Supplementary Material (ESI) for Chemical Communications

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

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Supplementary Information

Experimental details

General: All procedures were carried out under an inert atmosphere (N_2) using standard Schlenk line techniques unless otherwise specified. Chemicals were obtained from Aldrich or Fisher Scientific. Isoprene and 2,3-dimethylbut-1,3-diene were dried over 4Å molecular sieves, distilled and degassed prior to use; other chemicals were used without further purification. Methyl aluminoxane (MAO) was obtained from Aldrich as a 10 wt% solution in toluene. Ligands were synthesised by previously published methods.[1,2]

Typical trimerisation Run: $Ar_2PN(Me)PAr_2$ (Ar = 2-C_6H_4(MeO)) (11 mg, 20 μmol) and [$CrCl_3(THF)_3$] (8 mg, 20 μmol) were dissolved in tetrahydrofuran (3 ml) and stirred at room temperature for 10 minutes. Solvent was then removed under reduced pressure and toluene added (10ml). Methylaluminoxane (MAO, 10 wt% sol. in toluene, 300 eq, 6 mmol, 4 mL) was then added, to give a pale green solution. Isoprene (30 ml) was added and the solution was vigorously stirred for 1 h, during which time and temperature was moderated by an external water bath at 70 °C. After this time the tube was opened to air and a dilute aqueous solution of hydrochloric acid (10 %) slowly added to quench the reaction (*Caution: vigorous reaction of MAO and water!*). The organic layer was separated and dried over magnesium sulfate.

1,3-Butadiene Run: Essentially the same procedure was followed, only the catalyst solution was made up to a total volume of 44 ml with toluene and then saturated with 1,3-butadiene by bubbling this through the solution for 5 minutes.

Analysis of Products: Products were analysis by GC-MS and GC-FID (Hewlett Packard Series) using mesitylene as an internal standard. Conditions: Alltech Econo-CAP column, EC5, 30 m x 0.25 mm, IDX 0.25μm: starting temperature 40 ^oC, rising to 80 ^oC at 2 ^oC min^{-1} and then to 300 ^oC at 10 ^oC min^{-1}. Elusion times for the various isoprene oligomer products are given below:

Isomer	2,6,11-trimethyl-dodecatrienes	1,4,7-trimethyl-cyclododecatriene	Tetramers
Retention time (min)	28.4 - 28.9	30.0	33.8 – 39.0

The trimeric skeletal isomers obtained were confirmed by hydrogenation of a typical product distribution (run 2) and comparison with authentic commercially available samples. The hydrogenation of a portion of the product from run 2 was achieved by the following method: Solvent and residual isoprene were removed by distillation. The products were dissolved in toluene and 250 mg of 5 wt% Pt/C added. The resulting slurry was stirred under 1 bar of dihydrogen for 72 h, after which time the solution was filtered. The following product distribution was obtained (Run 2):

Isomer	2,6,11-trimethyl-dodecane	1,4,7-trimethyl-cyclododecane	Tetramers	Higher oligomers
Retention time (min)	26.2	28.1	36.3	39.8
Wt %	55.0	23.9	14.8	6.3

Products were also confirmed by ^{13}C NMR spectroscopy by comparison to authentic samples.

References

(1) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F.; *Chem. Comm*. **2002**, 858 .

(2) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuiness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S; Overett, M.; Slawin, A. M. Z.; Wasserscheid P.; Kuhlmann, S.; *J. Am. Chem. Soc.* **2004**, *126*, 14712.