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

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

Supplementary Information

Experimental details

General: All procedures were carried out under an inert atmosphere (N₂) 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: Ar₂PN(Me)PAr₂ (Ar = 2-C₆H₄(MeO)) (11 mg, 20 µmol) and [CrCl₃(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 °C, rising to 80 °C at 2 °C min⁻¹ and then to 300 °C at 10 °C min⁻¹. Elusion times for the various isoprene oligomer products are given below:
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):

<table>
<thead>
<tr>
<th>Isomer</th>
<th>2,6,11-trimethyl-dodecatrienes</th>
<th>1,4,7-trimethyl-cyclododecatriene</th>
<th>Tetramers</th>
<th>Higher oligomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retention time (min)</td>
<td>28.4 - 28.9</td>
<td>30.0</td>
<td>33.8 – 39.0</td>
<td></td>
</tr>
</tbody>
</table>

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

References
