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Discovery of a new family of chromium ethylene polymerisation catalysts using high throughput screening methodology†

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Following a discovery that salicylaldimines bearing bulky *ortho*-phenoxy substituents and small imine substituents give very active chromium catalysts for ethylene polymerisation, High Throughput Screening (HTS) methodology has been employed to facilitate a further discovery of exceptionally active catalysts based on tridentate salicylaldimine ligands with bulky triptycenyl groups.

Schiff base [N,O] chelates provide attractive stabilising ligands for catalysis due to their ready accessibility and amenability to modification. In recent years they have enjoyed notable success in the stabilisation of early (Ti[1]) and late (Ni[2]) transition metal catalysts for olefin polymerisation. In our own work we have been exploring this ligand family for chromium-based polymerisation systems. We have reported bis(chelate) complexes as ethylene polymerisation catalyst precursors, but these gave only modest activities ($\sim$100 g mmol^{-1} h^{-1} bar^{-1}).[3] Since the required salicylaldimines are readily formed by simple condensation chemistry, they are ideal candidates for ligand libraries in HTS programmes. Such programmes are of interest for catalyst discovery since they allow large numbers of diverse ligands to be tested efficiently.[4] Here, we describe the discovery of a new family of chromium catalysts containing bidentate [N,O] ligands for olefin polymerisation, **I** Fig.1. This led us to screen a ligand library by HTS methods resulting in the discovery of a further exceptionally active chromium catalyst system based on tridentate [O,N,N] ligands, **II** Fig.1.

Recent reports have shown that nickel complexes bearing [N,O] chelates with bulky *ortho*-phenoxy substituents are highly active for ethylene polymerisation.[2] We thought that bulky [N,O] chelates could be used to stabilise complexes of the type $LCrCl_2$ and that these may show a different reactivity profile to reported chromium catalysts. Simple modelling (MMFF94 MacSpartan-Pro), however, indicated that the bulky 2,6-^{i}Pr-phenyl groups, commonly used to stabilise square planar late transition metal complexes, may be poorly placed to stabilise tetrahedral or trigonal bipyramidyl geometries, and less sterically demanding imine substituents may be necessary. To test this hypothesis, three salicylaldimines were synthesised by reacting 2,6-^{i}Pr$_2$PhNH$_2$, PhNH$_2$ or ^{i}PrNH$_2$ with *o*-(9-anthracenyl)salicylaldehyde (**A**, Fig. 2). The new ligands were tested *in situ* by reacting them in toluene with the soluble metal precursor (*p*-tolyl)$CrCl_2(thf)_3$ (**2**) followed by removal of excess thf and solvent *in vacuo*. The resulting complexes were dissolved in toluene and activated with 200 equivalents of MAO, Scheme 1. In line with our reasoning, complex **3a** showed little activity (<40 g mmol^{-1} h^{-1} bar^{-1}) whilst the progressively less bulky complexes **3b** and **3c** afforded activities of 95 and 1760 g mmol^{-1} h^{-1} bar^{-1}, respectively.

On the basis of the encouraging results for catalyst **3c**/MAO, a ligand library was designed (i) to optimise the activity and performance of the bidentate mono-chelate ligand system, (ii) to explore the potential of tridentate Schiff base ligand systems, and (iii) to probe the steric and electronic effects of substituents attached to the salicylaldimine backbone. To this end, three further salicylaldehydes were synthesised‡ (see Fig. 2), and coupled with 55 commercial amines.§ The library was screened using a modification to the protocol outlined in Scheme 1: for the purposes of the HTS experiment, residual thf was not removed *in vacuo* from the reaction mixture. This affords lower absolute activities than for the base free catalyst systems, but parallel trends in activities are seen for the two systems. The results of the ligand library screen are summarised in Fig 3.

The HTS experiment confirmed the high activity of derivatives of **A** containing small alkyl substituents attached to the imino donor, especially 2° alkyls, cycloalkyls and phenyl-substituted alkyls, Fig 3. By comparison, ligands based on backbone **B** showed slightly lower activities to those of **A** while ligands based on backbone **C** showed no significant catalysis. Ligands based on backbone **D** showed in general no activity except, we were surprised to find, in combination with 2-aminopyridine (ligand **32D**) where the highest activity of the screen was recorded. Ligand **32D** was re-synthesised on a larger scale in order to further investigate the HTS result. The analogous ligand **32A**, which was not screened with the original library, was also prepared. When tested under *in-situ* conditions ligand **32A** was almost inactive while **32D** gave an activity of 1860 g mmol^{-1} h^{-1} bar^{-1} (Table 1).[5] Further testing in a 1L batch reactor at 4 bar ethylene and 50 °C afforded an activity of 3410 g mmol^{-1} h^{-1} bar^{-1}. This led us to synthesise the

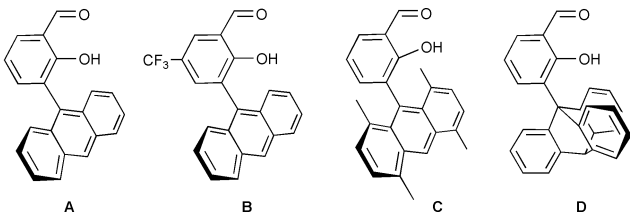


Fig. 2 Salicylaldehyde backbones used to generate the ligand library.

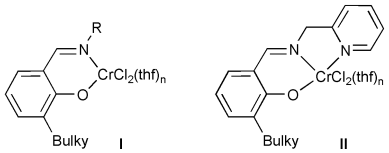
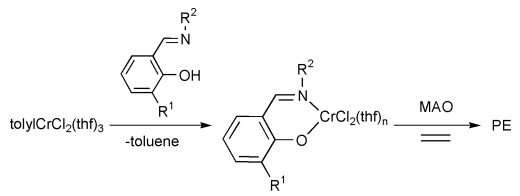


Fig. 1 Bidentate and tridentate Schiff's base complexes of chromium as pre-catalysts for ethylene polymerisation.



R^1 = Anthracenyl, R^2 = 2,6-^{i}Pr$_2$Ph (**3a**) : R^2 = Ph (**3b**) : R^2 = ^{i}Pr (**3c**)

Scheme 1 *In situ* catalyst precursor formation and MAO activation. *Reagents and conditions*: (i) vacuum, (ii) MAO (200 equiv.), toluene, (iii) C_2H_4 (1 atm), RT, 60 min.

† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b2/b202037h/

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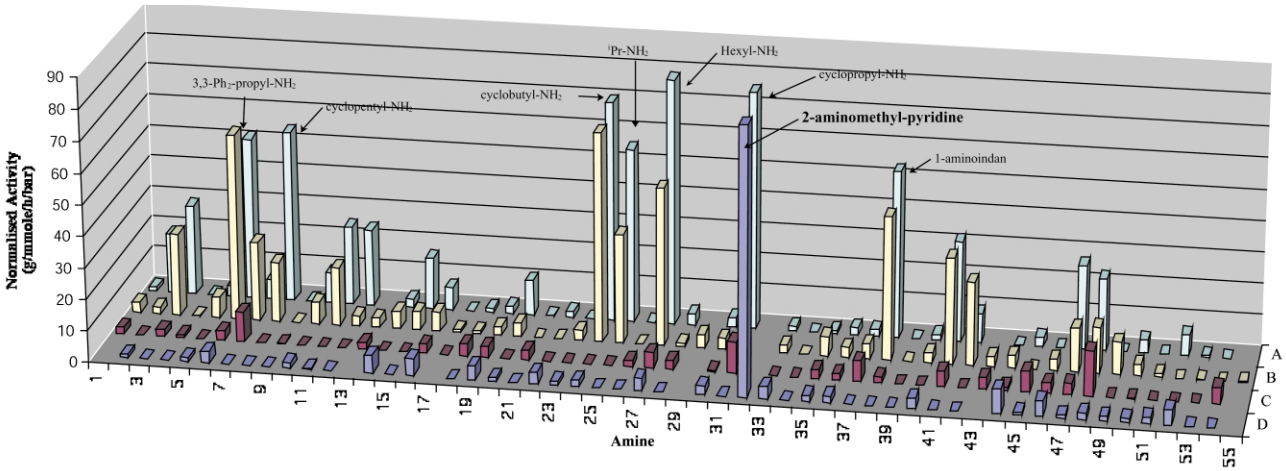

Fig. 3 HTS results for ethylene polymerisation tests using the ligand library generated from the four bulky salicylaldehydes and 55 commercial amines. *Reagents and conditions*: 0.005 mmol ligand + (tolyl)$CrCl_2(thf)_3$, Al:Cr = 200:1, toluene 5 ml, RT, 10 min. Actvities are normalised to the average activity for **3c**/**MAO** (ligand **25A**) in each set of tests. The single hit for the tridentate *o*-triptycenyl-salicylaldimine, ligand **32D**, is highlighted.

Table 1 Ethylene polymerisation tests for chromium complexes of the form $LCrCl_2(thf)_n$; summary of catalytic and polymer chracterisation data (Anth = anthracenyl, Tript = triptycenyl)

	R^1	R^2	Test method	Cr/mmol	Al:Cr	*T*/°C	*P*/bar	Yield/g	Activity[a]	M_n	M_w	M_w/M_n	Me's/per 1000C)	Vinyls/per 1000C)
1	Anth	$^iPr_2Ph$	*In situ*	0.005	200	RT	1	—	<40					
2	Anth	Ph	*In situ*	0.015	200	RT	1	1.42	95	213000	934000	4.4	0.8	0.3
3	Anth	^iPr	*In situ*	0.002	200	RT	1	0.88[b]	1760	is[c]	is[c]	is[c]	is[c]	is[c]
4	Anth	2-$PyCH_2$	*In situ*	0.005	200	RT	1	—	<40					
5	Tript	2-$PyCH_2$	*In situ*	0.005	200	RT	1	9.31[d]	1860	1100	1900	1.8	16.3	11.6
6	Tript	2-$PyCH_2$	*In situ*	0.005	600[e]	50	4	68.14	3410	600	1200	2.0	26.0	21.7
7	Tript	2-$PyCH_2$	$LCrCl_2$	0.001	2200[e]	50	4	27.87	6970	600	1100	2.1	24.8	22.3

[a] g(PE) $mmol^{-1}$ h^{-1} bar^{-1}. [b] Catalysis stopped after 15 min (standard 60 min). [c] Polymer not soluble, high molecular weight. [d] Includes 1.44 g of soluble material which is not included in the polymer analysis, GC analysis indicates linear α-olefins. [e] MAO (2 mmol) used as scavenger in the 1L batch reactor.

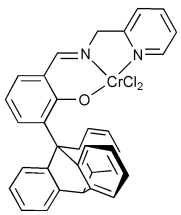

Fig. 4 Complex **3d** showing the bulky tryptycenyl substituent.

complex containing ligand **32D** *via* its treatment with (*p*-tolyl)$CrCl_2(thf)_3$ followed by precipitation from thf. This base free complex, **3d** (R^1 = triptycenyl, R^2 = 2-pyridylmethyl) Fig. 4, was tested at 4 bar and 50 °C and gave an activity of 6970 g $mmol^{-1}$ h^{-1} bar^{-1}, which compares favourably with the most active molecular chromium olefin polymerisation systems.[6] It is presumed that traces of thf remain in the *in situ* tests resulting in suppressed activities, as seen in the HTS experiments.

Polymer analysis indicates that the new complex (**3d**, Fig. 4), bearing a tridentate [O,N,N] chelate, generates low molecular weight linear polyethylene, $M_w \approx 1200$, while the complexes (**3b** & **3c**) formed with bidentate [N,O] ligands form high to very high molecular weight material.

In summary, we have used HTS methods to examine a library of salicylaldimine ligands bearing bulky *o*-substituents. The screening has confirmed our initial discovery that bidentate [N,O] chelates with small alkyl imine substituents can be used to generate highly active chromium ethylene polymerisation catalysts which produce high molecular weight polyethylene. The value of the screening methodology was further demonstrated by the identification of a new tridentate [O,N,N] ligand system which gives an exceptionally active chromium catalyst for the production of low molecular weight polyethylene.

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Notes and references

‡ The large-scale synthesis of these salicylaldehydes and related compounds will be reported elsewhere.

§ The ligand library was synthesised on a 0.2 mmol scale; a numbered list of amines is provided in the ESI.† Note that not all amine/salicylaldehyde combinations were made to the required purity or quantity to be included in the library.

All new compounds gave satisfactory analytical and spectroscopic analysis.

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