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Novel Cr-PNP complexes as catalysts for the trimerisation of ethylene

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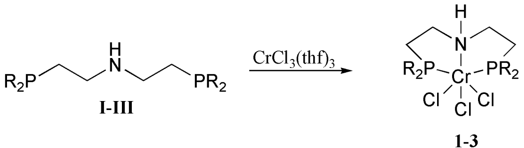
Cr(III) complexes of tridentate PNP ligands have been prepared and evaluated as catalysts for ethylene trimerisation, with several giving high activity and excellent selectivity towards 1-hexene when activated with methylaluminoxane.

While the oligomerisation of ethylene generally gives a broad range of α-olefins, there is increasing interest in the development of catalysts which are able to give greater selectivity toward more desirable olefins. Of particular interest is the linear trimerisation of ethylene to 1-hexene, due to the importance of this co-monomer in the production of polyethylene. Of the systems known to trimerise ethylene, most are based on homogeneous Cr catalysts, although several catalysts based on Ti[1] and Ta[2] have recently been reported. The most successful of the Cr based complexes appear to be pyrrolyl-Cr complexes[3] as well as complexes of neutral phosphorus containing ligands,[4,5] while neutral tridentate NNN ligands have been applied in the trimerisation of α-olefins.[6] In the course of investigations on alternative catalysts for ethylene trimerisation, we became interested in tridentate PNP ligands in combination with Cr as procatalysts for this reaction. Here we report new complexes of Cr(III) that, in combination with methylaluminoxane (MAO), selectively convert ethylene to 1-hexene with TOFs in ethylene up to *ca.* 70 000 h^{-1}.

The tridentate PNP ligands **I–III** were prepared *via* literature procedures or *via* adaptation of these.[7] When reacted with $CrCl_3(thf)_3$ the immediate formation of complexes **1–3** was observed, which were isolated as deep blue-purple powders in 92–100% yield after workup (Scheme 1).‡ Complex **1** was the first to be prepared and tested for ethylene trimerisation, and when activated with 120 equivalents of MAO was found to give reasonable activity with excellent selectivity toward 1-hexene (Table 1, entry 1). Attempts to improve the system centred first on modification of the phosphorus substitution. Highly basic but sterically demanding dicyclohexylphosphino substituents (complex **2**) led to a dramatic decrease in activity, with the product being predominately polymer (entry 2). In contrast, under comparable conditions basic but compact diethylphosphino substituents (complex **3**) led to a large increase in activity with excellent 1-hexene selectivity (entry 3).

When a greater amount of MAO was introduced (680 equiv.) along with complex **1** activity doubled, however a higher proportion of polymer and 6% 1-butene was formed at the expense of hexene selectivity (entry 4). In contrast, at higher MAO loadings (300–700 equiv.) complex **3** led to a pronounced increase in activity while high hexene selectivity was maintained (entries 5 and 6). The highest activity achieved with complex **3** was 69 340 turnovers h^{-1} (37400 gProduct per gCr per h) when activated with 850 equivalents of MAO, however a somewhat lower hexene selectivity resulted (entry 7). Increasing the amount of MAO beyond this does not significantly further increase the activity of the complexes. ^{13}C NMR analysis of polymer samples resulting from runs 2, 3 and 7



R=phenyl (**I**, **1**)
R=cyclohexyl (**II**, **2**)
R=ethyl (**III**, **3**)

Scheme 1

Table 1 Ethylene trimerisation with complexes **1–3**[a]

Entry	Catalyst (amount μmol)	MAO (equivalents)	Temperature (°C)	Run time (min)	PE (wt%)	Hexenes (wt%)	1-Hexene selectivity (wt%)[b]	Productivity (h^{-1})[c]
1	**1** (40.2)	120	100	30	0.1	98	99.2	8 670
2	**2** (42.3)	120	100	30	85.7	14	80.0	580
3	**3** (50.0)	100	100	30	0.2	98	99.2	17 300
4	**1** (11.0)	680	100	30	10.2	83	99.1	17 620
5	**3** (23.0)	340	100	30	0.3	98	98.9	48 060
6	**3** (10.8)	690	100	30	0.7	98	98.9	58 570
7	**3** (8.8)	850	100	30	2.1	94	99.1	69 340
8	**3** (12.0)	630	100	60	0.3	92	99.2	31 220
9	**3** (13.0)	600	50	60	21.9	78	98.8	2 950
10	**3** (11.0)	680	80	30	0.4	97	99.2	50 770
11	**3** (11.8)	640	80	60	0.3	97	99.3	39 890
12	**3** (11.3)	660	120	30	0.2	93	99.3	49 620

[a] 40 bar ethylene, 25mL toluene. [b] Selectivity for 1-Hexene as a percentage of total hexenes. [c] Average turnover frequency of ethylene conversion.

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showed no evidence for 1-hexene incorporation in the polyethylene chain.

It was noted in all runs conducted at 100 °C with complex **3** that ethylene uptake dramatically decreases towards the end of a run (30 min), suggesting deactivation of the catalyst. This is verified by a 1 h run (entry 8), in which the average activity obtained is roughly half of that for a 30 min run conducted under the same conditions. At 50 °C the catalytic activity drops significantly, and a high proportion of polymer is formed (entry 9). At 80 °C the high activity and selectivity of the catalyst is restored (entry 10). Furthermore, towards the end of this 30 min run ethylene uptake continues, suggesting a greater catalyst stability at this temperature. In a 1 h run at 80 °C (entry 11) the average activity of the catalyst is somewhat lower, however the total turnover number obtained (39 890) is higher than in all other runs, reflecting a longer catalyst lifetime at this temperature. To further verify a thermally induced catalyst deactivation at higher temperatures, when run at 120 °C (entry 12) the catalyst was virtually inactive after only 15 min, a lower total activity relative to runs at 80–100 °C resulted, and the formation of higher oligomers occurred which reduced the hexene selectivity to 93%. These results reveal a high sensitivity of the catalyst system towards varying reaction conditions, both in terms of activity and selectivity. Careful optimisation of the reaction conditions is ongoing.

Crystals of complexes **1** and **2** suitable for X-ray diffraction studies were grown by slow evaporation of a solution of the complex in DMSO (**1**) or acetone (**2**). The molecular structure of **1**, along with selected bond distances and angles, is shown in Fig. 1, while that for complex **2** is shown in Fig. 2§ Both complexes display a slightly distorted octahedral geometry, with the tridentate ligand coordinated in a meridional fashion. The chelate bite angles of the PNP ligand in both complexes are similar [81.08(8), 82.07(8)° (**1**); 82.54(7), 81.99(7)° (**2**)], as are the Cr–P distances, which for the Cr–P1 bond of each complex are the same within experimental error. The Cr–N distances in each complex [2.139(3) Å (**1**); 2.137(3) Å (**2**)] are likewise equal within experimental error and are within the range of Cr(III) amine bond lengths (*ca* 2.05–2.19 Å).[8] The greater steric demand of the cyclohexyl relative to the phenyl group, which represents the main difference between the two structures, is reflected in the larger angles C5–P1–C11 and C17–P2–C23 (Figs. 1 and 2).

Given the similarities in the molecular structures of **1** and **2** it is difficult to reconcile the remarkable differences in activity that each gives. It must be borne in mind however that these structures represent only that of the procatalyst, and it is possible that in the active catalyst the ligand is coordinated in a manner that is more sensitive to greater steric bulk of the phosphine, such as a facial coordination geometry. This is under further investigation. We are also exploring the use of alternate tridentate ligands, incorporating different donor atoms, such that the use of phosphines can be avoided. The results of this work will be published in due course.

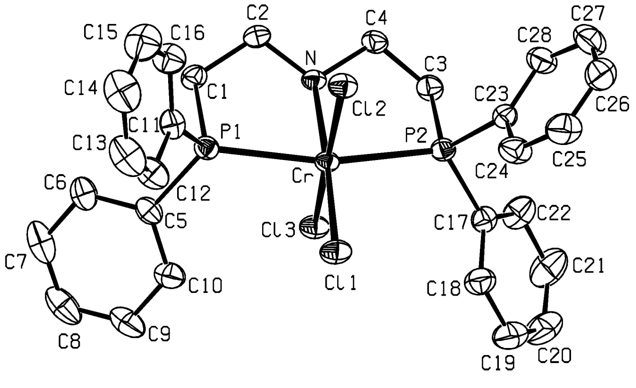

Fig. 1 Molecular structure of **1**, 30% probability ellipsoids, H atoms omitted for clarity. Selected bond distances (Å) and angles (°): Cr–P1 2.4660(12), Cr–PP2 2.4678(12), Cr–PN 2.139(3), Cr–PCl1 2.2934(11), Cr–PCl2 2.3081(11), Cr–PCl3 2.3480(11), N–PCr–PP1 81.08(8), N–PCr–PP2 82.07(8), P1–PCr–PP2 163.10(4), N–PCr–PCl1 176.74(8), N–PCr–PCl2 87.59(8), N–PCr–PCl3 85.00(8), C5–PP1–PC11 103.42(18), C17–PP2–PC23 104.40(17).

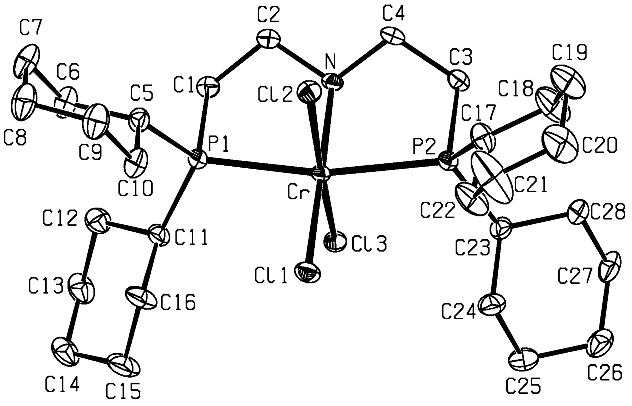

Fig. 2 Molecular structure of **2**, 30% probability ellipsoids, H atoms omitted for clarity. Selected bond distances (Å) and angles (°): Cr–PP1 2.4662(10), Cr–PP2 2.4736(10), Cr–PN 2.137(3), Cr–PCl1 2.2898(10), Cr–PCl2 2.3090(11), Cr–PCl3 2.3616(11), N–PCr–PP1 82.54(7), N–PCr–PP2 81.99(7), P1–PCr–PP2 164.49(4), N–PCr–PCl1 178.96(8), N–PCr–PCl2 86.63(8), N–PCr–PCl3 84.95(8), C5–PP1–PC11 112.51(16), C17–PP2–PC23 112.19(18).

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Notes and references

‡ Elemental analysis and mass spectral (+FAB) data for **1**–**3**. **1**: $C_{28}H_{29}Cl_3CrNP_2$ calcd. (found) C 56.07 (55.84), N 2.34 (2.14), H 4.87 (5.16)%. *m/z* 598 [M]$^+$, 563 [M − Cl]$^+$. **2**: $C_{28}H_{53}Cl_3CrNP_2$ calcd. (found) C 53.89 (54.10), N 2.24 (2.14), H 8.56 (8.54)%. *m/z* 624 [M]$^+$, 589 [M − Cl]$^+$. **3**: $C_{12}H_{29}NP_2Cl_3Cr$ calcd. (found) C 35.36 (35.29), N 3.44 (3.21), H 7.17 (7.49). *m/z* 352 [M]$^+$, 315 [M − Cl]$^+$.

§ **1**·DMSO: $C_{30}H_{35}Cl_3CrNOP_2S$, M = 677.95, monoclinic, a = 27.667(7), b = 14.751(4), c = 16.512(4) Å, β = 100.923(7)°, U = 6617(3) Å^3, T = 293(2) K, space group $C2/c$ (no. 15), Z = 8, μ (Mo-K$_\alpha$) = 0.772 mm^{-1}, 28626 reflections measured, 6532 unique (R_{int} = 0.0662) which were used in all calculations. The final $R(F)$ and $wR(F^2)$ were 0.0521 ($I > 2\sigma(I)$) and 0.1512 (all data), respectively. CCDC 179726. **2**·acetone: $C_{31}H_{59}Cl_3CrNOP_2$, M = 682.08, monoclinic, a = 10.340(3), b = 16.2779(11), c = 21.3434(18) Å, β = 90.757(13)°, U = 3592.1(11) Å^3, T = 223(2) K, space group $P2_1/n$ (no. 14), Z = 4, μ (Mo-K$_\alpha$) = 0.655 mm^{-1}, 10559 reflections measured, 7031 unique (R_{int} = 0.0494) which were used in all calculations. The final $R(F)$ and $wR(F^2)$ were 0.0520 ($I > 2\sigma(I)$) and 0.1399 (all data), respectively. CCDC 179727. See http://www.rsc.org/suppdata/cc/b2/b210878j/ for crystallographic files in CIF or other electronic format.

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