FULL PAPER

Synthesis, characterisation and catalytic behaviour of a novel class of chromium(III) and vanadium(III) complexes containing bi- and tri-dentate imidazole chelating ligands: a comparative study

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Received 24th July 2002, Accepted 7th October 2002 First published as an Advance Article on the web 14th November 2002

The syntheses and characterisation of tri- and bi-dentate coordinated chromium(III) and vanadium(III) complexes of the general composition [MCl₃(N^D^N)], [MCl₃(N^N)]₂ {M = Cr, (N^D^N) = (mim)₃COCH₃ **2a** [mim = 1-methylimidazolyl], (mim)₂CHCH₂PPh₂ **2b**, (mim)₂CHCH₂C(O)But **2c**, (tBupim)₃P **2d** [tBupim = 1-isopropyl-4*tert*-butylimidazolyl], (N^N) = (mim)₂CH₂ **3e**, (mim)₂CH₂PPh₂ **3f**, (mim)₂CO **3g**, (Bzmim)₂CO **3h** [Bzmim = 1-methybenzimidazolyl], (tBupim)₂CO **3i**, (mim)₂C=NPh **3j**; M = V: (N^D^N) = (mim)₃COCH₃ **5a**; (N^N) = (mim)₂CO **5g**}, [CrCl₃(mim)₃] **4k**, and [CrCl₃(MeTAM]] **6** (MeTAM = 1-methyltriacetylmethane) is described. Crystallisation of **3g** from CH₃CN/Et₂O gave the mononuclear complex [CrCl₃{(mim)₂CO}{(CH₃CN)] **3g'**. The molecular structure of **3g'** shows the chromium atom is quasi-octahedral, six-coordinate, the three coordinated chlorine atoms disposed *mer* in the coordination sphere. The electronic spectra of the chromium complexes exhibit d-d transitions typical of a pseudo-octahedral coordinated d³ ion, falling into the region $v_1 {}^4A_{2g} \rightarrow {}^4T_{2g} 600-700$ nm and $v_2 {}^4A_{2g} \rightarrow {}^4T_{1g}(F) 430-470$ nm, and 10Dq values between 14400 and 16700 cm⁻¹. In the presence of MMAO the complexes give active catalyst systems for the conversion of ethylene into 1-alkenes or polymers, with activities and selectivities depending on the electronic and steric factors of the ligand system and the metal centre, respectively.

Introduction

Numerous middle and late transition metal complexes bearing chelating imidazole ligands are known and they play a major role as models to mimic the active sites of metallo enzymes.¹ Applications outside this area, such as catalytic hydroamination, hydrosilylation and Heck coupling reactions have recently been reported by Field and coworkers and our group for imidazole chelated rhodium² and palladium³ complexes, respectively. By contrast and despite the fact that chromium(III) complexes with unidentate and chelating N-heterocyclic ligands (e.g. pyridine, phenanthroline, pyrazolylborate) are well established,4-10 very few examples with non-histidine type imidazole ligands¹¹⁻¹⁵ are known.¹⁶ Sanchez and Losada¹⁴ have reported chromium(III) halogen complexes of the type $[CrL_6]Cl_3$, $[CrXL_5]X_2$ (X = Cl, Br), cis- and trans- $[CrCl_2L_4]Cl$, and *trans*-[$CrCl_2(L)_4$]Cl with unidentate imidazoles (L = imidazole, 1-methylimidazole or 2-methylimidazole). Structurally characterised complexes bearing chelating benzimidazole ligands have been described recently by Castillo-Blum and coworkers.15

Apart from the lack of a well established chemistry for chromium imidazole complexes, our interest in such combinations has been stimulated by recent developments in homogeneous catalysis. Most notably these led to a great variety of new *N*-ligated transition metal complexes capable of catalysing the oligo- and poly-merisation of olefins,^{17,18} and it has been demonstrated that steric and electronic variations in the ligand system govern their activity and product selectivity.¹⁹⁻²²

More recently, these studies have also furnished a number of nitrogen chelated chromium olefin polymerisation^{23,24} and trimerisation^{25,26} catalysts that can be regarded as homogeneous non-cyclopentadiene model systems for industrial heterogeneous processes²⁷ (Phillips catalyst). In a previous note we have reported the synthesis and catalytic behaviour of six chromium(III) complexes bearing bi- and tri-dentate ligands based on a bis(imidazole) framework containing additional functional groups which differ in their electronic properties and chemical hardness (HSAB concept).28 With the aim of gaining a better understanding of how variations of the ligand system within a class of catalysts influences the electronic properties of the coordinated metal centre or impacts on their catalytic performance, we have extended our previous studies to other imidazole chelates, two imidazole chelated vanadium(III) complexes, and two chromium(III) complexes bearing the podand ligands 1-methyltrisacetylmethane (MeTAM) and trisaminotriethylamine (tren). In this paper we describe in greater detail the synthesis and characterization of this new class of chromium(III) chloro complexes, including their magnetic properties, electronic spectra, and electrochemical investigation (the ligands used in this work are shown in Fig. 1). We also report a rare example of a structurally characterized chromium(III) complex where the imidazole ligand is an integral part of the coordination environment.

Results and discussion

Synthesis of the complexes

The ligands have been synthesized according to published procedures^{2,29-31} or by methods developed in our laboratories.³²

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Fig. 1 Ligands used in this work.

The complexes have been prepared by adding a solution of the respective ligand to a solution of CrCl₃(THF)₃. Using CH₂Cl₂ or THF as a solvent, this method of preparing $CrCl_3(mim)_n$ complexes in high yields (*ca.* 90%) is generally applicable for the majority of the complexes presented in this work (Scheme 1). The reactions proceeded smoothly at ambient temperature and in most cases the green or grey-green products precipitated from the reaction medium. We note however that extensive trituration with CH₂Cl₂ is essential to obtain pure products. The, compared to the other ligands, relatively bulky ligand $(tBupim)_3P$, did not react under these conditions; even on refluxing the reaction mixture in CHCl₃ for one day in the presence of a trace amount of zinc dust, the purple colour persisted and most of the ligand was recovered. Complex 2d has been prepared by addition of a methanol solution of the ligand to a mixture of solid CrCl₃ and a trace amount of zinc dust. The reaction mixture gradually developed a green colour and was heated to 60 °C for 1-2 h prior to work up. Different reactivity of related ligand systems towards transition metal THF adducts is not uncommon. In order to demonstrate the advantage of using chelating ligands to support catalytically active metal centres we have also prepared the previously unknown [CrCl₃(1-methylimidazole)₃] 4k, containing three unidentate imidazole units.

The complexes **2**, **3** and **4** have been characterized by IR, MS, UV-vis and microanalysis. FAB and ESI mass spectrometry proved to be a particularly useful analytical method in that it allowed the quick and sufficient determination of the chemical composition. Satisfactory microanalyses were often difficult to obtain due to the moisture sensitivity of the complexes, leading

to drastically diminished C and N microanalytical values. In this regard we have undertaken controlled studies on an analytically pure sample of complex **2a**. Although the green colour of the complex did not change upon exposure to air, the analytical results demonstrate the problem regarding water absorption: water free $C_{14}H_{18}N_6OCl_3Cr$ (**2a**) requires C, 37.81; H, 4.09; N: 18.90; exposure to air for a few hours forming $C_{14}H_{18}N_6OCl_3Cr \cdot 2.5H_2O$ —requires: C, 34.32; H, 4.74; N, 17.16; found: C, 34.89; H, 5.36; N, 17.26; exposure to air for 1 day, forming $C_{14}H_{18}N_6OCl_3Cr \cdot 6H_2O$ —requires: C, 30.41; H, 5.48; N, 15.21; found: C, 30.54; H, 4.95; N, 14.81%.

Crystals suitable for X-ray diffraction separated from an acetonitrile solution of **3g** upon slow diffusion of diethyl ether at -20 °C. Instead of the anticipated dinuclear [CrCl₃{(mim)₂-CO}]₂ **3g**, the crystal structure (see below) reveals a mononuclear complex [CrCl₃(mim)₂CO}(CH₃CN)]·CH₃CN **3g**', in which one solvent molecule occupies the sixth coordination site and one solvent molecule is occluded in the crystal. **3g**' represents the first example of a structurally characterized chromium(III) complex bearing a bis(imidazole) chelating ligand. Together with the complexes [CrCl₂{tris(2-benzimidazolylmethyl)amine}]Cl·2H₂O and [Cr₂(2-guanidinobenzimidazole)(μ -OH)₂](ClO₄)₄·5H₂O reported by Castillo-Blum and coworkers,¹⁵ these are the only structurally characterized examples for chromium(III) in which the imidazole heterocycle is not a sub-unit of a more complex ligand environment.

Although five-coordinate chromium complexes bearing nitrogen ligands have been described,^{8,24,33} we favour a dinuclear structure^{6,7} for complexes **3** on the basis of their MS spectra, showing dinuclear pentachloro molecular ions, their electronic



spectra, which are distinct from those of five-coordinate chromium(III) complexes,³⁴ and their magnetic properties (see below).⁷ However, from the crystal structure of 3g' it follows, that the dimeric complexes 3 are cleaved when dissolved in coordinating solvents such as CH₃CN.

Molecular structure of 3g'

The results of the low-temperature single crystal X-ray structure determination (Fig. 2) are consistent with the above formulation of 3g', in terms of stoichiometry and connectivity, as [Cl₃CrL(NCCH₃)]·CH₃CN. One formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. The chromium atom is quasi-octahedral, sixcoordinate, the three coordinated chlorine atoms disposed mer in the coordination sphere. Their Cr-Cl distances exhibit only minor differences, with the difference between Cr-Cl(1,2) trans to different atoms, similar to that between Cr-Cl(2,3) trans to each other, although Cr-Cl(1), trans to an imidazole-nitrogen is the longest. The difference in the Cr-imidazole-N distances, trans to Cl and MeCN, is more substantial. Their mean is similar to that found in hydridotris(1-pyrazolyl)borate Cr(III) complexes^{9,10} and to that for the Cr-benzimidazole-N distances (2.047(4)-2.062(4) Å) in the cis-dichloro {tris(2-benzimidazolyl-



Fig. 2 Projection of complex 3g'. 50% probability amplitude displacement ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

methyl)amine}chromium(III) cation;¹⁵ in the latter Cr–N *trans* to Cr–Cl is 2.047(4), and *trans* to itself 2.050(3), 2.062(4) Å. Although the Cr–central N of the tripod is appreciably longer (2.153(4) Å), Cr–Cl *trans* to the two different types of nitrogen therein are relatively insensitive (2.318(1), 2.291(1) Å) to that difference.

Table 1 The chromium environment. r (Å) is the chromium–ligand atom distance; other entries in the matrix are the angles (°) subtended at the chromium by the relevant atoms at the head of the row and column

Atom	r	Cl(2)	Cl(3)	N(11)	N(21)	N(101)
Cl(1) Cl(2) Cl(3) N(11) N(21) N(101)	2.3290(3) 2.3199(3) 2.3090(3) 2.063(1) 2.0394(9) 2.070(1)	92.04(1)	91.60(1) 176.23(2)	177.79(4) 87.75(3) 88.65(3)	95.12(3) 88.11(3) 90.60(3) 87.07(4)	89.59(3) 89.64(3) 91.35(3) 88.21(4) 174.85(4)

The dihedral angle between the C_3N_2 planes of the bidentate ligand is 24.63(5)°, chromium atom deviations being 0.126(2), 0.303(2) Å. The C_3N_2 dihedral angles to the central C_2CO plane are 21.30(5), 24.63(5)°. O(0) \cdots H(16a, 26a) are 2.53(2), 2.62(1) Å. H(15) \cdots N(101) is 2.62(2), H(25) \cdots Cl(1,2) 2.89(1), 2.93(1) Å.

Table 2	Magnetic moments and	electronic spectral	data of 2a-c, 3e-h,j; 4k and 6
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Complex	$\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$	v ₁ /nm	v ₂ /nm	Shoulder/nm	$10Dq/cm^{-1}$	$\varepsilon_1; \varepsilon_2 / \mathrm{M}^{-1} \mathrm{cm}^{-1}$
2a	3.77	623	457	725	16051	83; 143
2b	4.2	601	431		16638	95; 78
2c	3.61	650	453	732	15384	37; 84
3e	3.57	642	445	718	15576	37; 63
3f	n. d.	693	468	719, 753	14423	174; 198
$3f^a$		666	451	,	15000	_
3g	3.68	645	~425 (sh)		15503	67
$3\mathbf{g}^{e}$		621, 544	_ ``		_	_
$3\mathbf{g}^{b}$		615			16250	_
3g'	3.63	n. d.	n. d.		n. d.	n. d.
3ĥ	3.5	648	obsc.		15432	108
3j	n. d.	637	obsc.	720	15701	65
4k	n. d.	613	447	700, 710	16313	23; 40
6	n. d.	678	440	,	14737	54; 210

In the present complex, the pair of imidazole C_3N_2 rings are appreciably inclined to each other, being folded about the central CO pivot (Table 1). This may be a consequence of some incompatibility between the 'bite' angle of a planar ligand *vizà-viz* the pair of sites available for its accommodation. A further relevant determinant may be accommodation of steric interactions between H(n5) and the adjacent equatorial ligands (H(15) \cdots N(101) 2.62(2); H(25) \cdots Cl(1) 2.89(1) Å) and/or those between the carbonyl pivot and the methyl substituents (H(16a, 26a) \cdots O(0) 2.53(2), 2.62(1) Å); some asymmetry is evident in the deviations of the chromium atom from the two C_3N_2 planes.

Magnetic properties

We have reviewed the magnetic properties of imidazole chromium complexes reported in our previous note,²⁸ and collected magnetic susceptibility data for powdered samples of complexes **2a–c,3e,g,g',h** in the temperature range 4–300 K on a SQUID magnetometer, allowing more accurate determination of μ_{eff} values than in the previous measurements (Evans balance). The complexes have μ_{eff} values typically between 3.5 and 4.2 μ_{B} (Table 2), which are in agreement with three unpaired electrons. Above $T \sim 25$ K essential temperature-independent behaviour (**2a,c; 3g,g',h**) or very little (**2b**: μ_{eff} 3.85–4.2; **3e**: μ_{eff} 3.25–3.57) temperature-dependence is observed, and thus none of the complexes shows antiferromagnetic coupling.

Electronic spectra

UV-vis spectra have been recorded for $1-5 \times 10^{-3}$ solutions of complexes **2a–c,e;3e–g,h,j** in CH₃CN or MeOH. The results are summarised in Table 2. The majority of the complexes exhibit d–d transitions typically observed^{5,34} for pseudo-octahedral chromium in the oxidation state +3, with $v_1 \, {}^{4}A_{2g} \rightarrow {}^{4}T_{2g} \, 600-700$ nm, $v_2 \, {}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$ (F) 430–470 nm and the third absorption, $v_3 \, {}^{4}A_{2g} \rightarrow {}^{4}T_{1}$ (P) being obscured by charge transfer (CT)

bands of the ligand systems, which are centred at approximately 300 nm. A low energy shift of the CT bands is observed for those ligands containing additional chromophoric groups in the backbone, so that the ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(F)$ transition in 3g appears as a shoulder, or is obscured in 3h,j. In addition shoulders at the low energy tail of the first transition (720-730 nm), observed in most cases, may be attributed to spinforbidden transitions and to LMCT bands.^{12,13} Since the molecular structure of 3g' suggests that the complexes containing bidentate ligands are mononuclear in acetonitrile solution with one solvent molecule occupying the sixth coordination site, we have recorded the diffuse reflectance spectra for complexes 3f,g. They exhibit bands characteristic of a pseudooctahedral chromium(III) chromophore, supporting the proposed dimeric structure of 3e-i with both bridging and terminal chlorines. Similar observations have been made for [CrCl₃-(bipy)].⁷ However, the visible spectrum of 3g at 19 K shows (bipy)]. However, the visible spectrum of 3g at 19 K shows splitting of the ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ transition, indicating lowering of the symmetry from $O_{\rm h}$, a common feature of a number of other chromium(III) complexes.^{5,34} The observation of the lowest energy spin-allowed transition for the chromium(III) centre allows us to estimate the splitting parameter 10Dq to lie between 14 737 and 16 640 cm⁻¹.

However, the positions of transitions found in this series of chromium(III) complexes, all based on a bis(1-methylimidazole) framework, merit some further comment. Among the imidazole complexes, the additional donor moiety in complexes **2** causes an approximately 500 cm⁻¹ greater splitting parameter relative to **3** which bear bidentate ligands. Values for v_1 and v_2 are similar to those observed for recently reported chromium(III) chloro complexes bearing tridentate benzimidazole chelating ligands.¹⁵ Changes in the individual Dq values of complexes containing the tripod ligands are in agreement with the nature of the third donor function, linked to the bis(imidazole) framework (N^N^N; N^O^N; N^P^N). Thus the highest Dq value is observed for N^P^N system reflecting the σ -donor/

Table 3 Peak potentials E_p observed in the cyclic voltammograms of complexes **2a–c**, **4k** and **3e–h**,**j**^{*a*}

Complex	$E_{\rm p}^{\rm red}/{\rm V}$	$E_{\rm p}^{\rm ox1}/{\rm V}$	$E_{\rm p}^{\rm ox2}/{\rm V}$
2a	-1.8	-0.67	0.69
2b ^v 2c	-1.5 -1.71	-0.91 -0.63	0.51 0.74
3e ^c	-1.42	-0.72	0.75
3f" 3g	-1.41 -1.33	-0.72	0.74
3h	-1.06	-0.94	0.56 ^e
3j° 4k	-1.58 -1.61	-0.53	0.85
	1.01	0.00	0.07

^{*a*} Conditions: scan rate $v = 500 \text{ mV s}^{-1}$; c = 5 mM; supporting electrolyte 0.1 M Bu₄NPF₆. ^{*b*} $E_p^{\text{ox3}} = 1.37 \text{ V}$. ^{*c*} $E_p^{\text{red2}} = 1.66 \text{ V}$. ^{*d*} $E_p^{\text{ox3}} = 1.39 \text{ V}$. ^{*c*} Quasi-reversible potential given as $E_{1/2}$.

 π -acceptor properties of the phosphine ligand. The low Dqvalue in 2c can be attributed to the strong electron withdrawing and hard nature of the oxygen ligand. Interestingly, in the series of bidentate coordinated complexes, reduced Dq values are observed for those ligands containing electron-accepting groups in the bridge. Generally the positions of d-d bands seen in the present complexes are very similar to those reported for the related chromium(III) chloro 2, 2'-bipyridine complexes $[CrCl_3(bipy)]_n$ and $[CrCl_3(bipy)L]$ (L = CH₃CN, py, pyO, OPPh₃).⁷ In the latter a low energy shift of the ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ band upon replacing the third pyridine donor with oxygen donors (pyO, OPPh₃) has also been observed. The electronic transitions in the tripod imidazole complexes 2 are similar to those reported for the tris(pyrazol-1-yl)borate complex [CrCl₃(Tp)]-[AsPh₄],⁹ but shifted to lower energy compared to [CrCl₃(Tp)]-[HPMe₃]¹⁰ and the related complexes [CrCl₃(Tp)(L)], bearing additional donors L = THF,¹⁰ py, Hpz.⁹ Given the relative ease with which the bis(1-methylimidazol-1-yl) framework can be functionalised, these ligands represent a valuable opportunity for the tuning of ligand field parameters and offer interesting applications in coordination chemistry.

Electrochemistry

Cyclic voltammograms (CV) for the complexes 2a-c;3e-g,h,j;4k and the ligands (mim)₃COCH₃ and (mim)₂CO have been recorded in CH₃CN containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte at a glassy carbon working electrode at various scan rates (50-2000 mV s^{-1}). All redox potentials are referenced in volts vs. the ferrocenium/ferrocene couple (Fc⁺/Fc). The results are collected in Table 3 and representative cyclic voltammograms for the complexes and ligands are shown in Fig. 3 and Fig. 4, respectively. Both ligands undergo a reversible reduction at $E_{1/2} = -1.76$ $[(\min)_3 COCH_3]$ and -1.73 V $[(\min)_2 CO]$ where $E_{1/2}$ is calculated as the average of the reduction and oxidation peak potentials in this process. These values can be compared to those found for substituted 2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazole-2-yl]pyridine ligands³⁵ (-1.84 to -1.98 V) under similar conditions.

The cyclic voltammograms of the complexes containing tripodal ligands and three unidentate imidazole units respectively exhibit complex irreversible ligand based reduction processes with peak potentials $E_p^{\text{red}} - 1.5$ to -1.84 V. The relative ease with which reduction occurs in **2b** is due to the π -acceptor properties of the PPh₂ group. The irreversible reductions in complexes **3** containing bidentate ligands are observed at less negative potentials (-1.06 to -1.58 V). Thus, as a result of coordination to chromium(III) the potentials are less negative than in the free ligands. At scan rates ≥ 500 mV a second irreversible reduction is found in complexes **3e**, **j** (-1.74, -1.77 V). After switching the potential, products resulting from the irreversible reductions give rise to one or two



Fig. 3 Cyclic voltammograms of 2a recorded in CH₃CN (0.1 M Bu₄NPF₆) at various scan rates using a 3 mm diameter glassy carbon electrode.



Fig. 4 Cyclic voltammogram of $(\min)_2$ CO **1g** recorded in CH₃CN (0.1 M Bu₄NPF₆) at a scan rate of v = 500 mV s⁻¹ using a 3 mm diameter glassy carbon electrode.

irreversible oxidation waves $(E_p^{ox1} = -0.59 \text{ to } -0.94 \text{ and } E_p^{ox2} = 0.70 \text{ to } 0.89 \text{ V})$, apart from **3h**, which displays a quasi-reversible oxidation at 0.56 V ($\Delta E_p^{ox} = 0.34 \text{ V}$). When the voltammograms of complexes **2** and **3** are scanned in the positive direction, the second oxidation process E_p^{ox2} is not detected or of very low intensity. In the bidentate coordinated complexes **3**, E_p^{ox1} is either absent (**3g**,**j**) or only observed at scan rates $\geq 100 \text{ mV}$ (**3e**,**f**,**h**). A third irreversible oxidation is observed in **2b** (1.37 V) and **3f** (1.39 V), which may be assigned to an oxidation of the phosphine group in these ligands.

Synthesis of [VCl₃{(mim)₃COCH₃}] 5a, [VCl₃{(mim)₂CO}-(THF)] 5g and [CrCl₃(MeTAM)] 6 (see Scheme 2)

Several groups have reported non-cyclopentadiene vanadium(III) complexes and their different catalytic behaviour compared to other systems.³⁶ In addition, the role of the number of valence electrons in transition metal pre-catalysts used in the olefin polymerisation has been pointed out by Britovsek and co-workers.¹⁷ With a view to contrasting the properties of d³ (mim)_nCr systems with their d² vanadium counterparts, we have attempted to synthesise related complexes containing the bidentate (mim)₂CO and tridentate (mim)₃COCH₃ ligand. The reaction of VCl₃(THF)₃ with these ligands in CH₂Cl₂ proceeds sluggishly resulting in green–brown reaction mixtures. Replacing CH₂Cl₂ with THF leads to the precipitation of green solids. The isolated complexes are very air sensitive and decompose on standing at room temperature under nitrogen. Published on 14 November 2002. Downloaded by The University of Auckland Library on 30/10/2014 00:03:22.



They analyse to the general compositions $[VCl_3\{(\min)_2CO\}-(THF)]$ (5g) and, less satisfactorily, $[VCl_3\{(\min)_3COCH_3\}]$ (5a). For both products the presence of the ligand system is confirmed by MS and IR (5g) ($v_{(C=O)}$ 1655 cm⁻¹), the former showing ions at m/z = 407 and 311 for the fragments $[(\min)_3-COCH_3VCl_2]^+$ and $[(\min)_2COVCl_2]^+$, respectively. High air sensitivity, instability and difficulties in characterisation of this type of complexes has also been reported by other groups.³⁶

Since in industrially utilised heterogeneous chromium poly-olefin catalysts (Phillips catalyst)^{26,27} the metal centre resides in a hard oxygen donor environment and closely related homogeneous model systems are scarce,³⁷ we have chosen 1-methytriacetylmethane (MeTAM) as a hard, albeit neutral tripodal oxygen ligand. Addition of one equivalent of MeTAM dissolved in CH₂Cl₂ to CrCl₃(THF) in THF resulted in an immediate colour change to green. The product [CrCl3-(MeTAM)] (6) was isolated as a green moisture sensitive solid upon repeated precipitation from CH₂Cl₂/hexanes at -20 °C and characterized by IR, MS, UV-vis and microanalysis. The IR spectrum of 6 (KBr; $v_{(CO)} = 1572 \text{ cm}^{-1}$) shows a low frequency shift of approximately 140 cm⁻¹ of the carbonyl band, relative to the free ligand, confirming its coordination. The electronic spectrum of 6 exhibits two transitions at $v_1 = 678$ nm and $v_2 = 440$ nm, characteristic of a pseudo-octahedral chromium(III) chromophore. The ligand field splitting parameter 10Dq (14737 cm⁻¹) is considerably smaller than in the tripod imidazole complexes 2.

Catalysis

In our previous note we have reported that exposure of toluene solutions of 2,3/modified methylaluminoxane (MMAO) to 40 bar ethylene resulted in the formation of linear 1-alkenes in the range of C_4 - C_{30} (maximum at C_8) with selectivities of up to 79%.²⁸ Catalytic test experiments for the conversion of ethylene have now been extended to the novel complexes 2d, 3i,j, 4k, 5 and 6. The catalytic results are summarised in Tables 4–6 and the data reported earlier have been included for convenient comparison (Table 4).

Generally, all of the new imidazole coordinated complexes give, upon activation with MMAO, active catalysts for the conversion of ethylene. Among the bidentate coordinated complexes lacking bulky substituents the benzimidazole derivative **3h** (Table 4, entry 10) exhibits the highest activities. The low activity observed for the precursor $4\mathbf{k}$ (entry 13) bearing three monodentate 1-methylimidazole ligands clearly demonstrates the advantage of chelating ligands in stabilizing intermediates occurring in catalytic cycles.

The test runs with complexes 2d and 3i bearing ligands containing bulky substituents provide interesting insight into how steric bulk placed in proximity to the metal centre affects selectivities in this type of reaction. Theoretical studies on the recently developed Ni(II), Pd(II), Fe(II) and Co(II) catalysts containing sterically demanding nitrogen ligands have revealed, that subtle placing of bulky substituents in the ligand system allows the blocking of axial coordination sites, thus suppressing β-hydride transfer as a chain termination mechanism.^{20,21} Hence it has been shown experimentally that, by varying the steric properties of the ligand system, each class of catalysts is capable of producing a great variety of products, ranging from linear and highly branched polymers to short chain oligomers.^{19,38} Our results obtained for the pre-catalysts 2d and 3i (entries 5 and 11) are in agreement with these studies. Although the bulky tBu substituents in the ligand system of 3i are situated close to the metal center as shown in the proposed structure in Fig. 5, their position does not allow reaching across the



Fig. 5 Steric situation at the metal centre in complexes 2d and 3i.

coordination plane to block axial sites. As a consequence, 1-alkenes ranging from C_4 to C_{30} rather than polyethylene (12 wt%) are produced. We note however that the maximum is found at C_{14} – C_{16} , whereas pre-catalysts lacking bulky substituents give 1-alkenes with a maximum at C_8 . The activity and selectivity is the highest observed among the series of complexes tested. By contrast, complex 2d in which the metal centre is embraced by the three *t*Bu groups of the tripod ligand (Fig. 5) gives mainly polyethylene. The relatively encumbered steric situation may account for the reduced activity compared to 3i and 2a. On the other hand the considerable polymer build-up hampered effective stirring, thus preventing obtaining higher activities.

Complex 2a, as a representative example in the series of imidazole based catalyst precursors, has been tested under various conditions (Table 5). Upon reducing the pressure the activity of 2a/MMAO decreases with decreasing monomer concentration. Surprisingly, but not unusually, when toluene is replaced with chlorobenzene as a solvent, polyethylene is produced with similar activity and only trace amounts of low molecular weight hydrocarbons have been detected in the GC samples.

 Table 4
 Ethylene oligomerisation and polymerisation in toluene^a

Entry	Catalyst/mmol	MMAO/equiv. ^b	Activity ^b /g mmol ⁻¹ h ⁻¹ bar ⁻¹	1-Alkenes	Isoalkenes	^c Alkanes	Isoalkanes	Polymer (wt%)
1	2 a/0.11	400	5.2	79	9	12		3.4
2	2b /0.1	400	2.7	65	10	21	4	9
3	2b /0.12	182	2.3	77	11	12		3.3
4	2c /0.1	400	2.3	65	13	20	2	15
5	2d/0.093	400	2.7	d				70
6	3e /0.09	400	1.4	50	16	25	9	1.7
7	3f /0.06	170	1.4	70	15	15		2.1
8	3f /0.04	408	2.3	60	20	18	2	2.6
9	3g /0.06	414	1.5	57	17	24	2	5.5
10	3h /0.047	400	3.6	68	15	16	1	6.5
11	3i /0.053	400	10.8	81	6.5	11	1.5	12
12	3i /0.11	400	0.8	26	23	29	22	2
13	4k /0.1	400	0.5		_			2
a 50 1	(01)	NII (0.1 / TE 1/		11 00 14	0 1 1 1	.1 .1	• , 1	

^{*a*} 50 ml toluene; $p(CH_2=CH_2)$ 40 bar, T = 100 °C, 1 h. ^{*b*} Per [Cr]. ^{*c*} Determined by GC–MS. ^{*d*} 1-Alkenes are the predominant products of the liquid phase.

Entry	Catalyst/ mmol	MMAO/ equiv.	Conditions	Act. ^{<i>b</i>} /g mmol ⁻¹ h^{-1} bar ⁻¹	1-Alkenes	Isoalkenes	Alkanes	Isoalkanes	Polymer (wt%)
1	0.11	400	C ₆ H ₅ Cl ^c	4.9	_			_	100
2	0.12	400	14 bar CH ₂ =CH ₂	5.8	62	18	20		1.5
3	0.11	400	6 bar $CH_{2}=CH_{2}$	3.2		n.d.			0.2
4	0.11	200	40 bar $CH_2 = CH_2$	1.3	67	13	20	_	6.6
^a 50 ml	toluene (excep	pt entry 1), T	= 100 °C, 1 h. ^{<i>b</i>} Per [0	Cr]. $^{c} p(CH_2 = CH_2) =$	40 bar.				

 Table 6
 Catalytic testing of 3–6 in toluene^a

Entry	Catalyst/mmol	<i>T/</i> °C	Act. ^{<i>b</i>} /g mmol ^{-1} h ^{-1} bar ^{-1}	1-Alkenes	Isoalkenes	Alkanes	Polymer (wt%)
1	5a /0.11	100	0.5	_		_	100
2	5a/0.12	1-40	1.3	С	с	с	64
3	5g/0.1	30-45	1.1				100
4	5g/0.09	1-40	2.2	n.d.	n.d.	n.d.	93
5 ^{<i>d</i>}	6/0.01	100	6.6	88 ^e		6	8
6	7/0.11	80	7.7	80	8.5	11.5	13.5

" 400 equivalents MMAO; 50 ml toluene, $p(CH_2=CH_2) = 40$ bar, 1 h. " Per [Cr]. " C₄ hydrocarbons only." 400 equivalents MAO instead of MMAO used as activator." Odd numbered 1-alkenes were also detected.

The vanadium complexes 5a,g, although not carrying bulky ligands, give predominantly polymer (Table 6) whereas their chromium counterparts under similar conditions produce oligomers. They also appear to be less stable, *e.g.* considerably higher activities have been obtained at low temperatures (entries 2 and 4) and a significant exothermic reaction has been observed on pressurising solutions of 5a,g/MMAO with 40 bar ethylene. Quite different behaviour of vanadium complexes compared to other early transition metals supported by the same ligand system, and deactivation of vanadium precatalysts due to reduction during the catalytic cycle, has been reported recently by other groups.³⁶

Complex 6, containing a tripodal oxygen ligand as a neutral mimic for the hard oxygen environment in heterogeneous supporting materials, shows somewhat higher activity than its imidazole chelated counterparts (Table 6, entry 5).

To further probe how electronic and binding properties of the supporting ligand system in chromium(III) complexes impacts on their performance as catalysts in the conversion of olefins we have chosen the reported ³⁹ complex [CrCl₂(tren)]Cl (7) containing the tetradentate amino ligand triaminotriethylamine. Catalytic testing of 7 under the conditions used for the imidazole systems gave improved selectivities and enhanced activity (Table 6, entry 6). The better performance of 7 may be partly attributed to the unique geometric properties of the tren ligand, which have been shown to greatly affect the kinetics of substitution reactions in chromium complexes.^{39,40} Generally, from these studies it is clear that tripod ligands are better suited to stabilise and protect the metal centre during the catalytic cycle than related bidentate ligands. The results from the catalytic testing of the imidazole chelated complexes show that, in agreement with the metal centres residing in a bis(imidazole) framework, these complexes display similar activities and selectivities, with the observed differences arising from variations in the additional substituents and donor centres respectively.

Conclusion

A number of novel chromium(III) complexes bearing bi- and tridentate imidazole chelate ligands as an integral part of the coordination environment have been prepared and characterised, adding to the very limited number of such complexes known to date. The complex [CrCl₃{mim}₂CO}(CH₃CN)] represents a rare example of a structurally characterized chromium(III) complex where the imidazole ligand is integral to the coordination environment. A particular feature of this series of complexes is, that the electronic properties of the central metal may be tuned by introducing different substituents and functional groups or additional donor groups into the bis(imidazole) ligand framework. The chromium complexes have been probed in the catalytic conversion of ethylene into higher molecular weight products. Upon activation with MMAO, 1-alkenes or polyethylene are produced with activities Published on 14 November 2002. Downloaded by The University of Auckland Library on 30/10/2014 00:03:22.

and selectivities largely depending on the steric and electronic nature of the ligand system. Two isostructural, albeit less well characterised, vanadium(III) complexes containing bi- and tridentate ligands, respectively, generated mainly polymer under similar conditions.

Experimental

Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox (Innovative Technology Inc.). All solvents for use in an inert atmosphere were purified by standard procedures and distilled under nitrogen immediately prior to use. The metal chlorides [CrCl₃(THF)₃],⁴¹ [VCl₃(THF)₃],⁴² and the ligands^{2,29-32} were prepared according to literature procedures, except for MeTAM, which was a loan from Dr S. B. Wild (ANU/ Canberra). For the preparation of $[CrCl_3(tren)]$ (7) a literature procedure³⁹ was followed, except that [CrCl₃(THF)₃] was used as a starting material and CH₂Cl₂ as a solvent. Anhydrous CrCl₃, 1-methylimidazole and triaminotriethylamine (tren) were purchased from Aldrich and used as received. Modified methylaluminoxane (MMAO) solution in heptane was purchased from AKZO. Ethylene was purchased from BOC gases. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) (Aldrich) was recrystallised from ethanol prior to use.

Catalytic test experiments were carried out in a 300 ml stainless steel autoclave (Parr) fitted with a glass liner and magnetic stir bar.

Solution phase voltammetric experiments in CH₃CN using $Bu_4NPF_6(0.1 \text{ M})$ as a supporting electrolyte were carried out in a standard three-electrode arrangement with a glassy carbon (GC) disk working electrode, a platinum wire as the counter electrode and an Ag/Ag⁺ (CH₃CN, 10 mM AgNO₃) double junction reference electrode. A BAS100B (Bioanalytical Systems) electrochemical workstation was used to conduct the voltammetric experiments. Magnetic susceptibility measurements were carried out in the temperature range 4-300 K on a Quantum Design MPMS SQUID magnetometer and electronic spectra were recorded using either a Cary 17 or 5 spectrometer. IR spectra were recorded on a Bruker IFS-66 FTIR spectrometer. Gas chromatography was performed on a Hewlett-Packard 5890 series II gas chromatograph fitted with a flame ionisation detector. Elemental analysis (Carlo Erba EA 1108 elemental analyser), MS (LSIMS: Kratos Concept ISQ MS, 10 kV Cs ions, m-nitrobenzyl alcohol (mnba) matrix; ESI: Finnigan LCO, direct infusion 3 µl min⁻¹, needle voltage 4.5 kV, capillary voltage 20 V, sheath gas 30 psi), and GC-MS were carried out by the Central Science Laboratory (CSL), University of Tasmania. Extreme water sensitivity leads to poor microanalytical data for some of the complexes.

General synthetic procedure for chromium imidazole complexes [CrCl₃{(Bzmim)₂CO}]₂ 3h, [CrCl₃{(mim)₂CNPh}]₂ 3j and [CrCl₃(mim)₃] 4k

1.03 equivalents of the respective ligand dissolved in CH_2Cl_2 were added to a CH_2Cl_2 solution of $(THF)_3CrCl_3$. The products started to precipitate within minutes. After stirring for 12 h the solvent was separated and the crude product stirred again in CH_2Cl_2 overnight. Removal of the CH_2Cl_2 followed by washing with CH_2Cl_2 , three portions of hexanes and drying *in vacuo* gave the respective complexes as green solids (*ca.* 90%).

3h. Found: C, 45.56; H, 3.67; N, 11.30. $C_{34}H_{28}Cl_6Cr_2N_8O_2$ requires C, 45.51; H, 3.15; N, 12.49%; v_{max}/cm^{-1} (C=O) 1680 (KBr); m/z 465 (LCrCl₃ + H₂O, 100%), 429 (LCrCl₂ + OH, 100%), 343 (LCrH, 8%) (FAB MS).

3j. Found: C, 42.84; H 4.77; N, 14.31. $C_{30}H_{30}Cl_6Cr_2N_{10}$ requires C, 42.84; H; 3.58; N, 16.53%; v_{max}/cm^{-1} (C=NPh) 1622 (KBr); m/z 810 (M – Cl, 5%), 387 (LCrCl₂, 100%), 352 (LCrCl, 65%) (FAB MS).

4k. Found: C, 35.69; H 4.70; N, 20.68. $C_{12}H_{18}Cl_3CrN_6$ requires C, 35.61; H; 4.49; N, 20.77%; *m/z* 403 (M⁺, 30%), 368 (M - Cl, 100%), 333 (M - 2Cl, 8%), 286 (L₂CrCl₂, 89%), 251 (L₂CrCl, 56%) (FAB MS).

[CrCl₃{(*t*Bupim)₃P}] 2d. The ligand 1d (0.122 g, 0.23 mmol), CrCl₃ (0.037 g, 0.23 mmol) and a trace of Zn dust were mixed as solids and 8 ml methanol added. Upon stirring and heating to 45 °C the colour of the slightly turbid reaction mixture changed to green–turquoise. After 4 h and cooling to room temperature the reaction mixture was filtered through Celite and the solvent removed under reduced pressure. Washing of the crude product with hexanes (2 × 5 ml) and drying under vacuum gave [CrCl₃{(*t*Bupim)₃P}] 2d as a mint green solid (0.142 g, 90%). Found: C 50.34, H 8.58, N 11.72. $C_{30}H_{51}$ -Cl₃CrN₆P·2H₂O requires C, 49.96; H, 7.7; N, 11.66%; *m*/*z* 630 (LCrCl + O, 18%); 327 (L, 100%) (FAB MS).

[CrCl₃{(*t*Bupim)₂CO}]₂ 3i. (*t*Bupim)₂CO 1i (0.095 g, 0.26 mmol) in tetrahydrofuran (7 ml) was added to a stirred solution of [CrCl₃(THF)] (0.099 g, 0.26 mmol) in tetrahydrofuran (10 ml). The solution turned brown and some solid material formed after a few hours. After stirring overnight the olive brown reaction mixture was filtered through Celite and the solvent removed under reduced pressure. Washing of the crude product with Et₂O (2×5 ml) and drying under vacuum gave [CrCl₃(*t*Bupim)₂CO}]₂ 3i as a green solid (0.118 g, 88%). Found: C, 48.65; H, 7.84; N, 9.54. C₄₂H₆₈Cl₆Cr₂N₈O₂ requires C, 48.79; H, 6.64; N, 10.84%; *m*/*z* 874 (L₂Cr₂Cl₂ – O), 1%) 359 (LH, 100%) (ESI MS).

[VCl₃{(mim)₃COCH₃}] **5a.** (mim)₃COCH₃ **1a** (0.091 g, 0.32 mmol) in tetrahydrofuran (7 ml) was added to a stirred solution of [VCl₃(THF)₃] (0.119 g, 0.32 mmol) in tetrahydrofuran (3 ml). A pale purple precipitate forms immediately. Upon stirring overnight the reaction mixture turns pale green. The product was allowed to settle and the almost colorless tetrahydrofuran phase decanted. Washing with tetrahydrofuran (2 × 5 ml), Et₂O (2 × 5 ml) and drying under vacuum gave [VCl₃{(mim-)₃COCH₃}] **5a** as a green solid. (0.14 g, 99%). Found: C, 34.36; H, 3.71; N, 17.20. C₁₄H₁₈Cl₃N₆OV requires C, 37.87; H, 4.10; N, 18.95%; *m/z* 408 (M – Cl, 9%); 388 (LVCl + O, 42%); 322 (LV–CH₃ – 3Cl, 12%); 255 (L – OCH₃) (FAB MS).

[VCl₃{(mim)₂CO}(THF)] 5g. A suspension of (mim)₂CO 1c (0.085 g, (0.44 mmol) in tetrahydrofuran (15 ml) was added to a stirred solution of [VCl₃(THF)₃] (0.166 g, 0.44 mmol) in tetrahydrofuran 5 ml. A bright green precipitate begins to form after a few minutes. After 2 h the product was allowed to settle and the almost colourless tetrahydrofuran phase decanted. Washing with tetrahydrofuran (2 × 5 ml), Et₂O (2 × 5 ml) and drying under vacuum gave [VCl₃{(mim)₂CO}(THF)] **5g** as a green solid (0.166 g, 90%). Found: C, 38.32; H, 3.98; N, 12.90. C₁₃H₁₈Cl₃N₄O₂V requires C, 37.20; H, 4.33; N, 13.35%; $v_{max}/$ cm⁻¹ (C=O) 1654 (KBr); *m*/*z* 428 (LVCl+mnba, 20%); 311 (LVCl₂, 14%); 292 (LVCl+O, 100%); 276 (LVCl, 23%); 191 (LH, 15%) (FAB MS).

[CrCl₃(MeTAM)] 6. MeTAM 1 (0.099 g, 0.63 mmol) in CH₂Cl₂ (3 ml) was added to a stirred solution/suspension of [CrCl₃(THF)₃] (0.235 g, 0.63 mmol) in tetrahydrofuran (4 ml). The solution gradually changes colour from purple to green. After 24 h the almost clear green reaction mixture was filtered through Celite and the solvents removed under reduced pressure. The remaining dark green sticky solid was stirred in hexanes for 24 h after which time the hexane phase was decanted and the green solid dried under vacuum. The crude [CrCl₃(MeTAM)] 6 was further purified by repeated precipitation from CH₂Cl₂/hexanes at -20 °C, followed by washing with hexanes and drying under vacuum (0.119–0.139 g,

60–70%). Found: C, 31.31; H, 4.07. $C_8H_{12}Cl_3CrO_3$ requires C, 30.55; H 3.85%; ν_{max}/cm^{-1} (C=O) 1571 cm⁻¹ (KBr); *m/z* 278 [M - Cl]⁺ (100%) (FAB MS).

Structure determination of 3g'

A full sphere of low-temperature CCD area-detector diffractometer data was measured (Bruker AXS instrument, ω -scans, $2\theta_{\rm max} = 75^{\circ}$; monochromatic Mo-K α radiation, $\lambda = 0.7107_3$ Å; $T \ ca. 153$ K) yielding 37346 reflections, merging to 9433 independent ($R_{\rm int} = 0.033$) after 'empirical'/multiscan absorption correction (proprietary software), 6992 with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinement, refining anisotropic displacement parameter forms for the non-hydrogen atoms and ($x,y,z,U_{\rm iso}$) for the hydrogen. Conventional residuals on |F| at convergence were R = 0.030, $R_{\rm w} = 0.035$ (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$). Neutral atom complex scattering factors were employed within the Xtal 3.7 program system.⁴³ Pertinent results are given below and in Table 1 and Fig. 2.

Crystal data: C₁₁H₁₃Cl₃CrN₅O·CH₃CN, M = 430.7, monoclinic, space group $P2_1/n$ (C_{2h}^5 , no. 14, variant), a = 6.9757(2), b = 14.6946(5), c = 17.5803(6) Å, $\beta = 94.419(1)^\circ$, V = 1797 Å³. D_c (Z = 4) = 1.592 g cm⁻³. $\mu_{Mo} = 11.0$ cm⁻¹; specimen: $0.5 \times 0.2 \times 0.1$ mm; $T_{min, max} = 0.72$, 0.83. $|\Delta \rho_{max}| = 0.55(7)$ e Å⁻³.

CCDC reference number 181231.

See http://www.rsc.org/suppdata/dt/b2/b207248c/ for crystallographic data in CIF or other electronic format.

General procedure for the catalysis

MMAO (1.82 M in heptane) was added slowly with stirring to a suspension of the selected complex in 5 ml toluene upon which the complexes dissolved. A colour change to olive or brown was observed. A 300 ml autoclave (dried at 100 °C, cooled to RT under vacuum and back-filled with nitrogen) was charged with 50 ml toluene and the catalyst solution added *via* a syringe. The reactor was immersed into a pre-heated oil-bath and pressurized with ethylene. The reactions were terminated by cooling the reactor in an ice salt-bath, and venting of excess ethylene followed by injection of *n*-nonane (internal standard), slow addition of a few ml of MeOH and dilute HCl. The solid material was collected on a frit, washed with MeOH, dilute HCl, MeOH and dried in a high vacuum at 60 °C. The filtrate was dried over Na₂SO₄ and analysed by GC and GC/MS.

Acknowledgements

The Australian Research Council (SPIRT Grant) and Orica Australia are gratefully acknowledged for financial support and for providing post-doctoral salaries for T. R. We thank Dr S. B. Wild (ANU/Canberra) for a generous loan of MeTAM. We also thank the staff from the Central Science Laboratory, University of Tasmania, for their assistance with elemental analyses, and in particular Dr Noel Davis for numerous MS measurements. We are grateful to Professor A. M. Bond (Monash University/Melbourne) for his helpful discussions and for providing the equipment to conduct electrochemical studies. Dr B. Moubaraki (Monash University/ Melbourne) is thanked for magnetic moment measurements.

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