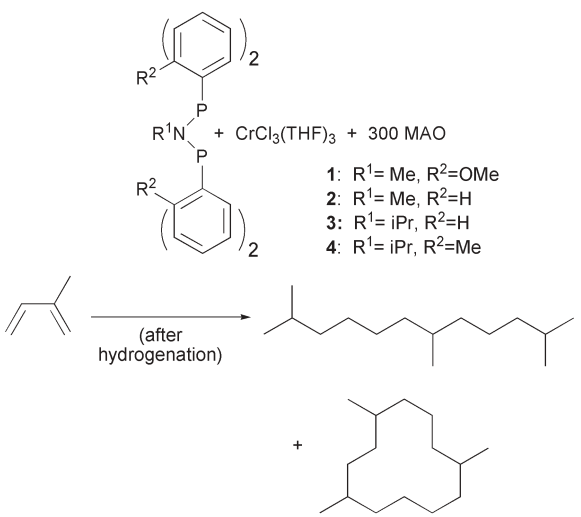


Fig. 1 Isoprene trimerisation.

School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS. E-mail: duncan.wass@bristol.ac.uk
† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/b702331f

Table 1 Trimerisation/polymerisation data

				Product distribution (wt%)			
				Trimers			
					Wt% within trimer fraction[c]		
Run[a]	Substrate	Ligand	TOF[b]/h	Total trimer	Linear	Cyclic	Other[j]
1[d]	1,3-Butadiene	**1**	1125	0.0	—	—	Polymerisation
2	Isoprene	**1**	660	79.1	70.0	30.0	20.9
3[e]	Isoprene	**1**	420	68.8	77.0	23.0	31.2
4[f]	Isoprene	**1**	280	68.2	87.2	12.8	31.8
5[g]	Isoprene	**1**	20	69.0	72.9	27.1	31.0
6[f,h]	Isoprene	**1**	240	70.0	85.3	14.7	30.0
7	Isoprene	**2**	300	6.6	[i]	[i]	93.4
8	Isoprene	**3**	240	28.7	[i]	[i]	71.3
9	Isoprene	**4**	530	94.9	74.3	25.7	5.1
10	2,3-Dimethylbuta-1,3-diene	**1**	695	89.9	[i]	[i]	10.1

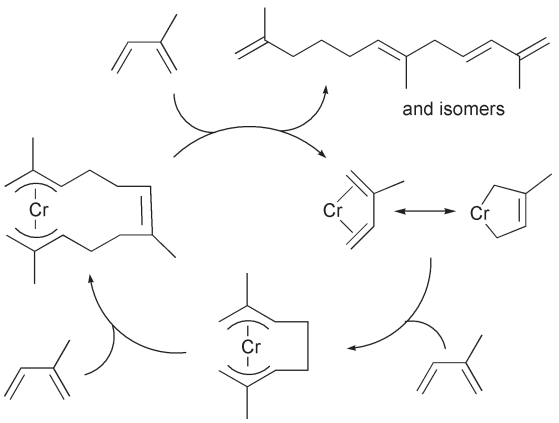
[a] Conditions unless stated otherwise: 20 μmol ligand, 20 μmol $CrCl_3(THF)_3$, 300 equivalents of MAO, 6.8 M substrate concentration, toluene diluent, 44 ml total volume; 70 °C controlled by external bath; 1 h run time. [b] Calculated from GC *vs.* internal standard (mesitylene). [c] Determined by GC and GCMS of hydrogenated products, products confirmed by NMR spectroscopy *vs.* authentic samples. [d] Toluene solution saturated with 1,3-butadiene; see ESI. TOF determined by mass of polymer. [e] 4.5 M substrate concentration. [f] Run at 45 °C. [g] Run at 25 °C. [h] Run for 4 h. [i] Could not be determined. [j] Tetramers are the major other products (>80%) in every case. See ESI for typical distribution.

Changing the ligand to **2**, in which methoxy substituents have been removed, gives a TOF approximately half that of **1** (compare runs 2 and 7) and a product distribution consisting largely (>90 wt%) of higher oligomers, C_{20} tetramers being the major product.

Ligand **3**, the most successful of those reported by Bollmann *et al.* for ethene tetramerisation,[8] gives a similar TOF to **2** (run 8) and again a product distribution favouring higher oligomers (>70 wt%). By contrast, ligand **4**, now with *ortho* tolyl P-substituents has a TOF approaching that of **1** (compare runs 2 and 9) and shows excellent selectivity to trimeric products of 94.9 wt%; selectivity to linear products is similar to **1**. These results suggest ligand steric bulk is an important factor in controlling trimerisation *vs.* tetramerisation/oligomerisation; this is also a crucial parameter for ethene trimerisation *vs.* tetramerisation with these catalysts.[7b,c]

With 2,3-dimethylbut-1,3-diene and ligand **1**, trimerisation is again observed with high selectivity (runs 2 and 10).

The high selectivities to trimeric products observed are consistent with a metallacyclic mechanism – simple insertion/elimination mechanisms would lead to a statistical distribution of products. A large number of regiochemical possibilities exist for isoprene trimerisation; however, the substitution pattern observed for the hydrogenated major isomer, 2,6,11-trimethyldodecane, indicates 1,4-insertion to be exclusively favoured. We propose a mechanistic scheme similar to that originally suggested for 1,3-butadiene trimerisation[3] (Scheme 1); this is clearly also closely related to the well-established metallacyclic mechanism for ethene trimerisation.[1] It is noteworthy that the head–tail–tail trimer produced is consistent with the more stable 2-methyl allyl intermediates being formed at each stage.



Scheme 1 Postulated trimerisation mechanism.

A full rationale for the change in selectivity from trimerisation to polymerisation with 1,3-butadiene remains elusive, although we note there is a very fine balance between trimerisation, tetramerisation, non-selective oligomerisation and polymerisation for chromium systems with more simple olefins.[1]

In conclusion, the catalysts described are efficient in selectively trimerising isoprene or 2,3-dimethylbut-1,4-diene *via* a metallacyclic mechanism. Currently, we are fully exploring ligand structure–property relationships in order to achieve selectivity to natural 2,6,10-trimethyldodecatriene isomers.

We would like to thank the University of Bristol for funding.

Notes and references

‡ See ref. 4*a*; TOF *ca.* 2.0 h^{-1} for Ni-based catalysts.

1 R. Baker, *Chem. Rev.*, 1973, **73**, 487.
2 For leading references, see: G. Wilke and A. Eckerle, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996, p. 359.
3 R. Benn, P. W. Jolly, R. Mynott and G. Schenker, *Organometallics*, 1985, **4**, 1136; G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 185.
4 (*a*) S. Akutagawa, T. Taketomi, H. Kumobayashi, K. Takayama, T. Someya and S. Otsuka, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1158; (*b*) S. Akutagawa, T. Taketomi and S. Otsuka, *Chem. Lett.*, 1976, 485.
5 D. F. Wass, *Dalton Trans.*, 2007, 816; J. T. Dixon, M. J. Green, F. M. Hess and D. H. Morgan, *J. Organomet. Chem.*, 2004, **689**, 3641.
6 A. Carter, S. A. Cohen, N. A. Cooley, A. Murphy, J. Scutt and D. F. Wass, *Chem. Commun.*, 2002, 858.
7 (*a*) T. Agapie, S. J. Schofer, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2004, **126**, 1304; (*b*) K. Blann, A. Bollmann, J. T. Dixon,

F. Hess, E. Killian, H. Maumela, D. H. Morgan, A. Neveling, S. Otto and M. J. Overett, *Chem. Commun.*, 2005, 622; (*c*) K. Blann, A. Bollmann, J. T. Dixon, F. M. Hess, E. Killian, H. Maumela, D. H. Morgan, A. Neveling, S. Otto and M. J. Overett, *Chem. Commun.*, 2005, 620.
8 A. Bollmann, K. Blann, J. T. Dixon, F. M. Hess, E. Killian, H. Maumela, D. S. McGuiness, D. H. Morgan, A. Neveling, S. Otto, M. Overett, A. M. Z. Slawin, P. Wasserscheid and S. Kuhlmann, *J. Am. Chem. Soc.*, 2004, **126**, 14712.
9 G. Ricci, M. Battistella and L. Porri, *Macromolecules*, 2001, **34**, 5766; G. Ricci, A. Forni, A. Boglia and M. Sonzogni, *Organometallics*, 2004, **23**, 3727.
10 L. E. Bowen and D. F. Wass, *Organometallics*, 2006, **25**, 555.