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Published on Web 07/16/2005

Discovery and Optimization of New Chromium Catalysts for Ethylene Oligomerization and Polymerization Aided by High-Throughput Screening

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Abstract: High throughput screening (HTS) of a 205 member Schiff base salicylaldimine ligand library derived from salicylaldehydes bearing bulky *ortho*-substituents, i.e., 9-anthracenyl, 1,4,5,8-tetramethylanthracenyl or triptycenyl, reacted in-situ with (*p*-tolyl)$CrCl_2(thf)_3$, identified two new classes of highly active chromium based systems for the oligomerization and polymerization of ethylene, respectively. The polymerization system comprises bidentate ortho-substituted anthracenyl Schiff bases bearing small primary or secondary alkyl imine substituents. The oligomerization catalysts are based upon tridentate *ortho*-triptycenyl-substituted Schiff bases with pyridylmethyl or quinolyl substituents. Validation tests confirmed polymerization productivities of up to 3000 g·mmol^{-1}h^{-1}bar^{-1} for the polymerization catalyst systems while the oligomerization catalysts gave productivities up to 10 000 g·mmol^{-1}h^{-1}bar^{-1}. Key catalyst precursors have been characterized by X-ray crystallography.

Introduction

Recent spectacular improvements in activities for nonmetallocene olefin polymerization systems have spurred efforts to develop new commercially viable catalyst systems for the production of polyolefins.[1] Among the transition metals, chromium holds special attraction due to its role in the commercial production of polyethylene using silica-supported Phillips[2] and Unipol[3] catalyst systems. In recent years, a number of molecular chromium catalysts have been reported, both for the oligomerization and polymerization of ethylene[4−18] as well as for ethylene trimerization,[19] and recently tetramerization.[20]

The rate of discovery and optimization of new catalyst systems has been enhanced significantly by the introduction of High Throughput Screening (HTS) methodologies.[21] For the Group 4 metals Tian and Coates applied a combinatorial 'catalyst pool' approach to discover a titanium catalyst supported by Schiff base ligands for the syndiotactic polymerization of propylene,[22] while workers at Symyx Technologies Inc. have disclosed stereoselective propylene polymerization catalysts based on dianionic tridentate chelate ligands,[23] as well as olefin polymerization catalysts based on monoanionic bidentate ligands.[24]

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More recently, Mountford and co-workers have utilized a HTS approach to discover imido-titanium catalysts for ethylene polymerization,[25] and GPC has been used as a screening method to discover hetero-ligated phenoxy-imine catalysts for syndiotactic propylene polymerization.[26] For the Group 6 metal chromium, we have communicated the discovery of new polymerization and oligomerization catalyst families assisted by an HTS approach.[12] Here, we describe the rationale behind the choice of ligand library, the synthesis and characterization of key pro-ligands and metal complexes, pre-screen validation chemistry as well as post-validation of hits from the library screen.

Ligand Library Design, Choice of Metal Precursor, and Initial Validation Experiments. An important consideration for high throughput catalyst screening is the accessibility of the pro-ligand library, specially its ease of synthesis and its amenability to variation at key substituent sites, combined with the availability of straightforward complexation procedures and catalyst screening protocols. Ligands such as phenoxy-imines, derivable by simple Schiff base condensation chemistry, hold special attraction for HTS programs, and have already been shown to afford highly active olefin polymerization catalysts for Group 4[22,26,27] and Group 10[28] metal systems. The productivities of the Group 10 metal system have been found to be enhanced dramatically by incorporating bulky *ortho*-anthracenyl substituents in the phenoxide donor.[28] The increased activities are attributed to steric protection of the salicylaldiminato oxygen by the *ortho*-anthracenyl group while the isopropyl substituents of the arylimino donor are positioned above and below the square plane of the nickel disfavoring associative displacement of olefin from the metal center. Contrastingly, the Group 4 metal systems employ salicylaldiminato (phenoxy-imine) ligands bearing small imine substituents and bis(chelation) is required to afford high activities. In our earlier work on salicylaldiminato chromium complexes, we found that bis(chelate) derivatives containing bulky imine substituents are not particularly active for ethylene polymerization, with productivities typically <150 $g \cdot mmol^{-1}h^{-1}bar^{-1}$.[11e] We reasoned that the relatively poor performance of the chromium system was most likely due to the unfavorable coordination environment afforded by binding two bulky N−O chelate ligands and that more highly active systems may be attainable by binding just one N−O chelate ligand decorated with judiciously selected ligand substituents.

It is relevant at this point to consider the relative merits of small versus large ligand substituents in salicylaldiminato ligands. It has generally been recognized that a bulky substituent such as anthracenyl positioned ortho to the phenoxide O-donor is beneficial since it disfavors interactions with the Lewis acidic centers of the activator or possibly other catalyst centers, both

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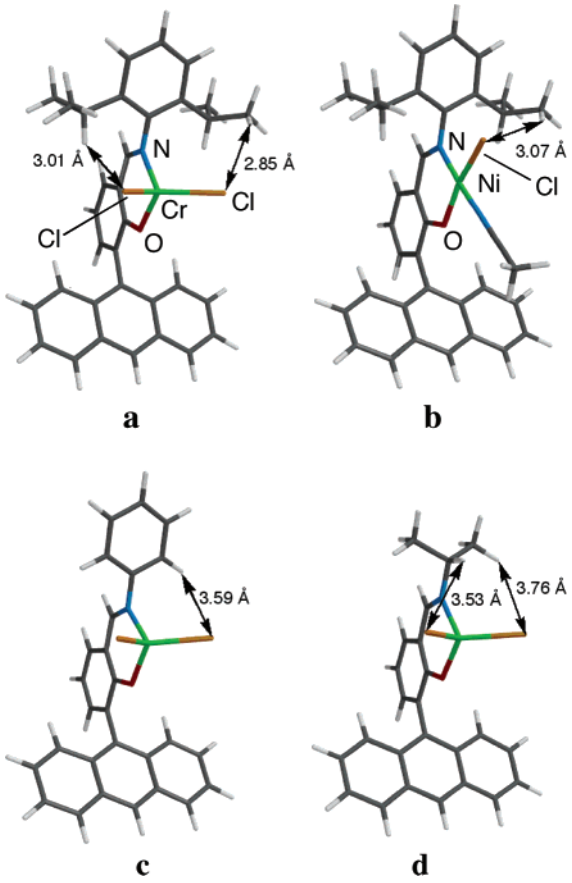

Figure 1. Comparison of energy-minimized structures for anthracenyl-salicylaldiminato ligands bearing different sized groups attached to the imine nitrogen donor: (**a**), (**c**), and (**d**) are modeled as (L)$CrCl_2$; (**b**) is modeled as (L)NiCl(NCMe).

of which may lead to catalyst deactivation. For the imine donor, the optimal size of the substituent would be expected to be dependent upon the coordination geometry. Thus, for square planar complexes based on the Group 10 metals, large 2,6-disubstituted aryl groups are advantageous for protecting the 'axial' coordination sites from associative displacement processes.

For tetrahedral, trigonal bipyramidal, and octahedral geometries, the steric requirements for protection of the active site will be substantially different and bulky substituents will not necessarily be required for optimal catalyst performance. The effect of large and small ligand substituents within a tetrahedral metal environment is illustrated using the energy-minimized MacSpartan Pro models shown in Figure 1, and compared with the square planar environment that predominates in divalent Group 10 metal systems. In the case of the tetrahedral environment containing bulky 2,6-diisopropylphenyl substituents (Figure 1a), the ligand isopropyl groups come into much closer contact with the metal-bonded chlorine atoms than for the square planar arrangement (Figure 1b). Indeed, for the tetrahedral coordination geometry, the Cl···H contacts are shorter than the Cl···H van der Waals contact of 2.95 Å. The steric conflict is removed for ligands containing smaller phenylimine and isopropylimine substituents (Figure 1c,d). Thus, the square planar environment is able to accommodate bulky groups at the imino nitrogen donor more readily than complexes or catalysts that adopt a tetrahedral coordination geometry. Such arguments also hold for trigonal bipyramidal and octahedral metal geometries, where the steric conflict would be anticipated to be similarly, if not more, severe.

For the metal precursor, several key properties are required: (a) ease of synthesis, (b) clean reactions with pro-ligands to generate complexes of targeted stoichiometry, (c) no reactive byproducts, d) good solubility in a nonreactive solvent, and (e) good stability in RT solution to allow standard solutions to be generated. Pre-evaluation tests may be needed to ensure pre-catalysts are formed from reaction of the pro-ligand and metal precursor complexes for the major classes of ligands tested; it also has to be recognized that complexation may occur upon treatment of the pro-ligand/metal precursor mix with activator, e.g. MAO. After examination of known alkyl- or aryl-chromium complexes it was decided that for this study the known complex, (*p*-tolyl)$CrCl_2(thf)_3$ (**I**),[29] matched the criteria, with the exception that it carries a coordinated donor solvent molecule which, if not removed, may suppress activities in the high throughput screen. The stability of alternative alkyl-chromium complexes has been reported to be significantly lower with $t_{1/2}$ values < 60 min at RT in noncoordinating solvents.[30] Similarly, potential alternative homoleptic chromium alkyls or aryls are poorly stable, more problematic to synthesize, stabilized by bulky ligands potentially reducing their reactivity,[31] retain coordinated solvent[32] or, as for tetravalent homoleptic chromium(IV) species, are often unreactive toward protic reagents.[33]

Since it seemed highly likely for chromium systems that trigonal bipyramidal or octahedral, but certainly not square-planar, coordination geometries would be preferred for the precatalysts and possibly the putative active sites, ligands with small, as well as large, substituents need to be considered. In a preliminary study, the three *ortho*-anthracenyl-salicylaldimines highlighted in the modeling study (Figure 1) were targeted to validate the synthetic approach to the pro-ligands, as well as to assess the potential for the new metal−ligand combinations to support polymerization-active metal centers.

Results and Discussion

Preliminary Validation Studies. A preliminary testing protocol was followed whereby the ligand and metal precursor (30 μmoles) were dissolved in 10 mL of toluene and the solvent immediately removed under vacuum to remove excess thf, Scheme 1. The residue was slurried/dissolved in toluene and activated with a methylalumoxane (MAO) solution in toluene (total volume 30 mL, 1 μmolmL^{-1}) from which an aliquot of the required volume was taken. Results for this preliminary screen are collected in Table 1; the ligands are numbered according to their position in the main ligand library—see Supporting Information. The metal precursor alone did not support significant catalysis (productivity 2.3 g·mmol^{-1}h^{-1}bar^{-1}), while the bulky diisopropylphenyl substituted imine **(28A)** also

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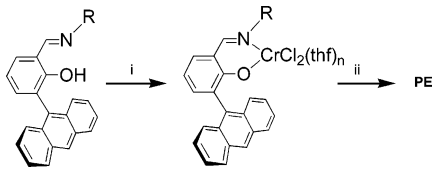
Scheme 1. Protocol for in Situ Catalyst Testing of New Schiff Base Ligands[a]



[a] (i) (*p*-tolyl)$CrCl_2(thf)_3$, vacuum, (ii) MAO/ethylene.

Table 1. Summary of Ethylene Polymerization Results for Salicylaldimines **28A**, **2A**, and **25A** Using the in Situ Ligand Screening Protocol Shown in Scheme 1[a]

ligand	Cr (mmol)	Cr:Al	*T* (°C)	*P* (bar)	yield (g)	prod.
no lig	0.030	1:100	RT	1	0.07	2.3
28A	0.030	1:400	RT	1	0.20	6.7
2A	0.015	1:100	RT	1	1.42	95
25A	0.002	1:200	RT	1	0.88[b]	1760

[a] Standard conditions: Schlenk test, 1 bar ethylene, 100 mL toluene, 60 min, productivity g.mmol^{-1}h^{-1}bar^{-1}. [b]run time 15 min.

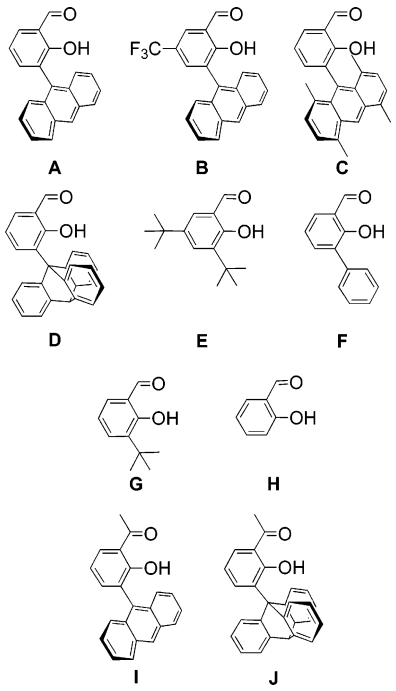


Figure 2. Salicyladehyde backbones used as part of this study. Backbones **A**−**D** used to generate the 205 member salicylaldimine library.

gave low productivity, 6.7 g·mmol^{-1}h^{-1}bar^{-1}. Phenyl substitution **(2A)** resulted in modest productivity, 95 g·mmol^{-1}h^{-1}bar^{-1}, comparable to values found for previously reported Schiff base chromium systems.[11e] Much higher productivity was found for the isopropyl derivative **(25A)**, an optimal catalyst loading affording a productivity of 1760 g·mmol^{-1}h^{-1}bar^{-1}.

These preliminary tests validated the reaction protocol and generated an initial lead for the ligand library. The success of the preliminary screening tests also made it possible to select a subset of small amines within the ligand library to allow a targeted ligand screen around this hit.

Ligand Synthesis. The salicylaldimine pro-ligand library required access to large quantities of the ortho-substituted salicylaldehydes shown in Figure 2. An earlier synthesis of **A**[28b,34] followed a multistep route with low yields for bulky ortho-substituents; therefore a simplified general route was investigated with a view to generating large quantities of the required ligand precursors[35] (Scheme 2). Backbone **A** was readily formed from anthraquinone by reaction with *ortho*-lithiated PhOMOM (or the related Grignard reagent MOMOPh-MgBr generated from the reaction of MOMOPhLi with $MgBr_2$; OMOM = OCH_2OCH_3).

The substituted anthraquinone **1** could be reduced using Zn dust in HOAc/H_2O at 60 °C without deprotection of the acid sensitive MOM group, leading to a general route to large quantities (100−200 g) of **2**. *Ortho*-lithiation of **2** to form **3**, and reaction of **3** with a range of electrophiles generated, after deprotection, substituted phenols including the required backbones **A** (**4a**) and **I** (**4b**). Reaction of **2** with benzyne resulted in the triptycenyl derivative (**7**) which could be functionalized by *ortho*-lithiation and reaction with an appropriate electrophile generating the backbones **D** (**9a**) and **J** (**9b**). Substituted phenols underwent similar reactions allowing the synthesis of **B (13)** containing an electron withdrawing CF_3 group *para* to the hydroxyl functionality (Figure 2), as well as presenting a simplified route to large quantities of salicylaldehydes from commercially available *ortho*-substituted phenols, e.g., the synthesis of **F** from 2-phenylphenol.

Formation of the tetramethylanthracenyl-salicylaldehyde, **C**, required more forcing conditions during reduction resulting in Lewis-Acid catalyzed deprotection of the phenol, Scheme 3. *Ortho*-formylation can be achieved by literature methods[36] or by reprotection and formylation using the conditions described above.

Crystals of **C** and **D** suitable for structural determination were isolated by vapor diffusion of hexane into benzene solutions of **C** or **D**. The views shown in Figure 3a,b illustrates the constrained nature of **C** with the salicylaldehyde wedged between the methyls C(22) and C(25) of the tetramethylanthracenyl group, forcing each of these units significantly away from their ideal positions. The steric protection of the phenolic oxygen afforded by the *ortho*-triptycenyl substituent is apparent from Figure 3c,d. Crystal data for **C** and **D** can be found in the Supporting Information along with data for the structure of **4e**.

Amines were selected to give salicylaldimines with a diverse range of steric and electronic properties, as well as additional donor functionalities. The ligands were synthesized using standard condensation chemistry, combining 55 amines with salicylaldehydes A−D to give a total of 205 salicylaldimines. The full list of pro-ligands is collected in the Supporting Information.

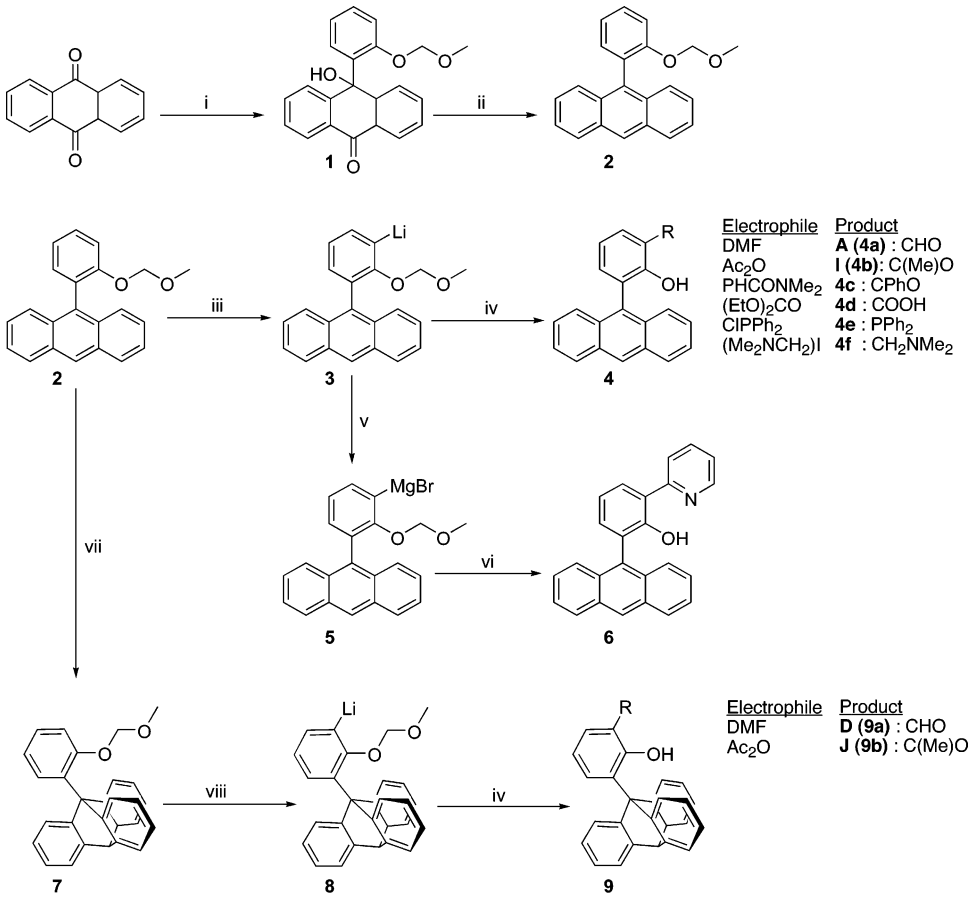
Screening Results. The ligands were screened under standard polymerization conditions in a 24 well reactor with each plate containing a solvent blank and two standard tests, ligand **25A** and the complex [*N*,*N*′-dimesityl diiminopyridine]iron dichloride.[37] The measured productivities were normalized to the average of the standard tests while the variation in the standard tests was used as a measure of error to aid in the identification of hits.

(34) (a) Rice, J. E.; Cai, Z. W. *Tetrahedron Lett.* **1992**, *33*, 1675.

(35) An alternative synthesis has been communicated for A.[28e] During the course of our ligand development program, we also examined a variation of this route. However, in our hands, we found that reaction of MOMOPhM (M = Li or MgBr) with anthrone gave yields varying between 0 and 90%, presumably due to the ability of MOMOPhM to act as a base or a nucleophile, and the sensitivity of its mode of action to minor changes in the experimental conditions.

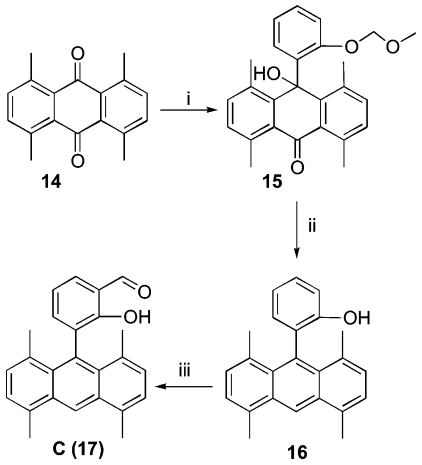
(36) Wang, R. X.; You, X. Z.; Meng, Q. J.; Mintz, E. A.; Bu, X. R. *Synth. Commun.* **1994**, *24*, 1757.

Scheme 2. Synthesis of Sterically Protected Salicylaldehydes[a]



[a] (i) MOMOPhM (M = Li or MgBr) in thf added over 3 h; (ii) Zn/cat. $ZnCl_2$ in $AcOH/H_2O$ (60/40) 60 °C, 16 h; (iii) BuLi 1.1 eq., ether 4 h; (iv) −78 °C DMF; Ac_2O, $PhCONMe_2$, $(EtO)_2CO$ or CO_2, excess Ph_2PCl or $[Me_2NCH_2]I$ 1.1 eq, then deprotection with thf/6M HCl reflux 4 h, (v) $MgBr_2$ (from Mg and BrC_2H_4Br), (vi) Br−Py/cat (dppe)$NiCl_2$, reflux 4 h then deprotection; (vii) diazobenzenecarboxylate (from anthranilic acid and isoamylnitrite) thf, reflux; (viii) BuLi (2.1 eq.), ether, RT, 4 h, −78 °C DMF or Ac_2O, then deprotection.

Scheme 3. Synthesis of Salicylaldehyde **C**[a]



[a] (i) MOMOPhM (M = Li or MgBr), thf added over 3 h; (ii) $LiAlH_4$/$BF_3.OEt_2$ in ether reflux, 4 h; (iii) EtMgBr (1.0 eq.), $(CH_2O)_n$ (2.5 eq), Et_3N (1.5 eq), toluene, 80 °C, 3 h then 2 M HCl.

The HTS results for amines condensed with anthracenyl-salicylaldehyde (**A**) are shown in Figure 4a. Several hits with productivities comparable to the standard isopropyl-amine derivative (**25**) are apparent. It is interesting to note that only primary or secondary alkyl substituents afford catalysts with significant productivities; neither tertiary alkyls, nor substituents with pendant O, N, or S donor units gave active systems.

Substitution of the salicylaldehyde in the para-position with the electron withdrawing CF_3 substituent, backbone **B**, gave hits for the same series of imine substituents (Figure 4b), but no improvement in productivity was observed. Productivities are generally slightly lower than for the parent ligands based on backbone **A**.

For the severely hindered ligands containing the tetramethyl-anthracenyl substituent (**C**), no productivity for ethylene polymerization or oligomerization was found. However, changing the ortho substituent to a triptycenyl unit gave the screen results shown in Figure 4c where, quite remarkably, a single active system, one containing a pyridylmethyl substituent, was identified.

Hit Validation. The six most active 'hits' from the library screen using salicylaldehyde **A**, i.e., ligands **6A** (3,3-diphenylpropyl), **8A** (cyclopentyl), **24A** (cyclobutyl), **25A** (isopropyl), **27A** (hexyl), and **31A** (cyclopropyl), were repeated on a preparative scale and the resultant polyethylene products analyzed by GPC. The results are collected in Table 2.

The isopropyl (**25A**), hexyl (**27A**) and cyclopropyl (**31A**) derivatives gave activities between 1000−3000 $g \cdot mmol^{-1}$-

(37) (a) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Stromberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728. (b) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849.

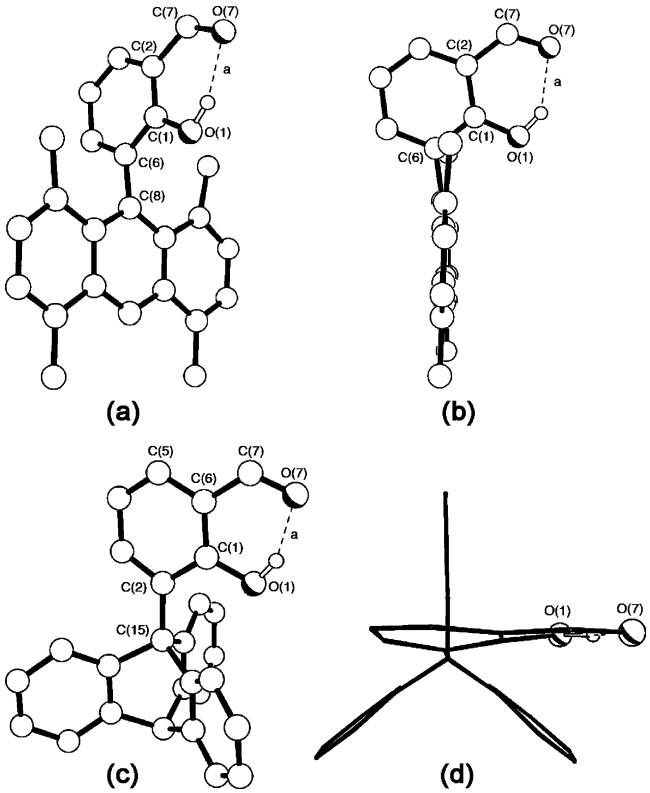


Figure 3. The molecular structures of **C (**a and b**)** and **D (**c and d**)**. View (b) shows distortions in **C** arising from steric constraints imposed by the tertramethylanthracenyl substituent; view (d) shows the molecular structure of **D** viewed down the C(2)···C(15) vector.

$h^{-1}bar^{-1}$. In all cases, high molecular weight linear polyethylene was formed with, in the two cases that could be determined, a narrow molecular weight distribution; in the case of **25A**, the polymer was insoluble indicating a MW > 2M Da. The cyclobutyl and cyclopentyl derivatives, **24A** and **8A**, gave activities comparable to each other, but with much lower molecular weight products than for their acyclic relatives. For the 3,3-diphenylpropyl derivative **6A**, polyethylene of intermediate molecular weight was produced and with a significantly broadened molecular weight distribution. Importantly, the relative activities of the catalysts obtained in the high throughput screen were reproduced in the preparative scale runs, validating the robustness of the HTS screen data.

Bidentate Salicylaldimines with Small Alkyl Groups. The success of the HTS screen and validation study led us to target a small, but more focused, ligand library to probe structure−activity relationships around the observed hits. Added diversity was achieved by reacting isopropylamine (**25**) with 3,5-di-*tert*-butyl-saliylaldehyde (**E**), phenyl-salicylaldehyde (**F**), and 3′-(9-anthracenyl)-2′-hydroxyacetophenone (**I**). The polymerization test results on in situ generated catalysts (Table 3) confirmed the requirement for a small alkyl group attached to the N-imino donor. Ligands based on the commercially available backbone **E** gave no active species (see also ref 39) while the phenyl substituted salicylaldimine **25F** gave low productivity (<10 $g{\cdot}mol^{-1}h^{-1}bar^{-1}$). The ketimine derivative (**25I**) also resulted in low productivity indicating a sensitivity of catalyst productivity to substitution at the imine carbon atom. Replacement of the imine by diphenylphosphino (**4e**), dimethylaminomethyl (**4f**) or pyridine (**6**) donor groups also resulted in no catalytic activity. On the basis of these results, it would appear that a combination of *ortho*-anthracenyl and imino donors bearing primary or secondary alkyl groups is optimal for catalyst performance.

The *N*-isopropyl and *N*-cyclopentyl derivatives of *o*-anthracenyl-salicylaldimine (complexes **II** & **III**) were readily formed by reaction of **25A** or **8A** with *p*-tolyl$CrCl_2(thf)_3$ (**I**) in toluene at RT (according to Scheme 1). Analytically pure complexes were recovered by solvent removal and washing with hexane. The pale yellow-green complexes have been fully characterized as the mono-thf adducts, $LCrCl_2(thf)$.

Crystals of **III** suitable for an X-ray structural analysis were grown from thf/benzene and show octahedral coordination at the chromium center with two *cis*-coordinated thf molecules and a single bidentate salicylaldiminato ligand (Figure 5). The anthracenyl moiety is oriented approximately orthogonally to the phenoxy ring (ca. 85°). The cyclopentyl substituent on N(7) is orientated such that the proton attached to C(8) is directed toward the metal center, with a [Cr,N(7),C(8),H(8A)] torsion angle of 18°.

Catalysts Containing Two Salicylaldiminato Ligands. For completeness, we decided to specifically target a bis(bidentate) chromium pre-catalyst containing small imine substituents as a direct analogue of the highly active Group 4 metal pre-catalysts of the type L_2MCl_2 (M = Ti, Zr) described by Fujita and coworkers.[27] In earlier work, we described bis(bidentate) derivatives of chromium containing bulky *N*-2,6-diisopropylphenyl substituents, but had found only modest ethylene polymerization activities.[11e] The bis(ligand) complex, $(\mathbf{L})_2CrCl$ (**IV**), containing salicylaldiminato ligands with an *o-tert*-butylphenoxy/N-phenylimino donor combination was prepared by treatment of the sodium salt of **2G** with $CrCl_3(thf)_3$ in thf to give a yellow-brown thf-free solid. Crystals of the six-coordinate acetonitrile adduct (**V**), suitable for an X-ray structure determination were obtained by slow cooling of a hot acetonitrile solution of **IV**. The molecular structure is shown in Figure 6; selected bond lengths and angles are given in the Figure caption. The positioning of the two N,O chelate ligands, with trans-O,O and cis-N,N dispositions, is virtually identical to that seen in the dichlorotitanium[24a] and dichlorozirconium precatalysts.[38]

IV was screened for ethylene polymerization using, separately, MAO and diethylaluminum chloride (DEAC) as activators. MAO afforded a low productivity of 6 $g{\cdot}mmol^{-1}h^{-1}bar^{-1}$, whereas DEAC gave a value of 70 $g{\cdot}mmol^{-1}h^{-1}bar^{-1}$. The more efficient activating effect of DEAC is consistent with our findings for bulky bis(ligand)Cr systems, and provides an indication that a neutral Cr-alkyl catalyst is formed. The clearly inferior productivity of the putative L_2CrR species versus $[L_2TiR]^+$ may be attributed, in part, to the lower electrophilicity of the neutral chromium center relative to the cationic, and therefore more electrophilic, titanium centers, but another important effect in Cr(III) systems is the kinetic stability of the d^3 configuration for octahedral (or pseudo-octahedral) species. This may lead to a large energetic barrier to ethylene insertion for a six-coordinate ethylene adduct of the type $[L_2CrR(C_2H_4)]$.

Ligands with Pendant π-Arene Groups. The initial series of 'hits' from the library screen revealed a beneficial effect of

(38) (a) Matsui, S.; Tohi, Y.; Mitani, M.; Saito, J.; Makio, H.; Tanaka, H.; Nitabaru, M.; Nakano, T.; Fujita, T. *Chem. Lett.* **1999**, 1065. (b) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Tanaka, H.; Fujita, T. *Chem. Lett.* **1999**, 1263.

(39) Ittel, S. D.; Wang, Y. E. I. Dupont De Nemours & Co., USA, WO 0144324, **2001**.

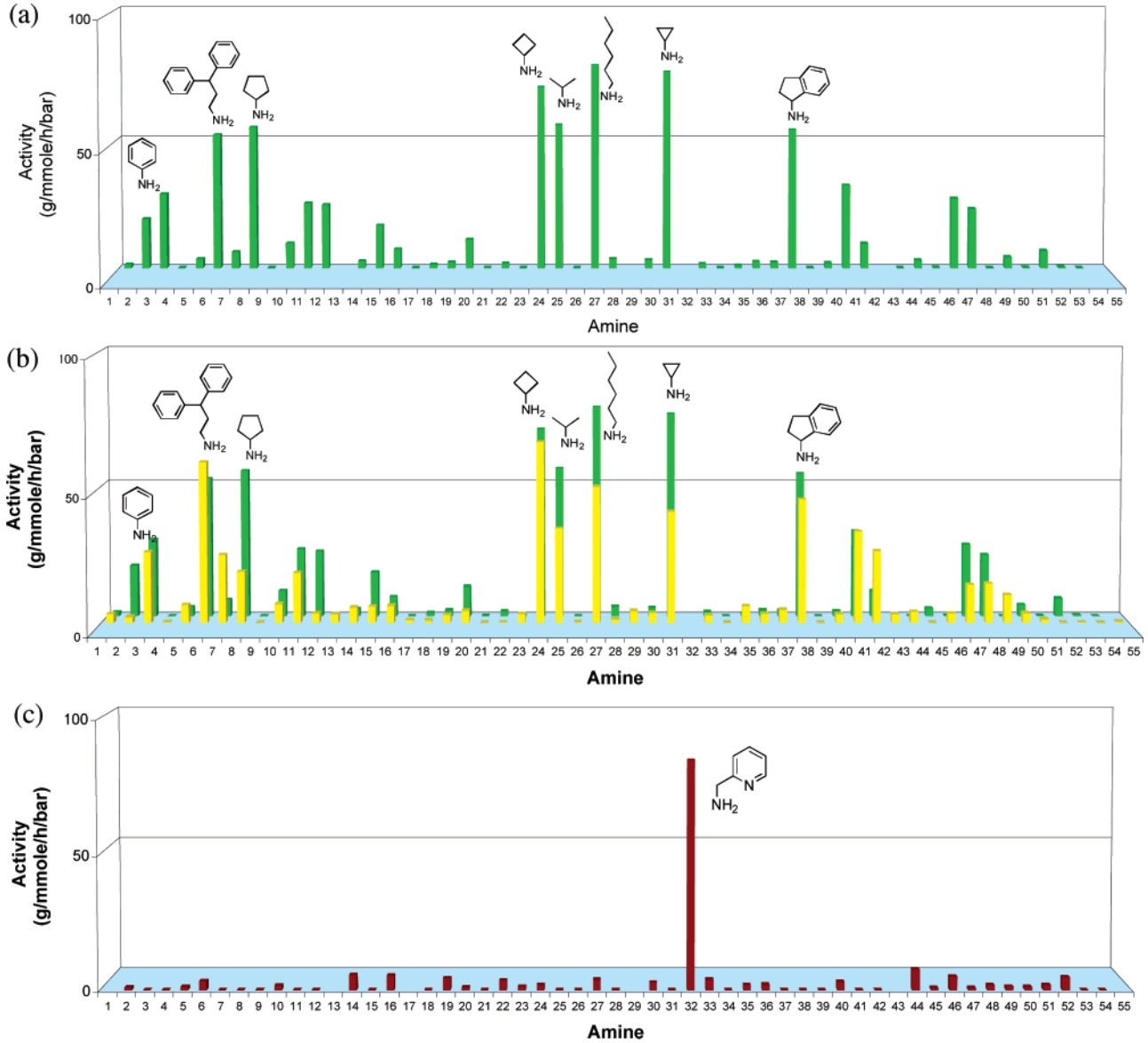


Figure 4. Ethylene polymerization screen using the ligand generated from 55 commercial amines and (a) *o*-anthracenyl-salicylaldehyde (**A**); (b) *o*-anthracenyl-CF_3-salicylaldehyde (hits for (**A**) shown in green for comparison) (**B**); (c) triptycenyl-salicylaldehyde (**D**). Conditions: metal precursor **I** (0.005 mmol), ligand (0.005 mmol), Al:Cr 200:1, toluene 5 mL, RT, 10 min.

Table 2. Summary of Productivity and Polymer Data for Selected Catalyst Systems Containing *N*-alkyl Salicylaldiminato Ligands[a]

ligand	prod. HTS	prod. in-situ	M_n	M_w	M_w/M_n
6A	51.6	672[b]	81000	611000	7.6
8A	54.6	920	26000	85000	3.2
24A	70.0	1288	30000	75000	2.5
25A	55.4	1760	$	$	$
27A	78.4	2960	728000	1550000	2.1
31A	75.8	2380	1370000	2360000	1.7

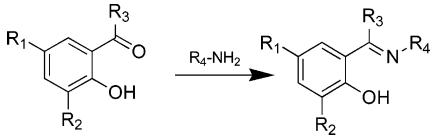
[a] Standard conditions: Schlenk test, 1 bar, 100 mL toluene, 15 min, productivity g.mmol^{-1}h^{-1}bar^{-1}. [b]run time 60 min. $ insoluble polymer, MW > 2M Da.

pendant arene substituents. High productivities were found for 1-indanyl (**38A**), 3,3-diphenylpropyl (**6A**), 1-methyl-3-phenyl-propyl (**41A**), 2-CF_3-benzyl (**47A**), and *p*-*tert*-butylbenzyl (**11A**) amines. Potentially stabilizing π-arene interactions have recently been identified in other systems,[40] leading to substantially improved catalyst lifetimes and altered product distributions.

Anthracenyl-salicylaldimines were synthesized containing one (**69A**), two (**70A**) and three (**71A**) methylene units separating a phenyl group from the imine nitrogen donor. Productivities for catalyst systems containing these salicylaldimines are collected in Table 4. A significant increase in productivity is found upon lengthening the link from zero (95 g·mmol^{-1}h^{-1}bar^{-1}) or one (94 g.mmol^{-1}h^{-1}bar^{-1}) to two methylene units (420 g·mmol^{-1}h^{-1}bar^{-1}). Also, the polymer obtained using **70A** is insoluble indicating very high molecular weight, and a significant increase over the molecular weight of PE isolated using ligand **2A** (M_w 93 4000, PDI 4.4). The productivity is raised further, to 650 g·mmol^{-1}h^{-1}bar^{-1}, for ligand **71A** containing a

(40) (a) Sassmannshausen, J.; Powell, A. K.; Anson, C. E.; Wocadlo, S.; Bochmann, M. *J. Organomet. Chem.* **1999**, *592*, 84. (b) Moody, L. S.; MacKenzie, P. B.; Killian, C. M.; Lavoie, G. G.; Ponasik, J. A., Jr.; Smith, T. W.; Pearson, J. C.; Barrett, A. G. M. Eastman Chemical Company, USA, WO. 2002022694, **2002**. (c) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Organometallics* **2002**, *21*, 5122. (d) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2516. (e) Gibson, V. C.; Tomov, A.; Wass, D. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.*, **2002**, 2261.

Table 3. Synthesis of Further Salicylaldimines for Examination of Structure−Activity Relationships for Bidentate Schiff Base Ligands on Chromium[a]



A (R_1 & R_3 = H, R_2 = Anthracenyl). **E** (R_1 = R_2 = ^{t}Bu, R_3 = H), **I** (R_1 = H, R_2 = Anth, R_3 = Me), **J** (R_1 = H, R_2 = Tript, R_3 = Me).

	Salicylaldimine	ligand	prod.
A	R_4 = -^{t}Butyl	**60A**	70
	-cyclohexyl	**61A**	<10
	-$CH(CH_2CH_2Ph)_2$	**62A**	14
	-NH_2	**63A**	76
	-$CHMeCH_2CHPh$	**64A**	80
	-$CH_2CH_2NMe_2$	**65A**	40
	-(2,5-dimethylpyrrolyl)	**66A**	26
	-CH_2CHMe_2	**67A**	94
	-adamantyl	**68A**	65
E	R_4 = -^{i}Pr	**25E**	<10
	-Ph	**2E**	<10
F	R_4 = -^{i}Pr	**25F**	<10
I	R_4 = -^{i}Pr	**25I**	<10

[a] Standard Schlenk polymerization conditions; RT, Cr:Al 1:200 (MAO), 1 bar ethylene, 100 mL toluene, 60 min.

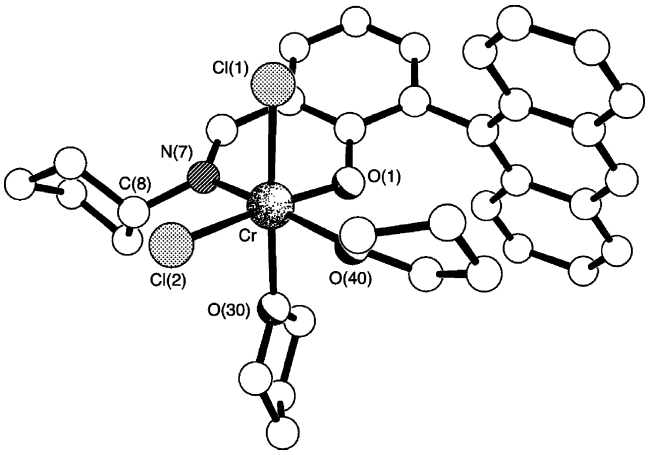


Figure 5. Molecular structure of **III**. Selected bond lengths (Å) and angles (°): Cr−Cl(1), 2.3266(16), Cr−Cl(2), 2.3402(16), Cr−O(1), 1.907(3), Cr−N(7), 2.038(4), Cr−O(30), 2.062(5), Cr−O(40), 2.071(4), Cl(1)−Cr−Cl-(2), 90.95(7), Cl(1)−Cr−O(1), 92.02(12), Cl(1)−Cr-N(7), 94.69(15), Cl(1)−Cr−O(30), 176.59(13), Cl(1)−Cr−O(40), 91.68(14), Cl(2)−Cr−O(1), 175.59(12), Cl(2)−Cr−N(7), 95.01(13), Cl(2)−Cr−O(30), 89.78(14), O(1)−Cr−N(7), 88.00(16), O(1)−Cr−O(30), 87.07(17), O(1)−Cr−O(40), 87.13-(15), N(7)−Cr−O(30), 88.56(18), N(7)−Cr−O(40), 172.1(2), O(30)−Cr−O(40), 85.00(18).

trimethylene spacer group. These results indicate a potential π-arene stabilization for >1 methylene linkers, affording higher productivities as a result of longer catalyst lifetimes, and significantly enhanced molecular weights, the latter arising from a lowering of the rate of β-H transfer due to competition with π-arene coordination.

Tridentate Salicylaldimine Ligands. The screen of triptycenyl-substituted salicylaldimines (Figure 4c) revealed a unique 'hit' for the pyridylmethylamine derivative **32D**. This ligand and its chromium complex were therefore scaled-up, along with its anthracenyl relative **32A**, and nonbulky 3,5-di-*tert*-butylphenoxy (**32E**) and 3-phenoxy **(32F**) derivatives. In addition 8-aminoquinoline (**73**), a rigid variation of **32**, was reacted with backbones **C** and **D** to generate **73C** and **73D**.

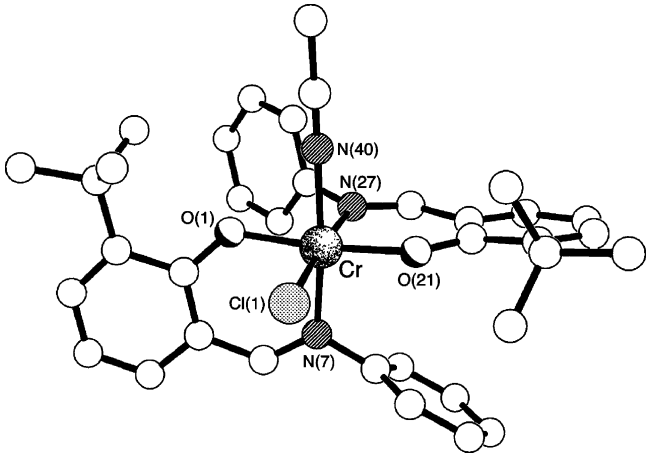


Figure 6. Molecular structure of **V**. Selected bond lengths (Å) and angles (°): Cr−Cl(1), 2.3395(11), Cr−O(1), 1.913(2), Cr−O(21), 1.923(2), Cr−N(7), 2.035(3), Cr−N(27), 2.057(3), Cl(1)−Cr−O(1), 92.21(8), Cl(1)−Cr−O(21), 88.49(8), Cl(1)−Cr−N(7), 90.42(9), Cl(1)−Cr−N(27), 175.68(9), Cl(1)−Cr−N(40), 91.76(9), O(1)−Cr−N(7), 88.82(11), O(1)−Cr−N(27), 91.76(11), O(1)−Cr−N(40), 85.98(11), O(1)−Cr−O(21), 173.47(11), N(7)−Cr−O(21), 97.67(11), N(7)−Cr−N(27), 87.96(12), N(7)−Cr−N(40), 174.43(12), O(21)−Cr−N(27), 87.76(11), O(21)−Cr−N(40), 87.52(11), N(27)−Cr−N(40), 90.22(11).

Table 4. Summary of Polymerization Tests for Catalysts Containing Pendant Arene Substituted Anthracenyl-Salicylaldimines with Zero (**2A**), One (**69A**), Two (**70A**), and Three (**71A**) Methylene Spacers between the Imine Donor and Phenyl Substituent[a]

ligand	Cr (mmole)	CH_2's	yield (g)	prod.[b]
2A	0.015	0	1.42	95
69A	0.005	1	0.42	94
70A	0.005	2	2.1	420
71A	0.002	3	1.3	650

[a] Standard Schlenk polymerization conditions; RT, Cr:Al 1:200 (MAO), 1 bar ethylene, 100 mL toluene, 60 min. [b] $g{\cdot}mol^{-1}h^{-1}bar^{-1}$.

Crystals of **32D** and **73C** suitable for structural analyses were isolated during purification and their structures are provided in the Supporting Information.

Ethylene polymerization tests on **32D** confirmed the results of the high throughput screen, i.e., that the triptycenyl analogue **32D** gave a catalyst with good productivity (1574 $g{\cdot}mmol^{-1}h^{-1}$-bar^{-1} under the test conditions employed), while the anthracenyl derivative **32A** is inactive. The more rigid ligands **73C** and **73D** gave productivities of 80 and 1858 $g{\cdot}mmol^{-1}h^{-1}bar^{-1}$, respectively, again showing the more beneficial effect of the triptycenyl substituent. The products afforded by these catalysts are typically low molecular weight solids (M_w 1700−1900; PDI 1.7−1.8) with 10−15 wt % being toluene soluble; GPC traces are shown in Figure 7. ^{13}C NMR analyses of the solid fractions show the presence of linear α-olefins while GC analysis on the soluble fraction indicates predominantly linear α-olefins, along with a small percentage of alkanes (depending on the Cr:Al ratio) which arise by chain transfer to aluminum.

Complexes were synthesized by reaction of **32D** and **73D** with metal precursor **I** in toluene. The poorly soluble red-brown solids were isolated as the thf-free species $LCrCl_2$, **VI** and **VII**. Complex **VI** dissolved in hot acetonitrile to give the crystalline acetonitrile adduct (**VIII**) which was found to be inactive for ethylene polymerization. Complex **VII** dissolved in hot pyridine to give the pyridine adduct (**73D**)$CrCl_2$(py) (**IX**) which was used in polymerization tests with no obvious influence on reactivity

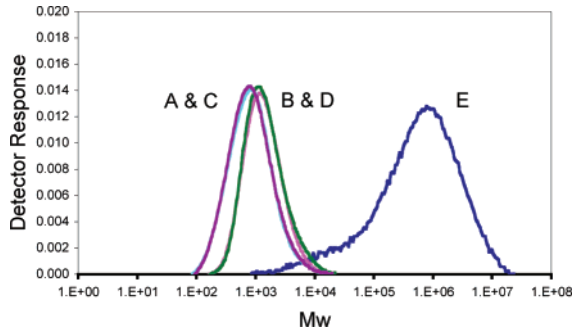


Figure 7. GPC traces of polyethylene samples generated by reacting **32D** (A&B) and **73D** (C&D) with (*p*-tolyl)$CrCl_2(thf)_3$ [the trace obtained using **25A** (E) is shown for comparison].

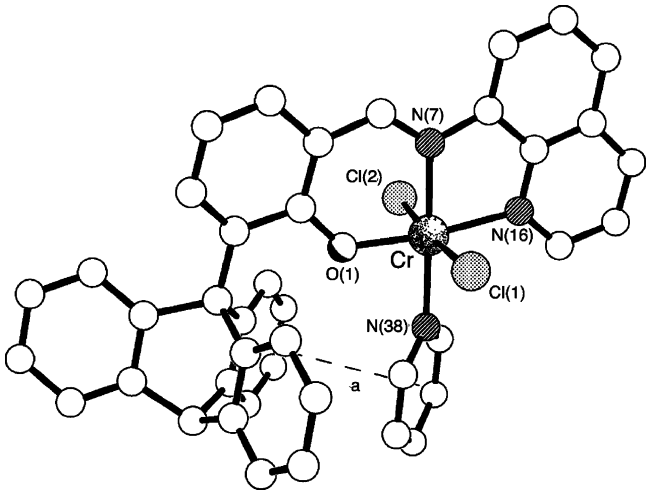


Figure 8. Molecular structure of **IX**. The intramolecular $\pi-\pi$ stacking interaction (**a**) has centroid···centroid and mean interplanar separations of ca. 3.71 and 3.64 Å respectively; the rings are inclined by only ca. 1°.[#]

or polymer distributions due to the coordinated pyridine. Crystals of **IX** suitable for X-ray structural analysis were grown by slow vapor diffusion of benzene (over 5−6 weeks) into a saturated pyridine solution of **VII**. The molecular structure (Figure 8) shows meridional binding of the tridentate ligand with the two chloride ligands occupying mutually trans positions. The coordinated pyridine lies trans to the imino nitrogen donor. In the closely related complex **VIII**, the acetonitrile ligand occupies a similar position between the two chloride ligands (see Supporting Information, Figure S9). Since **VIII** is inactive in catalysis, the acetonitrile ligand may interfere with the activation process or may even be retained by the metal center. In both

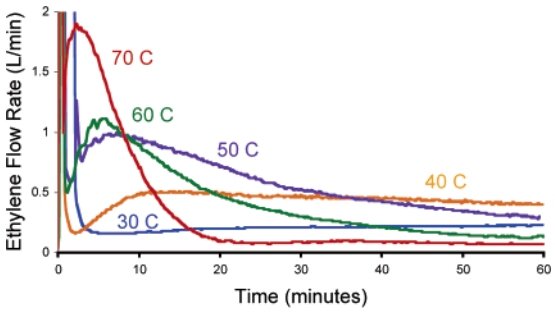


Figure 9. Ethylene uptake profiles for Complex **IX** activated with MAO at different temperatures.

VIII and **IX**, the steric protection of the salicylaldiminato oxygen by the triptycene is evident, though the orientations of the three C_6 rings in **VIII** and **IX** are slightly different, possibly a consequence of an intramolecular $\pi-\pi$ stacking interaction between the coordinated pyridine and one of the triptycene C_6 rings in **IX.**

The isolated complexes have been screened and all show high productivities with the exception of the acetonitrile complex. The presence of pyridine however has no detrimental affect on productivity (Table 5). The use of TiBAl as a scavenger led to poorer catalyst performance (cf. entries 10 and 12) while attempted activation with DEAC does not lead to an active system, unlike for previously reported Schiff base chromium complexes.[11e] Under optimized conditions, productivities of up to 7000 g·mmol^{-1}h^{-1}bar^{-1} are observed for complexes containing ligand **32D** while productivities in excess of 10 000 g·mmol^{-1}h^{-1}bar^{-1} were recorded for catalysts containing the quinolyl substituted ligand **73D**; these are among the highest productivities reported for homogeneous chromium based systems.

Kinetic profiles of ethylene uptake for **IX**/MAO, at differing reaction temperatures are shown in Figure 9. Performance optimizes ca. 50 °C and declines rapidly at higher temperatures. At 30−40 °C ethylene uptake continues for at least 1 h indicating a thermally stable, long-lived system. The catalysts exhibit first order dependence on ethylene concentration (as approximated by pressure) over a range of 1−5 bar, Figure 10. Unlike the bidentate systems described earlier, the tridentate system incorporates hexene to moderate levels (Table 6), reaching 3.7 butyl branches per 1000 carbons at high 1-hexene concentrations.

To explore further the potential of the tridentate triptycenylsalicylaldimine ligand family, a number of derivatives closely

Table 5. Ethylene Polymerization Results Using Triptycenylsalicylaldiminato Chromium Catalysts[a]

entry	complex	Cr (mmole)	Cr:Al	*T* (°C)	reactor	*P* (Bar)	yield (g)	prod.[b]
1	**32D**$CrCl_2$ **(VI)**	0.001	1:200	RT	Schlenk	1	3	3000
2	**32D**$CrCl_2$ **(VI)**	0.001	1:2200	50	FP	1	6.05	6050
3	**32D**$CrCl_2$ **(VI)**	0.001	1:2200	50	Large	4	27.87	6968
4	**32D**$CrCl_2$ **(VI)**	0.005	1:15[c]	RT	Schlenk	1	0	0
5	**32D**$CrCl_2(MeCN)_2$ **(VIII)**	0.005	1:600	50	Large	4	1.49	75
6	**73D**$CrCl_2$ **(VII)**	0.005	1:200	RT	Schlenk	1	10.9	2180
7	**73D**$CrCl_2$ **(VII)**	0.0005	1:2000	RT	Schlenk	1	5.06	10120
8	**73D**$CrCl_2$ **(VII)**	0.0005	1:4000	50	FP	4	18.7	9350
9	**73D**$CrCl_2$(Py) **(IX)**	0.001	1:700	50	FP	4	12.25	3063
10	**73D**$CrCl_2$(Py) **(IX)**	0.001	1:2200	50	FP	4	29.79	7448
11	**73D**$CrCl_2$(Py) **(IX)**	0.0005	1:4000	50	FP	4	20.32	10161
12	**73D**$CrCl_2$(Py) **(IX)**	0.001	1:2200[d]	50	FP	4	1.17	292

[a] Standard tests except entry 5, 6, 9, and 10 activated in situ by injecting the catalyst solution into the reactor scavenged with the required amount of MAO; [b] g·mol^{-1}h^{-1}bar^{-1}, [c] catalyst activated with DEAC, 15 equiv., [d] TiBAl used as scavenger, 2 mmol.

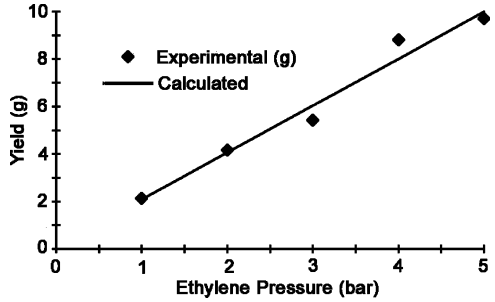


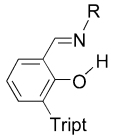
Figure 10. Pressure response for pre-catalyst **IX** activated with MAO showing a first order dependence on ethylene.

Table 6. Summary of 1-Hexene Incorporation Data for Complex **73D**$CrCl_2$·y (**IX**)[a]

Hexene (mL)	prod[b]	M_n	M_w	M_w/M_n	Butyl (/1000 C's)
0	9987	1000	1500	1.5	0
8	7685	1000	1500	1.5	0.8
16	6575	1000	1500	1.5	2.3
32	6005	1000	1400	1.4	3.7

[a] Polymerization conditions; Fischer Porter reactor, solvent = toluene 200 mL, Cr 0.0005 mmol, 2.0 mmol MAO scavenger (in situ activation), T = 50 °C, P = 4 bar, t = 60 min. [b] g·mol^{-1}h^{-1}bar^{-1}.

Table 7. Summary of Polymerization Tests on Catalysts Bearing Triptycenyl-Salicylaldiminato Ligands[a]



80D : R = Py
32D : R = CH_2Py
79D : R = CH_2CH_2Py
74D : R = CMe_2Py
75D : R = CPh_2Py
65D : R = $CH_2CH_2NMe_2$
76D : R = CH_2CH_2-pyrrolidine
72D : R = $PhPPh_2$

entry	ligand	Cr (mmol)	yield (g)	prod. g·mol^{-1}h^{-1}bar^{-1}
1	**80D**	0.005	0.59	118
2	**32D**	0.005	7.87	1574
3	**79D**	0.005	2.23	446
4	**74D**	0.005	5.9	1180
5	**75D**	0.005	0.576	115
6	**65D**	0.005	2.84	568
7	**76D**	0.005	2.86	572
8	**72D**	0.005	1.64	328

[a] Standard Schlenk polymerization conditions; RT, Cr:Al 1:200 (MAO), 1 bar ethylene, 100 mL toluene, 60 min.

related to **32D** were targeted. These encompass a series of ligands in which the linker to the pyridine donor is systematically lengthened, derivatives containing methyl and phenyl substituents attached to the methylene linker of **32D**, and derivatives containing other nitrogen donors and a phosphine donor (Table 7). Increasing the length of the spacer between the imine and the pyridine does not result in improved catalyst performance. The 2-pyridyl derivative **80D** gave a productivity of 118 g·mmol^{-1}h^{-1}bar^{-1}, which compares with a productivity of 1574 g·mmol^{-1}h^{-1}bar^{-1} for the pyridylmethyl derivative **32D** while the pyridylethyl derivative gave a productivity 446 g·mmol^{-1}h^{-1}bar^{-1} (entries 1−3, Table 7). Replacing the methylene bridge protons with either methyl or phenyl substituents resulted in a decrease in productivity (cf. entries 2, 4, and 5, Table 7). Changing the pendant nitrogen donor to a dimethylamino (**65D**) or pyrrolidino (**76D**) moiety gave catalysts with productivities approximately one-third the level achieved using **32D**. Altering the donor to a diphenylphosphino moiety (entry 8) resulted in a lower productivity catalyst. It is thus apparent that the pyridylmethyl and quinolyl donors afford the best catalyst performance for these tridentate Schiff base ligands.

Summary

In summary, we have used High Throughput Screening (HTS) methods to examine the catalytic performance for ethylene polymerization of a library of salicylaldiminato ligands attached to chromium. Systems based on bidentate 6-anthracenyl-salicylaldiminato ligands bearing small 1° or 2° alkylimino donors gave linear high molecular weight polyethylene with productivities of up to 3000 g·mmol^{-1}h^{-1}bar^{-1}. Contrastingly, ligands bearing large groups at the imine nitrogen donor afforded poor catalyst productivities, highlighting the importance of matching the ligand substituent size to the likely coordination geometry of the active species. Ligands containing pendant π-arene groups were found to exert a beneficial effect on catalyst performance, consistent with stabilization of the active site by weak π-arene-metal interactions. A bis(chelate) chromium analogue of the highly active titanium phenoxy-imine catalyst system was found to afford only low productivity which may be a consequence of the lower electrophilicity of the postulated neutral active site in the chromium system, and possibly the high kinetic stability of pseudo-octahedral Cr(III) (d^3) complexes. A second category of catalyst was discovered based on tridentate bulky *ortho*-triptycenyl substituted salicylaldimines containing pendant pyridylmethyl or quinolyl donors. These thermally robust catalysts oligomerize ethylene with productivities up to 10 000 g·mmol^{-1}h^{-1}bar^{-1} to give predominantly linear α-olefins.

Experimental Section

Full experimental details are provided in the Supporting Information package.

Acknowledgment. Innovene Ltd. is thanked for financial support. Tripos Receptor Research Ltd is thanked for assistance with the ligand library synthesis. Drs G. Audley and J. Boyle are thanked for GPC and NMR measurements, respectively.

Supporting Information Available: Complete listing of amines used to generate the ligand library; tables listing polymerization screen results and polymer data; GC data for the soluble oligomer fraction arising from tridentate ligand polymerization tests; full experimental details for ligand and complex syntheses and experimental data for ligands formed for in situ screening purposes; crystallographic data files for all reported structures. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0518171