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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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The syntheses and characterisation of tri- and bi-dentate coordinated chromium(III) and vanadium(III) complexes of the general composition [MCl$_3$(N^D^N)], [MCl$_3$(N^N)]$_2$ {M = Cr, (N^D^N) = (mim)$_3$COCH$_3$ **2a** [mim = 1-methylimidazolyl], (mim)$_2$CHCH$_2$PPh$_2$ **2b**, (mim)$_2$CHCH$_2$C(O)Bu*t* **2c**, (*t*Bupim)$_3$P **2d** [*t*Bupim = 1-isopropyl-4-*tert*-butylimidazolyl], (N^N) = (mim)$_2$CH$_2$ **3e**, (mim)$_2$CH$_2$PPh$_2$ **3f**, (mim)$_2$CO **3g**, (Bzmim)$_2$CO **3h** [Bzmim = 1-methybenzimidazolyl], (*t*Bupim)$_2$CO **3i**, (mim)$_2$C=NPh **3j**; M = V: (N^D^N) = (mim)$_3$COCH$_3$ **5a**; (N^N) = (mim)$_2$CO **5g**}, [CrCl$_3$(mim)$_3$] **4k**, and [CrCl$_3$(MeTAM)] **6** (MeTAM = 1-methyltriacetylmethane) is described. Crystallisation of **3g** from CH$_3$CN/Et$_2$O gave the mononuclear complex [CrCl$_3${(mim)$_2$CO}(CH$_3$CN)] **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 d^3 ion, falling into the region ν_1 $^4A_{2g} \longrightarrow {}^4T_{2g}$ 600–700 nm and ν_2 $^4A_{2g} \longrightarrow {}^4T_{1g}(F)$ 430–470 nm, and 10*Dq* 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 rhodium[2] and palladium[3] 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 ligands[11–15] are known.[16] Sanchez and Losada[14] have reported chromium(III) halogen complexes of the type [CrL$_6$]Cl$_3$, [CrXL$_5$]X$_2$ (X = Cl, Br), *cis*- and *trans*-[CrCl$_2$L$_4$]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 processes[27] (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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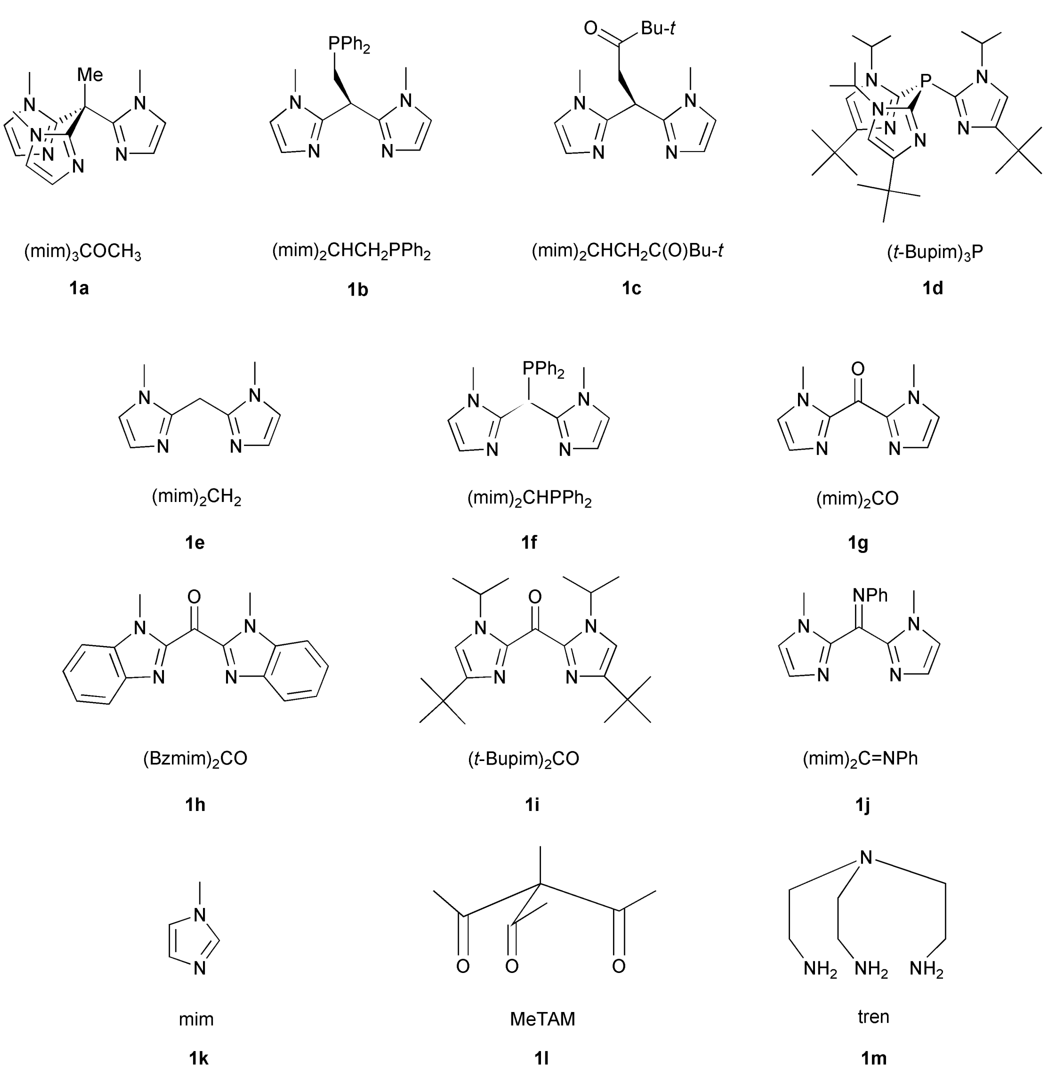


$(mim)_3COCH_3$ **1a**; $(mim)_2CHCH_2PPh_2$ **1b**; $(mim)_2CHCH_2C(O)Bu$-*t* **1c**; (*t*-Bupim)$_3$P **1d**; $(mim)_2CH_2$ **1e**; $(mim)_2CHPPh_2$ **1f**; $(mim)_2CO$ **1g**; $(Bzmim)_2CO$ **1h**; (*t*-Bupim)$_2$CO **1i**; $(mim)_2C{=}NPh$ **1j**; mim **1k**; MeTAM **1l**; tren **1m**

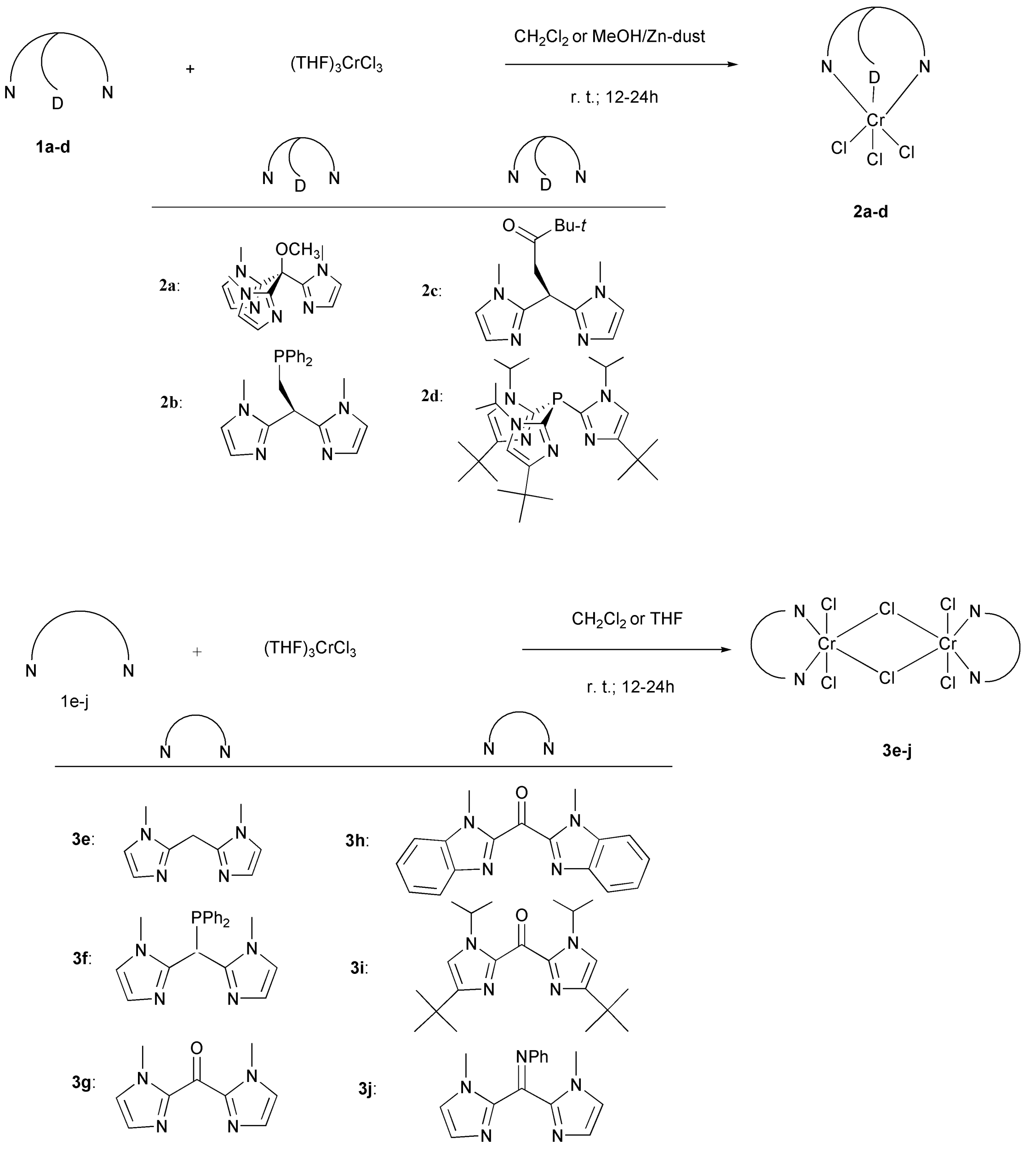
Fig. 1 Ligands used in this work.

The complexes have been prepared by adding a solution of the respective ligand to a solution of $CrCl_3(THF)_3$. Using CH_2Cl_2 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 CH_2Cl_2 is essential to obtain pure products. The, compared to the other ligands, relatively bulky ligand (*t*Bupim)$_3$P, did not react under these conditions; even on refluxing the reaction mixture in $CHCl_3$ 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 $CrCl_3$ 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 $[CrCl_3(1\text{-methylimidazole})_3]$ **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 $[CrCl_3\{(mim)_2CO\}]_2$ **3g**, the crystal structure (see below) reveals a mononuclear complex $[CrCl_3(mim)_2CO\}(CH_3CN)]\cdot CH_3CN$ **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 $[CrCl_2\{tris(2\text{-benzimidazolylmethyl})amine\}]Cl\cdot 2H_2O$ and $[Cr_2(2\text{-guanidinobenzimidazole})(\mu\text{-}OH)_2](ClO_4)_4\cdot 5H_2O$ 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



Scheme 1 Syntheses of the complexes.

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 CH_3CN.

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 $[Cl_3CrL(NCCH_3)]{\cdot}CH_3CN$. One formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. The chromium atom is quasi-octahedral, six-coordinate, 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-benzimidazolylmethyl)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.

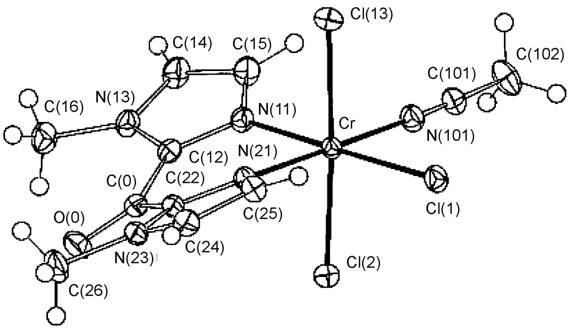


Fig. 2 Projection of complex **3g**′. 50% probability amplitude displacement ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

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

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) ··· H(16a, 26a) are 2.53(2), 2.62(1) Å. H(15) ··· N(101) is 2.62(2), H(25) ··· 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**

Complex	μ_{eff}/μ_B	ν_1/nm	ν_2/nm	Shoulder/nm	$10Dq$/cm^{-1}	ε_1; ε_2/ M^{-1} 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
3g[e]	—	621, 544	—		—	—
3g[b]	—	615	—		16250	—
3g′	3.63	n. d.	n. d.		n. d.	n. d.
3h	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

[a] Diffuse reflectance spectrum at 19 K. [b] Diffuse reflectance spectrum at r.t.

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 *viz-à-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) ··· N(101) 2.62(2); H(25) ··· Cl(1) 2.89(1) Å) and/or those between the carbonyl pivot and the methyl substituents (H(16a, 26a) ··· 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 × 10^{-3} solutions of complexes **2a–c**,**e;3e–g**,**h**,**j** in CH_3CN 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 ν_1 $^4A_{2g} \longrightarrow {}^4T_{2g}$ 600–700 nm, ν_2 $^4A_{2g} \longrightarrow {}^4T_{1g}(F)$ 430–470 nm and the third absorption, ν_3 $^4A_{2g} \longrightarrow {}^4T_1(P)$ 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 $^4A_2(F) \longrightarrow {}^4T_1(F)$ 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 spin-forbidden 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 pseudo-octahedral chromium(III) chromophore, supporting the proposed dimeric structure of **3e–j** with both bridging and terminal chlorines. Similar observations have been made for $[CrCl_3(bipy)]$.[7] However, the visible spectrum of **3g** at 19 K shows splitting of the $^4A_{2g} \longrightarrow {}^4T_{2g}$ transition, indicating lowering of the symmetry from O_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 ν_1 and ν_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_p^{red}/V	E_p^{ox1}/V	E_p^{ox2}/V
2a	−1.8	−0.67	0.69
2b[b]	−1.5	−0.91	0.51
2c	−1.71	−0.63	0.74
3e[c]	−1.42	−0.72	0.75
3f[d]	−1.41	−0.72	0.74
3g	−1.33	—	0.72
3h	−1.06	−0.94	0.56[e]
3j[c]	−1.58	—	0.85
4k	−1.61	−0.53	0.89

[a] Conditions: scan rate $v = 500$ mV s^{-1}; $c = 5$ mM; supporting electrolyte 0.1 M Bu_4NPF_6. [b] $E_p^{ox3} = 1.37$ V. [c] $E_p^{red2} = 1.66$ V. [d] $E_p^{ox3} = 1.39$ V. [e] Quasi-reversible potential given as $E_{1/2}$.

π-acceptor properties of the phosphine ligand. The low *Dq* value 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 = CH_3CN, py, pyO, $OPPh_3$).[7] In the latter a low energy shift of the $^4A_{2g} \longrightarrow {}^4T_{2g}$ band upon replacing the third pyridine donor with oxygen donors (pyO, $OPPh_3$) 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 $[CrCl_3(Tp)][AsPh_4]$,[9] but shifted to lower energy compared to $[CrCl_3(Tp)][HPMe_3]$[10] and the related complexes $[CrCl_3(Tp)(L)]$, 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 $(mim)_3COCH_3$ and $(mim)_2CO$ have been recorded in CH_3CN 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 $E_{1/2} = -1.76$ [$(mim)_3COCH_3$] and −1.73 V [$(mim)_2CO$] 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 ligands[35] (−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^{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 PPh_2 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 irreversible oxidation waves ($E_p^{ox1} = -0.59$ to -0.94 and $E_p^{ox2} = 0.70$ to 0.89 V), apart from **3h**, which displays a quasi-reversible oxidation at 0.56 V ($\Delta E_p^{ox} = 0.34$ 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 ≥100 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.

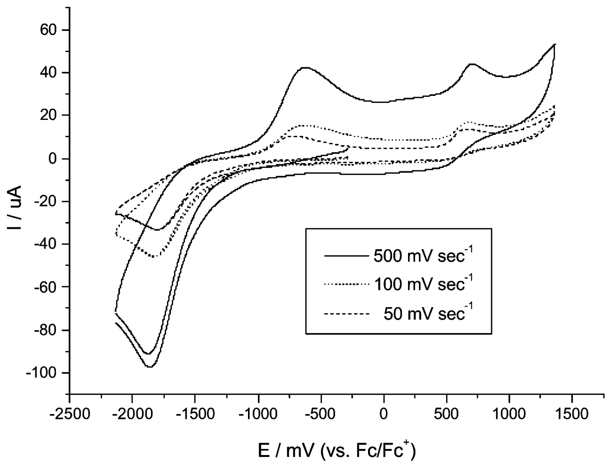


Fig. 3 Cyclic voltammograms of **2a** recorded in CH_3CN (0.1 M Bu_4NPF_6) at various scan rates using a 3 mm diameter glassy carbon electrode.

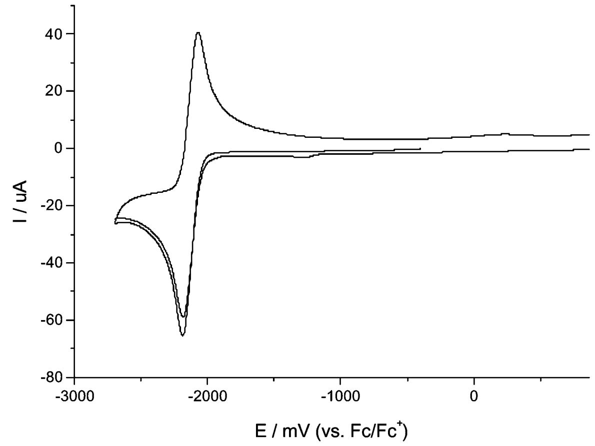
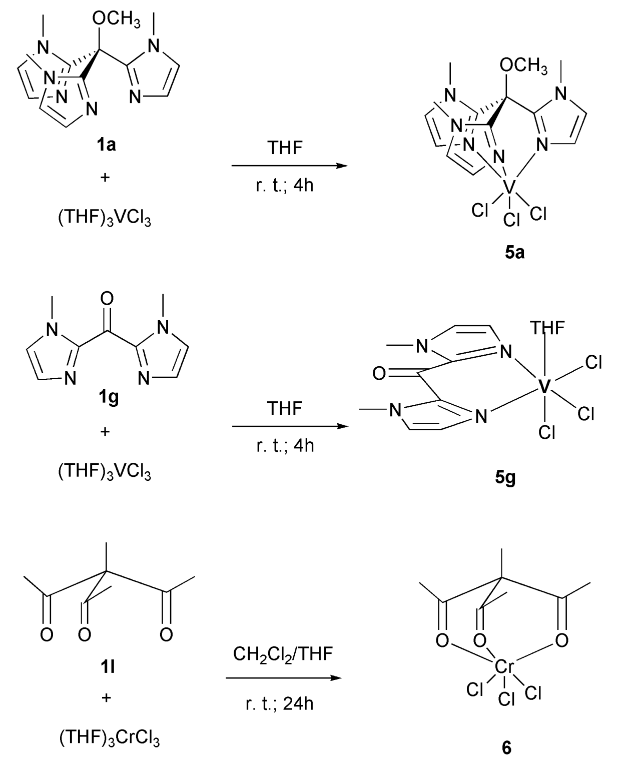


Fig. 4 Cyclic voltammogram of $(mim)_2CO$ **1g** recorded in CH_3CN (0.1 M Bu_4NPF_6) at a scan rate of $v = 500$ mV s^{-1} using a 3 mm diameter glassy carbon electrode.

Synthesis of $[VCl_3\{(mim)_3COCH_3\}]$ 5a, $[VCl_3\{(mim)_2CO\}(THF)]$ 5g and $[CrCl_3(MeTAM)]$ 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 d^3 $(mim)_nCr$ systems with their d^2 vanadium counterparts, we have attempted to synthesise related complexes containing the bidentate $(mim)_2CO$ and tridentate $(mim)_3COCH_3$ ligand. The reaction of $VCl_3(THF)_3$ with these ligands in CH_2Cl_2 proceeds sluggishly resulting in green–brown reaction mixtures. Replacing CH_2Cl_2 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.



Scheme 2 Syntheses of the complexes **5a**,**g** and **6**.

They analyse to the general compositions $[VCl_3\{(mim)_2CO\}(THF)]$ (**5g**) and, less satisfactorily, $[VCl_3\{(mim)_3COCH_3\}]$ (**5a**). For both products the presence of the ligand system is confirmed by MS and IR (**5g**) ($\nu_{(C=O)}$ 1655 cm^{-1}), the former showing ions at m/z = 407 and 311 for the fragments $[(mim)_3COCH_3VCl_2]^+$ and $[(mim)_2COVCl_2]^+$, 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 polyolefin 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 CH_2Cl_2 to $CrCl_3(THF)$ in THF resulted in an immediate colour change to green. The product $[CrCl_3(MeTAM)]$ (**6**) was isolated as a green moisture sensitive solid upon repeated precipitation from CH_2Cl_2/hexanes at −20 °C and characterized by IR, MS, UV-vis and microanalysis. The IR spectrum of **6** (KBr; $\nu_{(CO)}$ = 1572 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 ν_1 = 678 nm and ν_2 = 440 nm, characteristic of a pseudo-octahedral chromium(III) chromophore. The ligand field splitting parameter $10Dq$ (14 737 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 **4k** (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 *t*Bu 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 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.

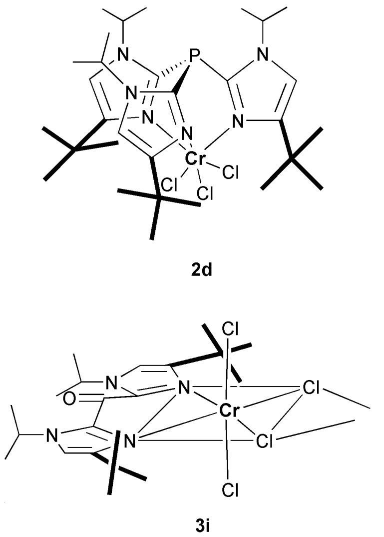


Fig. 5 Steric situation at the metal centre in complexes **2d** and **3i**.

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	**2a**/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	**3j**/0.11	400	0.8	26	23	29	22	2
13	**4k**/0.1	400	0.5	—	—	—	—	2

[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.

Table 5 Catalytic testing of **2a** under varying conditions[a]

Entry	Catalyst/ mmol	MMAO/ equiv.	Conditions	Act.[b]/g mmol^{-1} h^{-1} bar^{-1}	1-Alkenes	Isoalkenes	Alkanes	Isoalkanes	Polymer (wt%)
1	0.11	400	C_6H_5Cl[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 (except entry 1), T = 100 °C, 1 h. [b] Per [Cr]. [c] $p(CH_2{=}CH_2)$ = 40 bar.

Table 6 Catalytic testing of **3**–**6** in toluene[a]

Entry	Catalyst/mmol	T/°C	Act.[b]/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	[c]	[c]	[c]	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[d]	**6**/0.01	100	6.6	88[e]	—	6	8
6	**7**/0.11	80	7.7	80	8.5	11.5	13.5

[a] 400 equivalents MMAO; 50 ml toluene, $p(CH_2{=}CH_2)$ = 40 bar, 1 h. [b] Per [Cr]. [c] C_4 hydrocarbons only. [d] 400 equivalents MAO instead of MMAO used as activator. [e] 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 $[CrCl_2(tren)]Cl$ (**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 $[CrCl_3\{mim)_2CO\}(CH_3CN)]$ 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 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 $[CrCl_3(THF)_3]$,[41] $[VCl_3(THF)_3]$,[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 procedure[39] was followed, except that $[CrCl_3(THF)_3]$ was used as a starting material and CH_2Cl_2 as a solvent. Anhydrous $CrCl_3$, 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 (Bu_4NPF_6) (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 CH_3CN using Bu_4NPF_6 (0.1 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^+ (CH_3CN, 10 mM $AgNO_3$) 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 LCQ, 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 $[CrCl_3\{(Bzmim)_2CO\}]_2$ 3h, $[CrCl_3\{(mim)_2CNPh\}]_2$ 3j and $[CrCl_3(mim)_3]$ 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%; ν_{max}/cm^{-1} (C=O) 1680 (KBr); *m*/*z* 465 ($LCrCl_3 + H_2O$, 100%), 429 ($LCrCl_2 + OH$, 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%; ν_{max}/cm^{-1} (C=NPh) 1622 (KBr); *m*/*z* 810 (M − Cl, 5%), 387 ($LCrCl_2$, 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 (L_2CrCl_2, 89%), 251 (L_2CrCl, 56%) (FAB MS).

$[CrCl_3\{(tBupim)_3P\}]$ 2d. The ligand **1d** (0.122 g, 0.23 mmol), $CrCl_3$ (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 $[CrCl_3\{(tBupim)_3P\}]$ **2d** as a mint green solid (0.142 g, 90%). Found: C 50.34, H 8.58, N 11.72. $C_{30}H_{51}Cl_3CrN_6P{\cdot}2H_2O$ requires C, 49.96; H, 7.7; N, 11.66%; *m*/*z* 630 (LCrCl + O, 18%); 327 (L, 100%) (FAB MS).

$[CrCl_3\{(tBupim)_2CO\}]_2$ 3i. $(tBupim)_2CO$ **1i** (0.095 g, 0.26 mmol) in tetrahydrofuran (7 ml) was added to a stirred solution of $[CrCl_3(THF)]$ (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 Et_2O (2 × 5 ml) and drying under vacuum gave $[CrCl_3\{(tBupim)_2CO\}]_2$ **3i** as a green solid (0.118 g, 88%). Found: C, 48.65; H, 7.84; N, 9.54. $C_{42}H_{68}Cl_6Cr_2N_8O_2$ requires C, 48.79; H, 6.64; N, 10.84%; *m*/*z* 874 ($L_2Cr_2Cl_2$ − O), 1%) 359 (LH, 100%) (ESI MS).

$[VCl_3\{(mim)_3COCH_3\}]$ 5a. $(mim)_3COCH_3$ **1a** (0.091 g, 0.32 mmol) in tetrahydrofuran (7 ml) was added to a stirred solution of $[VCl_3(THF)_3]$ (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), Et_2O (2 × 5 ml) and drying under vacuum gave $[VCl_3\{(mim)_3COCH_3\}]$ **5a** as a green solid. (0.14 g, 99%). Found: C, 34.36; H, 3.71; N, 17.20. $C_{14}H_{18}Cl_3N_6OV$ requires C, 37.87; H, 4.10; N, 18.95%; *m*/*z* 408 (M − Cl, 9%); 388 (LVCl + O, 42%); 322 ($LV-CH_3 - 3Cl$, 12%); 255 ($L - OCH_3$) (FAB MS).

$[VCl_3\{(mim)_2CO\}(THF)]$ 5g. A suspension of $(mim)_2CO$ **1c** (0.085 g, (0.44 mmol) in tetrahydrofuran (15 ml) was added to a stirred solution of $[VCl_3(THF)_3]$ (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), Et_2O (2 × 5 ml) and drying under vacuum gave $[VCl_3\{(mim)_2CO\}(THF)]$ **5g** as a green solid (0.166 g, 90%). Found: C, 38.32; H, 3.98; N, 12.90. $C_{13}H_{18}Cl_3N_4O_2V$ requires C, 37.20; H, 4.33; N, 13.35%; ν_{max}/cm^{-1} (C=O) 1654 (KBr); *m*/*z* 428 (LVCl + mnba, 20%); 311 ($LVCl_2$, 14%); 292 (LVCl + O, 100%); 276 (LVCl, 23%); 191 (LH, 15%) (FAB MS).

$[CrCl_3(MeTAM)]$ 6. MeTAM **1** (0.099 g, 0.63 mmol) in CH_2Cl_2 (3 ml) was added to a stirred solution/suspension of $[CrCl_3(THF)_3]$ (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 $[CrCl_3(MeTAM)]$ **6** was further purified by repeated precipitation from CH_2Cl_2/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, $2\theta_{max} = 75°$; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; *T ca.* 153 K) yielding 37346 reflections, merging to 9433 independent ($R_{int} = 0.033$) 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_{iso}) for the hydrogen. Conventional residuals on $|F|$ at convergence were $R = 0.030$, $R_w = 0.035$ (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: $C_{11}H_{13}Cl_3CrN_5O{\cdot}CH_3CN$, $M = 430.7$, monoclinic, space group $P2_1/n$ (C^5_{2h}, no. 14, variant), $a = 6.9757(2)$, $b = 14.6946(5)$, $c = 17.5803(6)$ Å, $\beta = 94.419(1)°$, $V = 1797$ Å^3. D_c $(Z = 4) = 1.592$ g cm^{-3}. $\mu_{Mo} = 11.0$ cm^{-1}; specimen: 0.5 × 0.2 × 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 Na_2SO_4 and analysed by GC and GC/MS.

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