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A five-coordinate chromium alkyl complex stabilised by salicylaldiminato ligands

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The five-coordinate bis(salicylaldiminato)chromium(III) complex [3,5-(t-Bu)$_2$(O)C$_6$H$_2$CHN(2,6-i-Pr$_2$C$_6$H$_3$)]$_2$CrCl (2) reacts with triethylaluminium in THF at room temperature to give the air sensitive ethyl species [3,5-(t-Bu)$_2$-(O)C$_6$H$_2$CHN(2,6-i-Pr$_2$C$_6$H$_3$)]$_2$CrEt (3); in the presence of aluminium activators, 2 and 3 are moderately active ethylene polymerisation catalysts.

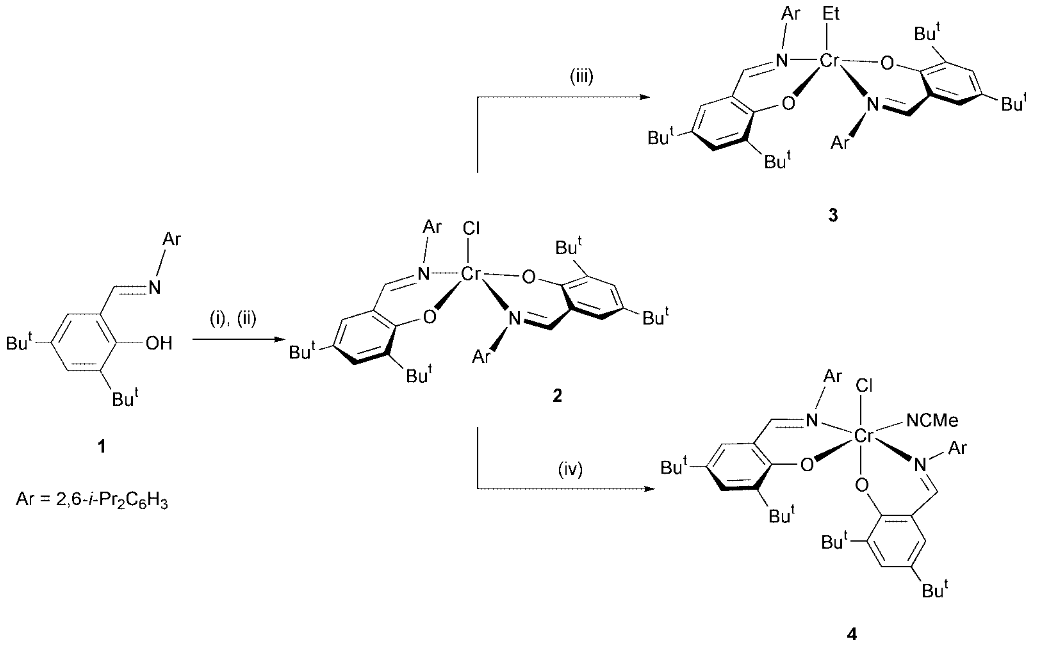
Much research effort has been devoted to the study of half-sandwich chromium complexes[1] as model systems for the Unipol family of silica-supported chromium catalysts[2] which have been commercially exploited for the production of high density polyethylene. More recently, a number of non-cyclopentadienyl ligand sets have been investigated including imido,[3] β-diketiminates[4] and reduced Schiff base [N,O] chelate derivatives,[5] with a view to generating new, tunable molecular chromium polymerisation systems.

The simple and readily accessible salicylaldiminato ligand family has played an important role in the development of transition metal coordination chemistry, and recently they have been shown to support highly active polymerisation centres for both the early[6] and late[7] transition metals. There are, however, no examples of olefin polymerisation catalysts bearing these ligands for the mid transition metals, and indeed, as far as we are aware, there have been no reports of chromium alkyl species stabilised by Schiff base [N,O] chelate ligands.† We therefore decided to target such species as potentially viable ethylene polymerisation catalysts. Here, we report the synthesis and characterisation of a five-coordinate chromium alkyl species bearing two bulky salicylaldiminato ligands and its performance, along with its precursor and a closely related derivative, as ethylene polymerisation catalysts.

The bis(salicylaldiminato)chromium(III) complex [3,5-(t-Bu)$_2$-(O)C$_6$H$_2$CHN(2,6-i-Pr$_2$C$_6$H$_3$)]$_2$CrCl (**2**) is prepared in high yield by treatment of [CrCl$_3$(THF)$_3$] with two equivalents of the lithium salt of **1** in THF (Scheme 1). Prolonged standing at −10 °C of a pentane solution gave **2** as a pale yellow microcrystalline solid.

Complex **2** is presumed to be a monomeric, square-based pyramidal complex with an apical chlorine atom (by comparison with the structure of **3** – *vide infra*);[8] microanalysis ‡ and the magnetic moment (3.94 μ_B, Evans Balance) are consistent with its formulation. The FAB$^+$ mass spectrum of **2** shows a molecular ion peak along with a fragmentation peak corresponding to loss of one chlorine atom. Attempts at preparing a mono(salicylaldiminato) chromium complex by reacting [CrCl$_3$(THF)$_3$] with one equivalent of the lithium salt of **1** also resulted in the isolation of **2** albeit in lower yield.

Treatment of **2** with triethylaluminium at room temperature in THF afforded the air sensitive green ethyl complex [3,5-(t-Bu)$_2$(O)C$_6$H$_2$CHN(2,6-i-Pr$_2$C$_6$H$_3$)]$_2$CrEt (**3**).‡ Crystals of **3** suitable for a single crystal X-ray determination § were grown from a saturated light petroleum (bp 40–60 °C) solution. The complex has crystallographic C_2 symmetry with a consequent *trans* disposition of the coordinated atoms of the chelating ligands; the apical ethyl substituent is disordered about this axis (Fig. 1).



Scheme 1 Reagents and conditions (i) n-BuLi, −78 °C, THF; (ii) [CrCl$_3$(THF)$_3$], −78 °C, THF, 71%; (iii) AlEt$_3$, THF, 70%; (iv) MeCN, 89%.

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Table 1 Results of ethylene polymerisation runs using pre-catalysts **2**–**4**[a]

Run	Precatalyst	Activator	T/°C	Ethylene pressure/bar	Polymer yield/g	Productivity/ g mmol^{-1} h^{-1} bar^{-1}	M_n	M_w	M_w/M_n	M_{pk}
1[b]	**2**	MAO	25	1	trace	<1	—	—	—	—
2[b]	**2**	DEAC	25	1	0.6	30	88 000	1 762 000	19.9	1 009 000
3	**2**	DEAC	35	10	24	96	351 000	1 784 000	5.1	916 000
4	**2**	DEAC	75	10	<1	<1	—	—	—	—
5	**2**	DMAC	35	10	21	84	[c]	[c]	[c]	[c]
6[d]	**2**	DEAC	35	10	20	80	4 900	41 000	8.3	18 000
7	**3**	DEAC	35	10	13	50	576 000	2 070 000	3.6	1 400 000
8	**4**	DEAC	35	10	17	66	375 000	1 420 000	3.8	1 137 000

[a] General conditions: 1 L autoclave, 0.025 mmol pre-catalyst dissolved in 2 ml of toluene, isobutane solvent (500 ml), diethylaluminium chloride (DEAC) or dimethylaluminium chloride (DMAC) scavenger, 0.0625 mmol activator (25 eq.), 60 min, autoclave vented, polymer washed with dilute HCl (40 ml) and MeOH (100 ml) and dried in a vacuum oven at 40 °C. [b] Performed in toluene in a Schlenk tube over 60 min, MAO (200 eq.) or DEAC (25 eq.). [c] Polymer insoluble in the GPC solvent 1,2,4-trichlorobenzene. [d] 1 bar hydrogen.

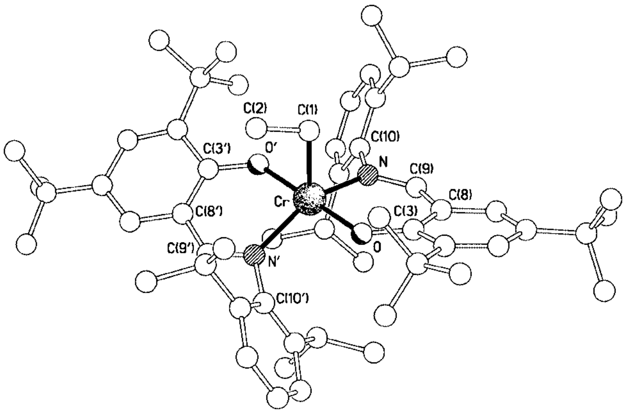

Fig. 1 The molecular structure of **3**. Selected bond lengths (Å) and angles (°) are: Cr–O 1.947(3), Cr–N 2.073(4), Cr–C(1) 2.065(12), O–C(3) 1.310(6), N–C(9) 1.308(7), N–C(10) 1.463(7), C(1)–C(2) 1.51(2); O–Cr–O′ 179.9(3), N–Cr–N′ 147.8(3), O–Cr–N 88.9(2), O–Cr–N′ 91.2(2), O–Cr–C(1) 93.9(4), N–Cr–C(1) 95.8(3), O′–Cr–C(1) 86.0(4), N′–Cr–C(1) 116.4(3), Cr–C(1)–C(2) 108.0(8).

The geometry at chromium is severely distorted square pyramidal with *cis* angles ranging between 86.0(4) and 116.4(3)°, and with the N/Cr/O and N′/Cr/O′planes inclined by 32° to each other. The coordination distances are typical, with the bonds to the nitrogen atoms [2.073(4) Å] reflecting their formal dative character, while the Cr–C bond length of 2.065(12) Å is comparable to the Cr–C distances of 2.037(9) and 2.042(8) found in related pyrrolide-imine and β-diketiminate systems,[4a] respectively. The double bond nature of the imine linkage [N–C(9) 1.308(7) Å] is clearly retained. The six-membered chelate ring has a slightly folded conformation [*ca.* 12°] about the O · · · C(9) vector.

The acetonitrile adduct of **2**, [3,5-(*t*-Bu)$_2$(O)C$_6$H$_2$CHN(2,6-*i*-Pr$_2$C$_6$H$_3$)]$_2$Cr(NCMe)Cl (**4**), can be prepared in high yield by stirring **2** in acetonitrile at room temperature (Scheme 1). Prolonged standing at room temperature gives dark green crystalline blocks of **4**. The X-ray analysis¶ shows (Fig. 2) an octahedral complex in which the chromium is bound to two *cis*-coordinated [N,O] chelating ligands [the nitrogens being *trans*-176.6(1)°], a chloride and the solvent derived acetonitrile. If one ignores the non-equivalence of the chloride and acetonitrile ligands, the geometry approximates closely to C_2, the axis bisecting the O(1)–Cr–O(2) angle, *cf.* the C_2-*trans* geometry observed in **3**. The Cr–N distances are slightly greater than those observed in **3**, and not surprisingly the Cr–O distances are asymmetric with that *trans* to chlorine [Cr–O(2) 1.949(3) Å] being significantly longer than that *trans* to acetonitrile [Cr–O(1) 1.917(3) Å]. As in **3**, the two imine linkages, N(1)–C(7) and N(2)–C(37), are both short reflecting a retention of their double bond character. Both six-membered chelate rings have folded, sofa conformations with the chromium atom lying 0.37 and 0.73 Å out of the "O(1) to N(1)" and "O(2) to N(2)" chelate planes respectively, a geometry that differs from that adopted in the structure of **3** (*vide supra*). An interesting feature of the coordinated acetonitrile is that it is inclined such that it lies over the plane of the C(8) 2,6-diisopropylphenyl ring, with C(61) lying 3.05 Å from the ring plane, suggesting a degree of π–π interaction.

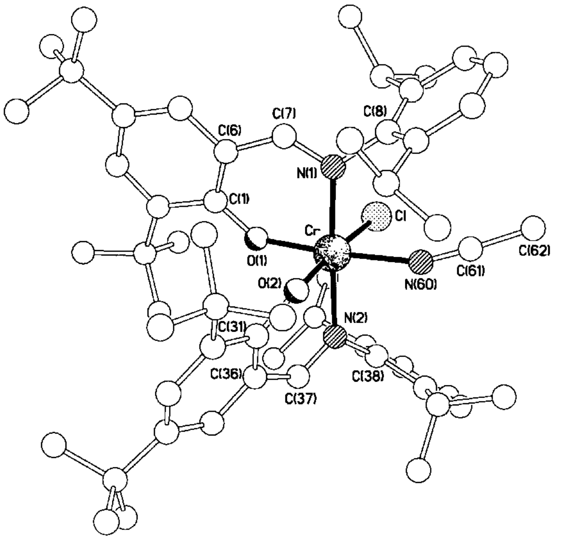

Fig. 2 The molecular structure of **4**. Selected bond lengths (Å) and angles (°) are: Cr–O(1) 1.917(3), Cr–O(2) 1.949(3), Cr–N(1) 2.102(4), Cr–N(2) 2.098(3), Cr–Cl 2.320(1), Cr–N(60) 2.089(4), O(1)–C(1) 1.310(6), N(2)–C(31) 1.323(5), N(1)–C(7) 1.283(6), N(2)–C(37) 1.287(5); O(1)–Cr–O(2) 90.26(14), O(1)–Cr–N(60) 175.4(2), O(2)–Cr–N(60) 93.0(2), O(1)–Cr–N(2) 92.48(13), O(2)–Cr–N(2) 86.90(13), N(60)–Cr–N(2) 90.91(14), O(1)–Cr–N(1) 90.62(14), O(2)–Cr–N(1) 91.76(14), N(60)–Cr–N(1) 86.06(14), N(2)–Cr–N(1) 176.62(14), O(1)–Cr–Cl 93.01(11), O(2)–Cr–Cl 175.83(10), N(60)–Cr–Cl 83.92(12), N(2)–Cr–Cl 90.37(10), N(1)–Cr–Cl 90.79(11).

As with **2** the derivatives **3** and **4** are paramagnetic exhibiting magnetic moments of *ca.* 3.9 μ_B and *g*-values in their EPR spectra of *ca.* 1.98 consistent with Cr(III) (d^3) centres.

The rearrangement of the salicylaldiminato ligands to accommodate the chloro and the donor acetonitrile groups of **4** in mutually *cis* positions was thought to be potentially significant for generating polymerisation-active metal centres since an important requirement for an active catalyst is to have the vacant site (occupied by acetonitrile in **4**) positioned adjacent to the growing alkyl chain (in place of the chloro group). The results of ethylene polymerisation tests on **2**–**4** are collected in Table 1. Solid polyethylene is obtained in all cases with all samples displaying high molecular weights, moderate polydispersities and virtually no branching (by NMR). Under similar conditions [10 bar ethylene, 35 °C, activator (25 eq.)] the productivities obtained are in the range 50–100 g mmol^{-1} h^{-1} bar^{-1}. Increasing the polymerisation reaction temperature results in a dramatic deactivation of the system, at 75 °C the catalyst system being almost inactive (run 4). Infrared (IR) analysis of the polymer produced in run 7 reveals a vinyl endgroup concentration of 0.19 per 1000 carbon atoms indicative of β-hydrogen transfer as the main termination pathway. Preliminary experiments performed on **2** show a positive hydrogen response (1 bar) with a reduction in M_w from 1,784,000 (run 3) to 41,000 (run 6); IR analysis of the polyethylene from run 6 is consistent with predominantly saturated end-groups. Notably, the mono(ethylated) complex **3** is not an active catalyst in the absence of activator, nor when **2** is employed with $AlEt_3$ as activator. It is thus possible that an important role of the activator is to remove one of the [N,O] chelate ligands.|| As we have observed elsewhere, the alkylaluminium chloride cocatalysts DEAC or DMAC are more compatible activators than methylaluminoxane (MAO) (see runs 1–3,5) with these low valent chromium pre-catalysts.[4a,5]

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Notes and references

† A search of the Cambridge Crystallographic Database revealed that no alkylchromium complexes bearing salicylaldiminato ligands have been structurally characterised up to January 2000.

‡ Elemental analysis data, for **2**: Calc. for $C_{54}H_{76}N_2O_2CrCl$; C, 74.35; H, 8.72; N, 3.21. Found: C, 74.61; H, 8.99; N, 3.01%. For **3**: Calc. for $C_{56}H_{81}N_2O_2Cr$; C, 77.69; H, 9.36; N, 3.24. Found: C, 77.09; H, 8.98; N, 2.99%. For **4**: Calc. for $C_{56}H_{79}N_3O_2CrCl$; C, 73.64; H, 8.66; N, 4.60. Found: C, 73.44; H, 8.56; N, 4.44%.

§ Crystal data for **3**: $C_{56}H_{81}N_2O_2Cr{\cdot}C_5H_{12}$, $M = 938.4$, monoclinic, $C2/c$ (no. 15), $a = 25.231(3)$, $b = 10.153(1)$, $c = 25.314(6)$ Å, $\beta = 90.01(1)°$, $V = 6485(2)$ Å^3, $Z = 4$ (the complex has crystallographic C_2 symmetry), $D_c = 0.961$ g cm^{-3}, μ(Mo-Kα) = 2.12 cm^{-1}, $F(000) = 2052$, $T = 203$ K; orange/red prisms, 0.53 × 0.47 × 0.32 mm, Siemens P4/PC diffractometer, ω-scans, 4236 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms of the complex were refined anisotropically using full matrix least-squares based on F^2 to give $R_1 = 0.083$, $wR_2 = 0.202$ for 2772 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 45°$] and 321 parameters. The high final residual is a consequence of highly disordered included solvent.

¶ Crystal data for **4**: $C_{56}H_{79}N_3O_2ClCr{\cdot}MeCN$, $M = 954.7$, monoclinic, $P2_1/c$ (no. 14), $a = 22.829(3)$, $b = 12.704(2)$, $c = 20.164(4)$ Å, $\beta = 90.73(1)°$, $V = 5847(2)$ Å^3, $Z = 4$, $D_c = 1.084$ g cm^{-3}, μ(Mo-Kα) = 2.82 cm^{-1}, $F(000) = 2060$, $T = 293$ K; deep orange prisms, 0.77 × 0.77 × 0.38 mm, Siemens P4/PC diffractometer, ω-scans, 10176 independent reflections. The structure was solved by direct methods and the major occupancy non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give $R_1 = 0.065$, $wR_2 = 0.141$ for 5565 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 50°$] and 619 parameters. CCDC reference number 186/1995. See http://www.rsc.org/suppdata/dt/b0/b002631j/ for crystallographic files in .cif format.

|| It is unlikely that both [N,O] ligands are removed since ligand-free precursors, such as $[CrCl_3(THF)_3]$, afford very low activities (typically < 3 g mmol^{-1} h^{-1} bar^{-1}).

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