Chromium complexes ligated by amino-salicylaldimine ligands: synthesis, structures and ethylene oligomerisation behaviour

Jin Cui and Mingjie Zhang*

Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, P.R.China

A series of amino-salicylaldimine ligands, 5-tert-butyl-3-(R-1-ylmethyl)-salicylaldimine (**L1-4**, R = morpholine, piperidine, pyrrolidine, 4-methylpiperazine) have been synthesised and structurally analysed. The molecular structure of compound (**L1,** R = piperidine) has been determined by single-crystal X-ray diffraction. These ligands reacted with $[CrCl_3(THF)_3]$ in THF to form chromium complexes, which were isolated in high yields as stable green solids and characterised by means of IR and elemental analysis. Activated with methylaluminoxane (MAO), these complexes showed moderate catalytic activities for ethylene oligomerisaton.

Keywords: amino-salicylaldimine, chromium(III) complexes, ethylene oligomerisation

Olefin polymerisation using transition-metal complex catalysts has received great attention over the past decade.[1] Especially, the development of chromium-based catalysts for olefin oligomerisation/polymerisation has received considerable attention.[2] In general, two classes of chromium-based catalysts are commercially used: Phillips catalyst[3] and Union Carbide catalyst.[4] Recently, various chromium complexes coordinated by anionic ligands such as NO (salicylaldiminato, amino-phenol),[5,6] NN (imino-pyrrolide, β-diketiminate, bis(phosphoranimine)methanide)[7,8,9] and NNN (salicylaldiminato, bis(imino)pyridines, (2-pyridylmethyl)amines, triazacyclohexane)[10,11,12,13] have been reported. Chromium complexes coordinated to various symmetrical ligands such as PNP (bridged-diphosphine),[14] PPP (triphosphacyclododecane),[15] SNS [amine bis(thioether)],[16] CNC [bis(carbine)pyridine][17] and NSN (iminodiphenylsulfide)[18] ligands have also been investigated. When combined with appropriate cocatalyst, some of those chromium complexes catalyse ethylene polymerisation to form oligomeric products with high catalytic activity.

We report here a series of new amino-salicylaldimine ligands that have been designed and synthesised. The chromium complexes were obtained by reaction of amino-salicylaldimine with $[CrCl_3(THF)_3]$. In the presence of methylaluminoxane (MAO), all the chromium complexes showed moderate ethylene oligomerisation activities. Here the synthesis, characterisation of the chromium complexes are reported with their catalytic properties for ethylene activation investigated under various reaction conditions.

The synthetic procedures for ligands 5-tert-butyl-3-(R-1-ylmethyl)-salicylaldimine (**L1-4**, R = morpholine, piperidine, pyrrolidine, 4-methylpiperazine) and their chromium complexes are shown in Scheme 1. Ligands were conveniently prepared in good yields (91–95%) by the condensation reaction of one equivalent of diisopropylaniline with one equivalent of 5-tert-butyl-3-(R-1-ylmethyl)-salicylaldehyde[19] in ethanol, yielding yellow crystals or oily products after purified through column chromatography on Al_2O_3. All the ligands were well characterised by IR spectrometry, ^1H NMR, elemental analysis and an X-ray structure of the representative compound (**L2**, R = piperidine). A perspective view of the molecular structure of **L2** with atom numbering scheme is shown in Fig. 1. The yellow crystal of **L2**, suitable for X-ray diffraction analysis was obtained by slow evaporation of a saturated ethanol

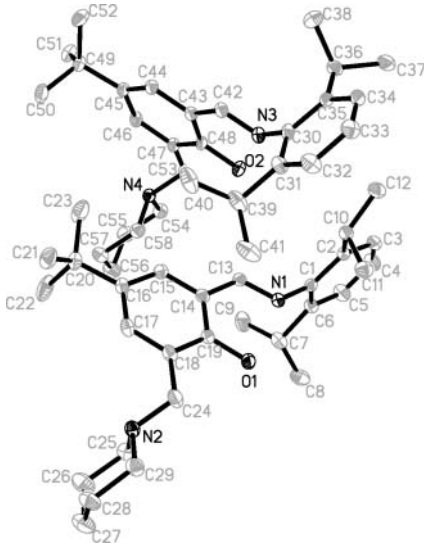
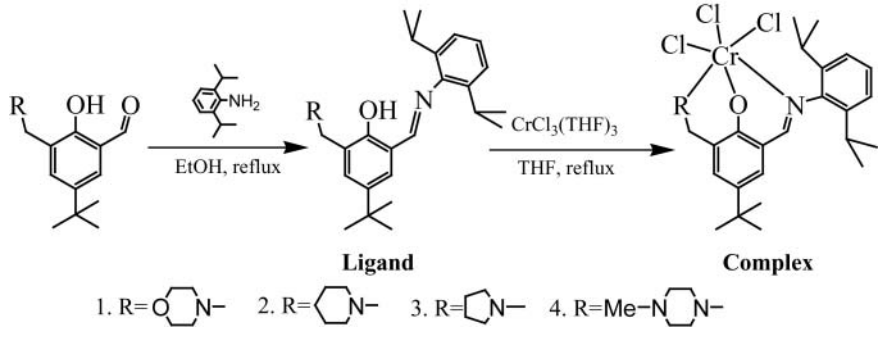


Fig. 1 Molecular structure of ligand 2. Hydrogen atoms are omitted for clarity.



Scheme 1 Synthesis of amino-salicylaldimine ligands **L1-4** and their Cr (III) complexes **C1-4.**

* Correspondent. E-mail: Mjzhangtju@163.com

solution at room temperature. In the molecular structure of **L2** (Fig. 1), the imino group in the solid state is in the E conformation with the typical imino C=N double-bond length of 1.281(2) Å. The dihedral angle between phenoxy and phenylimino rings is 85.43° (or 89.37°). The piperidine ring possesses a stable chair conformation.

The chromium complexes **C1–C4** were prepared by treating a THF solution of $[CrCl_3(THF)_3]$[20] with the corresponding ligands **L1–L4** under reflux. The obtained complexes were precipitated from the reaction solution by adding ethyl ether and separated as green powders in reasonable yields. These complexes showed high stability in both solution and solid and have been identified by FT-IR and elemental analysis. The IR spectra of the ligands showed that the C=N stretching frequencies appeared in the range of 1619–1624 cm^{-1}, while the C=N stretching vibrations shifted toward lower frequency, giving bands between 1600 and 1609 cm^{-1} with weak intensities for complexes **C1–C4**. The results indicate an effective coordination interaction between the imino nitrogen atom and the chromium centre.

To probe the effects of reaction parameters on the ethylene reactivity, oligomerisation behaviour was typically investigated *via* changing the amount of Al/Cr, reaction temperature and reaction time. The oligomers range from C4 to C18 with good selectivity for α-olefins, and the results are given in Table 1. Guided by the experience of the catalytic system with MAO, the various Al/Cr molar ratios were studied with complex **C1** at 30 atm of ethylene. When the Al/Cr molar ratio was varied from 300 to 1500 (entries 1–4), the catalytic activities initially increased and then decreased, with the optimum activity being at an Al/Cr molar ratio of 1000 (entry 3). This may be a consequence of MAO scavenging adventitious water and impurities in the solvent, and attained the highest value at an Al/Cr ratio of 1000. Increasing the Al/Cr molar ratio to 1500 led to lower activity.

As the ethylene oligomerisation is a highly exothermic reaction, the reaction temperature significantly affects the catalytic activity. The effect of temperature on oligomerisation activity was investigated (entry 5). Elevation of the reaction temperature from 40 to 60 °C resulted in a decrease of catalytic activity, which might be caused by instability of the active species or a lower concentration of ethylene in the reaction solution. The proportion of C_4 increased at higher temperature because β-hydrogen elimination was faster than ethylene propagation. The catalytic activity decreased along with the prolonged reaction time and meanwhile higher order olefins were obtained (entry 6).

The catalytic behaviour of these tridentate chromium complexes with MAO is rooted in their ligands with different substituents. In the presence of MAO as cocatalyst, complexes **C1–4** showed moderate activities for ethylene oligomerisation (entries 7–9). Changing the cyclic amine substituents on the phenol ring resulted in little differences in productivity and α-olefin selectivity. **C4** catalyst gave the highest activity of 2.97×10^5 g mol^{-1}(Cr)h^{-1}. Their corresponding amino-salicylaldimine chromium complexes displayed productivities in the range of 2.43×10^5–2.71×10^5 g mol^{-1}(Cr) h^{-1}.

In summary, a series of new amino-salicylaldimine ligands have been successively synthesised and characterised, and consequently used to form their chromium complexes. The molecular structure of the 5-tert-butyl-3-(piperidin-1-ylmethyl)-salicylaldimine ligand has been analysed. Upon activation with MAO, under mild conditions, the chromium complexes have moderate catalytic activities in the range of 2.43×10^5 to 2.97×10^5 g mol^{-1}(Cr)h^{-1}, in producing α-olefin (C4-C18) with good selectivity.

Experimental

Solvents were refluxed over an appropriate drying agent then distilled and degassed prior to use. All other chemicals were obtained commercially without purification unless stated otherwise. 5-tert-butyl-3-(R-1-ylmethyl)-salicylaldehyde precursors and $[CrCl_3(THF)_3]$ were prepared according to the established procedures.[20] IR spectra were obtained as KBr pellets on a Perkin-Elmer FTIR 2000 Spectrometer. Elemental analyses were performed on a Flash EA 1112 micro-analyser. ^{1}H NMR spectral data were recorded on a Varian Inova 500 MHz spectrometer using TMS as internal standard and $CDCl_3$ as solvent. The distribution of oligomers obtained was measured on a Varian VISTA 6000GC spectrometer and the yield of oligomers was calculated by referencing to the mass of the solvent on the basis of the prerequisite that the mass of each fraction was approximately proportioned to its integrated area in the GC trace.

Synthesis of ligands

2,6-diisopropylaniline (0.01mol) was added to a solution of 5-tert-butyl-3-(R-1-ylmethyl)-salicylaldehyde (0.01mol) in ethanol (30ml) and heated to reflux for 4 hours. TLC analysis showed completed conversion of starting materials. The solvent was removed under reduced pressure and the resulting yellow oil was eluted with petroleum ether/ethyl acetate (5:1) on an alumina column.

*(E)-4-*t*ert-butyl-2-{(2,6-diisopropylphenylimino)methyl)-6-(morph olinomethyl)}phenol* (**L1**)**:** Yellow oil, yield 95%. IR (KBr, cm^{-1}): 1619 (C=N). ^{1}H NMR (500 MHz, CDC13): δ 8.278 (s, 1H, Ar-C*H*=N), 7.534–7.539 (d, J = 2.5Hz, 1H, *H*-Ar-CH=N), 7.320–7.325 (d, J = 2.5Hz, 1H, *H*-Ar-CH=N), 7.204 (s, 3H, C=NArH), 3.792–3.810(t, J = 4.5Hz, 4H, NCH_2CH_2O), 3.694 (s, 2H, Ar-CH_2N), 2.933–2.995 (m, 2H, Ar($CH(CH_3)_2)_2$), 2.619 (s, 4H, NCH_2CH_2O), 1.384 (s, 9H, ArC($CH_3)_3$), 1.190–1.203 (d, J = 6.5Hz, 12H, Ar($CH(CH_3)_2)_2$. Calcd for $C_{28}H_{40}N_2O_2$: C, 77.02; H, 9.23; N, 6.42. Found: C, 77.15; H, 9.30; N, 6.53%. *(E)-4-tert-butyl-2-{(2,6-diisopropylphenylimino)methyl)-6-(piperidin-1-ylmethyl})phenol l*(**L2**)**:** Yellow crystal, yield 94%. IR (KBr, cm^{-1}): 1621 (C=N). ^{1}H NMR (500 MHz, CDC13): δ 8.410 (s, 1H, ArC*H*=N), 7.560 (s, 1H, *H*-ArCH=N), 7.451 (s,1H, *H*-ArCH=N), 7.183–7.217 (m, 3H, C=NAr*H*), 3.742 (s, 2H, ArCH_2N), 3.028–3.078 (m, 2H, Ar($CH(CH_3)_2)_2$), 2.587 (m, 4H, $NCH_2CH_2CH_2$), 1.690–1.711

Table 1 Ethylene oligomerisation with 1-4/MAO systems[a]

Entry	Cat.	Al/Ni	T/°C[b]	T/min[c]	Oligomer distribution[d] (wt%)				Activity[e]
					$C_4/\sum C$	$C_6/\sum C$	$C_8/\sum C$	$\geq C_{10}/\sum C$	
1	1	300	40	30	45.1	19.8	8.4	26.7	1.23
2	1	500	40	30	39.2	24.2	12.3	24.3	1.77
3	1	1000	40	30	31.3	33.6	13.1	22.0	2.55
4	1	1500	40	30	25.3	35.3	11.5	27.9	2.11
5	1	1000	60	30	37.7	30.4	12.2	19.7	0.93
6	1	1000	40	60	30.1	24.1	16.3	29.5	1.97
7	2	1000	40	30	38.4	28.7	13.1	19.8	2.71
8	3	1000	40	30	42.5	28.4	14.2	14.9	2.43
9	4	1000	40	30	34.1	30.8	14.6	20.5	2.97

[a]Conditions: 5μmol of catalyst; toluene (100ml); 30atm ethylene.
[b]Reaction temperature.
[c]Reaction time. [d]Determined by GC. [e]Oligomer activity: 10^5 g mol^{-1} (Cr) h^{-1}.

Table 2 Crystallographic parameters

	Ligand **2**
Empirical formula	C29 H42 N2 O
Formula weight	434.65
Temperature (K)	113(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	10.700(2)
b (Å)	14.447(3)
c (Å)	17.502(4)
α (°)	77.83(3)
β (°)	86.63(3)
γ (°)	88.34(3)
Vol.(Å^3)	2639.8(9)
Z	4
D_{calc}(Mg m^{-3})	1.094
μ(mm^{-1})	0.065
Reflections collected/unique [R_{int}]	19552/9261
F(000)	952
Crystal size (mm)	0.26 × 0.24 × 0.16
θ Range for data collection (°)	1.44–25.02
Data/restraints/parameters	9261/0/594
Final R indices [$I > 2\sigma(I)$]	R^1 = 0.0567, WR^2 = 0.1527
R indices (all data)	R^1 = 0.0739, WR^2 = 0.1671
Goodness-of-fit on *F2*	1.037
Largest differences in peak and hole(eÅ^{-3})	0.342 and –0.234

(t, 4H, $NCH_2CH_2CH_2CH_2$), 1.514 (m, 2H, $NCH_2CH_2CH_2CH_2$), 1.379 (s, 9H, $ArC(CH_3)_3$), 1.209–1.223 (d, *J* = 6.5Hz, 12H, $Ar(CH(CH_3)_2)_2$). Calcd for $C_{29}H_{42}N_2O$: C, 80.13; H, 9.74; N, 6.44. Found: C, 79.98; H, 9.68; N, 6.49%

(E)-4-tert-butyl-2-{(2,6-diisopropylphenylimino)methyl)-6-(pyrrolidin-1-ylmethyl}- phenol (**L3**): Yellow crystals, yield 91%. IR (KBr, cm^{-1}): 1620 (C=N). ^{1}H NMR (500 MHz, CDC13): δ 8.399 (s, 1H, ArCH=N), 7.578 (s, 1H, *H*-ArCH=N), 7.453 (s, 1H, *H*-ArCH=N), 7.199–7.211 (m, 3H, C=NAr*H*), 3.752 (s, 2H, $ArCH_2N$), 2.981–3.023 (m, 2H, $Ar(CH(CH_3)_2)_2$), 2.584 (m, 4H, NCH_2CH_2), 1.702(m, 4H, NCH_2CH_2), 1.388 (s, 9H, $ArC(CH_3)_3$), 1.198-1.211 (d, *J* = 6.5Hz, 12H, $Ar(CH(CH_3)_2)_2$). Calcd for $C_{28}H_{40}N_2O$: C, 79.95; H, 9.59; N, 6.66. Found: C, 79.83; H, 9.51; N, 6.63%. *(E)-4-tert-butyl-2-{(2,6-diisopropylphenylimino)methyl)-6-((4-methylpiperazin-1-yl)methyl)} phenol* (**L4**): Yellow oil, yield 95%. IR (KBr, cm^{-1}): 1624 (C=N). ^{1}H NMR (500 MHz, CDC13): δ 8.312 (s, 1H, ArCH=N), 7.533 (s, 1H, *H*-ArCH=N), 7.302 (s, 1H, *H*-ArCH=N), 7.182 (s, 3H, C=NArH), 3.786 (s, 2H, $ArCH_2N$), 2.977–3.005 (m, 2H, $Ar(CH(CH_3)_2)_2$), 2.582–2.887 (s, 8H, NCH_2CH_2N), 2.398–2.433 (m, 3H, $NCH_2CH_2NCH_3$), 1.345 (s, 9H, $ArC(CH_3)_3$), 1.172–1.186 (d, *J* = 7.0Hz, 12H, $Ar(CH(CH_3)_2)_2$). Calcd for $C_{29}H_{43}N_3O$: C, 77.46; H, 9.64; N, 9.34. Found: C, 77.66; H, 9.56; N, 9.28%.

Synthesis of complexes

0.20 mmol of $[CrCl_3(THF)_3]$ and 0.21 mmol of ligand were dissolved in THF (20 mL). The solution was refluxed for 2 h and then cooled to room temperature. The solution was filtered, then part of solvent was removed in vacuum. Ether (100 mL) was added to the reaction mixture, and this mixture was allowed to stand for an appropriate period of time, after which it was filtered and the solid was obtained.

[4-tert-butyl-2-{(2,6-diisopropylphenylimino)methyl)-6-(morpholinomethyl}phenol]CrCl$_3$ (**C1**)**:** Green solid, Yield 71%. IR (KBr, cm^{-1}): 1604 (C=N). Calcd for $C_{28}H_{39}Cl_3CrN_2O_2$: C, 56.62; H, 6.62; N, 4.72. Found: C, 56.87; H, 6.78; N, 4.79%.

[4-tert-butyl-2-{(2,6-diisopropylphenylimino)methyl)-6-(piperidin-1-ylmethyl}phenol]CrCl$_3$ (**C2**): Green solid, Yield 75%. IR (KBr, cm^{-1}): 1609 (C=N). Calcd for $C_{29}H_{41}Cl_3CrN_2O$: C, 58.84; H, 6.98; N, 4.73. Found: C, 58.95; H, 6.87; N, 4.86%.

[4-tert-butyl-2-{(2,6-diisopropylphenylimino)methyl)-6-(pyrrolidin-1-ylmethyl}phenol]CrCl$_3$ (**C3**): Green solid, Yield 69%. IR (KBr, cm^{-1}): 1600 (C=N). Calcd for $C_{28}H_{39}Cl_3CrN_2O$: C, 58.19; H, 6.80; N, 4.85. Found: C, 58.26; H, 6.88; N, 4.91%

[4-tert-butyl-2-{(2,6-diisopropylphenylimino)methyl)-6-((4-methylpiperazin-1-yl)methyl)}phenol]CrCl$_3$ (**C4**): Green solid, Yield 81%. IR (KBr, cm^{-1}): 1604 (C=N). Calcd for $C_{29}H_{42}Cl_3CrN_3O$: C, 57.38; H, 6.97; N, 6.92. Found: C, 57.45; H, 7.02; N, 6.98%

Procedure for ethylene oligomerisation

Ethylene oligomerisation at 30 atm ethylene pressure was carried out in a 250-mL autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. Toluene, the desired amount of cocatalyst and a toluene solution of the catalyst precursor (the total volume was 100 mL) was added to the reactor in this order under an ethylene atmosphere. Upon reaching the desired reaction temperature, ethylene with the desired pressure was introduced to start the reaction, and the ethylene pressure was kept by constant feeding of ethylene. After 30 min, the reaction was stopped. The catalytic reaction mixture was quenched with HCl-acidified ethanol (5%) in an ice-water bath in accordance with the oligomers produced. Then the solution was analysed by gas chromatography for determining the distribution of oligomers obtained.

X-ray crystallographic studies

Ligand **L2** intensity data sets were collected at 113(2) K on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by the global refinement of the positions of all collected reflections. Intensities were corrected by Lorentz and polarization effects and empirical absorptions were applied. The structure was solved by direct method, and refined by full-matrix least-squares on F^2 using SHELXS-97 package [G. M. Sheldrick, SHELXTL Version 5.1, Bruker Analytical X-rayInstruments Inc, Madison, WI, USA, 1998].

Received 13 October 2009; accepted 30 November 2009
Paper 090826 *doi: 10.3184/030823410X12628736648105*
Published online: 22 January 2010

References

1 V.C. Gibson and S.K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.
2 E. Groppo, C. Lamberti, S. Bordiga, G. Spoto and A. Zecchina, *Chem. Rev.*, 2005, **105**, 115.
3 A. Clark, *Catal. Rev.*, 1969, **3**, 145.
4 F.J. Karol, G.L. Karapinka, C. Wu, A.W. Dow, R.N. Johnson and W.L. Carrick, *J. Polymer. Sci., Part A: Polymer. Chem.*, 1972, **10**, 2621.
5 V.C. Gibson, S. Mastroianni, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White and D.J. Williams, *J. Chem. Soc., Dalton Trans.*, 2000, 1969.
6 V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White and D.J. Williams, *J. Chem. Soc., Dalton Trans.*, 1999, 827.
7 V.C. Gibson, P.J. Maddox, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White and D.J. Williams, *Chem. Commun.*, 1998, 1651.
8 L.A. McAdams, W.-K. Kim, L.M. Liable-Sands, I.A. Guzei, A.L. Rheingold and K.H. Theopold, *Organometallics*, 2002, **21**, 952.
9 P. Wei and D.W. Stephan, *Organometallics*, 2002, **21**, 1308.
10 D.J. Jones, V.C. Gibson, S.M. Green and P.J. Maddox, *Chem. Commun.*, 2002, 1038.
11 H. Sugiyama, G. Aharonian, S. Gambarotta, G.P.A. Yap and P.H.M. Budzelaar, *J. Am. Chem. Soc.*, 2002, **124**, 12268.
12 M.J. Carney, N.J. Robertson, J.A. Halfen, L.N. Zakharov and A.L. Rheingold, *Organometallics*, 2004, **23**, 6184.
13 R.D. Köln, M. Haufe, G. Kociak-Köhn, S. Grimm, P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.*, 2000, **39**, 4337.
14 D.S. McGuinness, P. Wasserscheid, D.H. Morgan and J.T. Dixon, *Organometallics*, 2005, **24**, 552.
15 R.J. Baker and P.G. Edwards, *J. Chem. Soc., Dalton Trans.*, 2002, 2960.
16 D.S. McGuinness, P. Wasserscheid, W. Keim, D. Morgan, J.T. Dixon, A. Bollmann, H. Maumela, F. Hess and U. Englert, *J. Am. Chem. Soc.*, 2003, **125**, 5272.
17 D.S. McGuinness, V.C. Gibson, D.F. Wass and J.W. Steed, *J. Am. Chem. Soc.*, 2003, **125**, 12716.
18 J. Liu, Y. Li, J. Liu and Z. Li, *J. Mol. Catal. A*: C, *hem*., 2006, **244**, 99.
19 M. Fennie, E. DiMauro, E. O'Brien, V. Annamalai and M. Kozlowski, *Tetrahedron*, 2005, **61**, 6249.
20 W. Herwig and H.H. Zeiss, *J. Org. Chem.*, 1958, **23**, 1404.