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Low valent chromium complexes bearing *N*,*O*-chelating pyridyl-enolate ligands $[OC(Bu^t)(=2\text{-}CHN_5H_3Me\text{-}x)]^-$ ($x = 3$–6)

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Treatment of $[CrCl_2(THF)]$ (THF = tetrahydrofuran) with the sodium salt of $HOC(Bu^t)(2\text{-}CH_2NC_5H_3Me\text{-}x)_2$ ($x = 6$) in refluxing THF results in fragmentation of the L_2X (L = neutral donor, X = anionic donor) ligand to afford the square planar bis(pyridyl-enolate) chromium(II) complex $[Cr\{OC(Bu^t)(=2\text{-}CHNC_5H_3Me\text{-}6)\}_2]$ (**1**) and the by-product *trans*-$[CrCl_2(2,6\text{-dimethylpyridine})_2]$ (**2**). On prolonged heating in refluxing toluene, oxidation of **1** occurs yielding the octahedral tris(pyridyl-enolate) chromium(III) complex $[Cr\{OC(Bu^t)(=2\text{-}CHNC_5H_3Me\text{-}6)\}_3]$ (**3**). Similar use of the sodium salts of $HOC(Bu^t)(2\text{-}CH_2NC_5H_3Me\text{-}x)_2$ ($x = 3$–5) also results in ligand fragmentation but gives solely the chromium(III) *tris*-chelated complexes $[Cr\{OC(Bu^t)(=2\text{-}CHNC_5H_3Me\text{-}x)\}_3]$ [$x = 3$ (**4**), 4 (**5**), 5 (**6**)]. Surprisingly, prolonged heating in a sealed tube of a mixture of $[CrCl_2(THF)]$ and the sodium salt of $HOC(Bu^t)(2\text{-}CH_2NC_5H_3\text{-}Me\text{-}x)_2$ ($x = 6$) in the presence of diphenylacetylene furnishes the bimetallic chromium(II) complex $[ClCr\{(\mu\text{-}OC(Bu^t)\text{-}(2\text{-}CH_2NC_5H_3Me\text{-}6)_2\}CrCl]$ (**7**), in which the two intact L_2X ligands bridge the Cr–Cr vector (2.92 Å), one acting as a bidentate ligand and the other as a tridentate ligand. Single crystal X-ray diffraction studies have been performed on **1**, **2**, **3**, **6** and **7**.

Introduction

Recent years have seen considerable research effort dedicated to the design of new bidentate spectator ligands for complexation to transition metals. This interest has been stimulated, in some measure, by their use as supports for olefin polymerisation catalysts with examples now plentiful for both early and late transition metal systems.[1–3] In particular, sterically variable monoanionic *N*,*O*-chelating ligands such as salicylaldiminato (**A** in Fig. 1) have been leading the developments with active catalysts formed with metals drawn from group 4,[4,5] group 6[6,7] and group 10.[8–11]

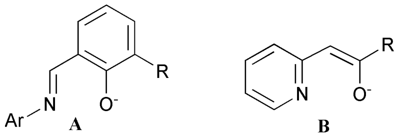

Fig. 1 Monoanionic salicylaldiminato (**A**) and pyridyl-enolate (**B**) ligand frames.

In the course of examining the coordination chemistry of the sodium salt of bis(methylpyridine)-substituted alcohol, $HOC(Bu^t)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2$, we have found that ligand fragmentation (with concomitant loss of 2,6-dimethylpyridine) can occur to generate complexes containing another class of *N*,*O*-chelating ligands, the pyridyl-enolate (**B** in Fig. 1).[12] Somewhat surprisingly this type of monoanionic bidentate ligand has not been the subject of greater interest and indeed examples of structurally characterised complexes containing pyridyl-enolates are rare.[13–15] In this paper we explore this ligand fragmentation reaction in the presence of $[CrCl_2(THF)]$, with particular regard being paid to the steric attributes of the starting bis(methylpyridine)-substituted alcohol. In addition, the application of one of the resultant chromium complexes as an olefin polymerisation catalyst is reported.

Results and discussion

Addition of one equivalent of $[CrCl_2(THF)]$ to the sodium salt of $HOC(Bu^t)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2$ in THF afforded, after work-up, the paramagnetic (μ_{eff} = 3.2 BM at ambient temperature) chromium(II) complex $[Cr\{OC(Bu^t)(=2\text{-}CHNC_5H_3\text{-}Me\text{-}6)\}_2]$ (**1**) in good yield (Scheme 1). Also isolated in the reaction was the by-product *trans*-$[CrCl_2(2,6\text{-dimethyl-pyridine})_2]$ (**2**). Both complexes have been subject to single crystal X-ray diffraction studies.

Table 1 Selected bond lengths [Å] and angles [°] for complex **1**

Cr–O	1.962(2)	Cr–N	2.093(2)
O–C(7)	1.312(3)	C(6)–C(7)	1.367(4)
O′–Cr–O	165.04(11)	O′–Cr–N	92.24(8)
O–Cr–N	87.11(8)	O′–Cr–N′	87.11(8)
O–Cr–N′	92.24(8)	N–Cr–N′	174.98(11)

Blue/green crystals of **1** suitable for an X-ray crystal structure determination were grown from a saturated acetonitrile solution at room temperature. The molecular structure is shown in Fig. 2; selected bond lengths and angles are listed in Table 1. The complex is seen to have a substantially folded geometry which has crystallographic C_2 symmetry. The geometry at chromium is slightly distorted square planar with *cis* angles in the range 87.11(8) to 92.24(8)°, the acute angle being associated with the bite of the chelating ligand. Whereas the *trans* N–Cr–N′ angle

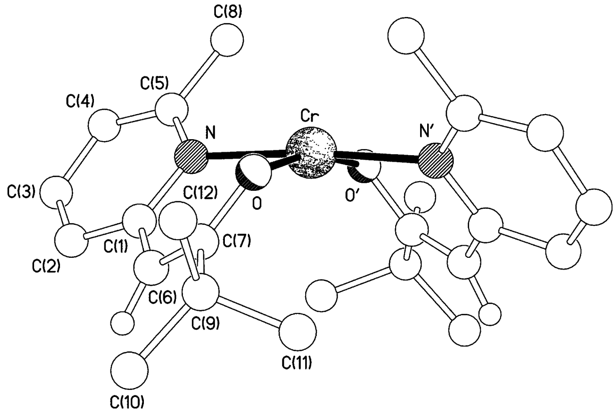

Fig. 2 The molecular structure of **1**.

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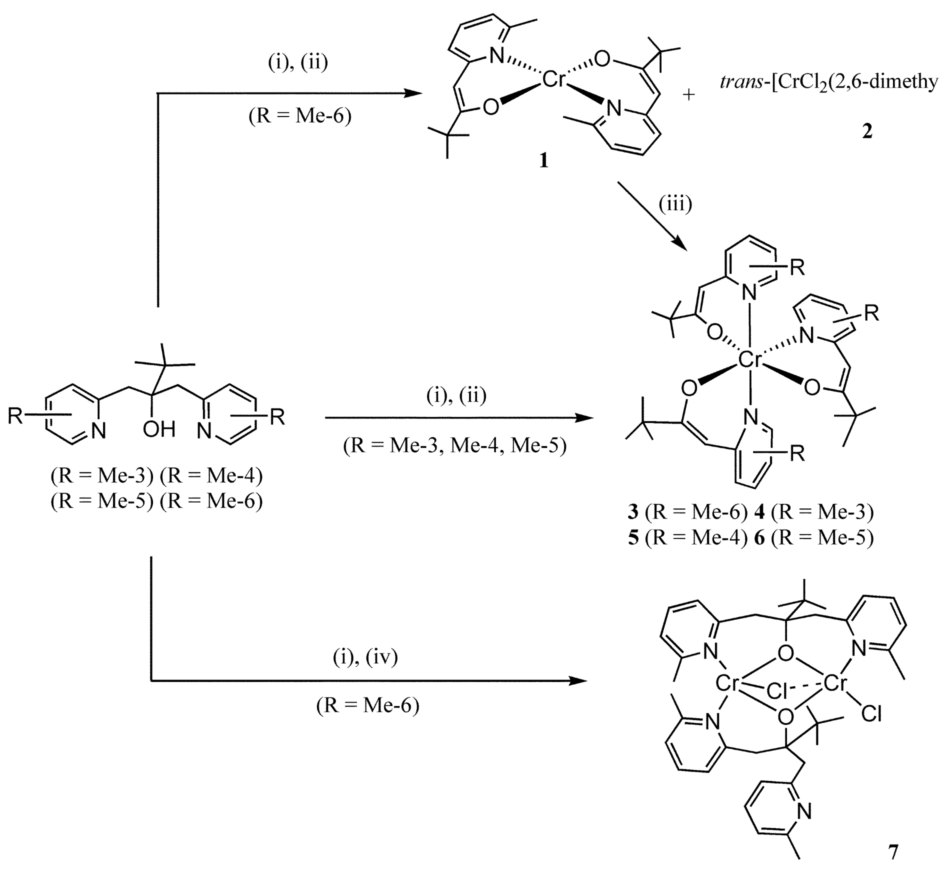

Scheme 1 *Reagents and conditions*: (i) NaH, THF, 12 h, heat; (ii) [CrCl$_2$(THF)], THF, 12 h, RT; (iii) C$_6$H$_5$CH$_3$, 48 h, heat; (iv) [CrCl$_2$(THF)], PhCCPh, THF, sealed ampoule, 1 week, heat.

is nearly linear [175.0(1)°], the O–Cr–O′ angle is noticeably bent [at 165.0(1)°, Table 1]. The Cr–O and Cr–N bond lengths are unexceptional, with those to the nitrogens [2.093(2) Å] being significantly longer than those to the oxygens [1.962(2) Å] reflecting the pyridyl nature of the nitrogen donor. There is a noticeable lengthening of the C(6)=C(7) linkage [1.367(4) Å] indicating appreciable delocalisation of the double bond into the adjacent C–O bond. The distinctly arched geometry of the molecule is a consequence of the very large fold angles [46°] about the N ··· O vectors in the two six-membered chelate rings. This geometry results in a shielding of the chromium centre from attack from 'beneath' but appears to leave the upper surface exposed. However, inspection of a space-filling representation of the molecule shows that the upper surface is also partially obscured by the two inwardly directed methyl substituents [C(8)] on the pyridyl rings. Inspection of the packing reveals loosely linked chains of molecules held together by weak C–H ··· π interactions between one of the methyl hydrogens on C(8) in one molecule and the pyridyl ring of the next [H ··· π 2.88 Å, C–H ··· π 135°].

Purple crystals of *trans*-[CrCl$_2$(2,6-dimethylpyridine)$_2$] (**2**) were formed on prolonged standing of an acetonitrile solution containing the reaction mixture employed to give **1**. The structure of **2** was determined and shown to be very similar to that of the 2,4,6-trimethylpyridyl analogue.[16] In both of these C_i symmetric structures the pyridyl ring is inclined almost orthogonally to the coordination plane [88° in **2** and 86° in ref. 16]; the Cr–Cl distances are essentially the same [2.336(1) and 2.328(1) Å in **2** and ref. 16, respectively] but there is significant lengthening of the Cr–N bond to 2.117(2) Å [*cf.* 2.101(3) Å in ref. 16] reflecting the change in the electron donating character of the substituted pyridyl ring (Table 2).

The structure of **2** confirms the formation of 2,6-dimethylpyridine during the synthesis of **1**. A similar degradation of [HOC(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-6)$_2$] has been observed previously during the reaction of [HOC(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-6)$_2$] with an 'inadvertent' mixture of [Sm{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] and [NaSm{N(SiMe$_3$)$_2$}$_3$], although no experimental details were reported.[14a] In this latter reaction free 2,6-dimethylpyridine was identified by GC mass spectrometry.

Table 2 Selected bond lengths [Å] and angles [°] for complex **2**

Cr–N	2.117(2)	Cr–Cl	2.3361(6)
N′–Cr–N	180.0	N–Cr–Cl′	90.38(5)
N–Cr–Cl	89.62(5)	Cl′–Cr–Cl	180.0

On refluxing **1** in toluene for 48 hours, ligand redistribution and oxidation occurs to give the octahedral tris(pyridyl-enolate) chromium(III) complex [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-6)}$_3$] (**3**) in good yield (Scheme 1). Complex **3** has been characterised by EI mass spectrometry, EPR and by microanalysis. In addition, **3** has been subject to a single crystal X-ray diffraction study.

A crystal of **3** suitable for an X-ray crystal structure determination was grown from the slow cooling of a hot acetonitrile solution. The molecular structure is shown in Fig. 3; selected bond lengths and angles are listed in Table 3. The X-ray analysis of **3** shows the crystal to contain two independent molecules in the asymmetric unit. Both molecules have very similar conformations, with an rms deviation of only 0.08 Å for the fit of the whole molecule excluding the methyl and *tert*-butyl groups. The geometry at chromium is slightly distorted octahedral with the three pyridylenolate ligands coordinated in a *mer* configuration. Although the isomer illustrated in Fig. 3 has a Λ configuration, the complex crystallises in a space group containing a glide plane and there are thus equal numbers of Δ and Λ forms present in the crystal. In each chelate ring the bite angle is near optimal, the respective O–Cr–N angles being in the range 87.1(4) to 89.4(4)° (Table 3). Surprisingly, despite the different *trans* environments of the oxygen and nitrogen atoms, there is no apparent *trans* influence, the Cr–O and Cr–N distances not being significantly different, though, as in **1**, the bonds to

Table 3 Selected bond lengths [Å] and angles [°] for complex **3**

Cr–O(1)	1.921(8)	Cr–O(2)	1.899(7)	Cr–O(3)	1.914(8)
Cr–N(1)	2.161(9)	Cr–N(2)	2.149(10)	Cr–N(3)	2.160(11)
O(1)–C(7)	1.32(2)	O(2)–C(27)	1.28(2)	O(3)–C(47)	1.294(14)
C(6)–C(7)	1.35(2)	C(26)–C(27)	1.36(2)	C(46)–C(47)	1.37(2)
Cr′–O(1′)	1.937(9)	Cr′–O(2′)	1.904(8)	Cr′–O(3′)	1.945(9)
Cr′–N(1′)	2.164(9)	Cr′–N(2′)	2.144(9)	Cr′–N(3′)	2.160(10)
O(1′)–C(7′)	1.294(14)	O(2′)–C(27′)	1.30(2)	O(3′)–C(47′)	1.33(2)
C(6′)–C(7′)	1.35(2)	C(26′)–C(27′)	1.36(2)	C(46′)–C(47′)	1.35(2)
O(2)–Cr–O(3)	88.7(3)	O(2)–Cr–O(1)	88.0(3)	O(3)–Cr–O(1)	173.9(4)
O(2)–Cr–N(2)	87.1(4)	O(3)–Cr–N(2)	88.3(4)	O(1)–Cr–N(2)	86.4(4)
O(2)–Cr–N(3)	83.4(4)	O(3)–Cr–N(3)	89.4(4)	O(1)–Cr–N(3)	95.3(4)
N(2)–Cr–N(3)	170.3(4)	O(2)–Cr–N(1)	176.1(4)	O(3)–Cr–N(1)	94.2(3)
O(1)–Cr–N(1)	89.4(3)	N(2)–Cr–N(1)	95.6(4)	N(3)–Cr–N(1)	93.9(4)
O(2′)–Cr′–O(1′)	88.6(4)	O(2′)–Cr′–O(3′)	88.3(4)	O(1′)–Cr′–O(3′)	173.9(4)
O(2′)–Cr′–N(2′)	88.2(3)	O(1′)–Cr′–N(2′)	86.7(4)	O(3′)–Cr′–N(2′)	88.0(3)
O(2′)–Cr′–N(3′)	175.3(4)	O(1′)–Cr′–N(3′)	95.2(4)	O(3′)–Cr′–N(3′)	88.2(4)
N(2′)–Cr′–N(3′)	94.9(3)	O(2′)–Cr′–N(1′)	83.7(3)	O(1′)–Cr′–N(1′)	88.8(4)
O(3′)–Cr′–N(1′)	96.0(4)	N(2′)–Cr′–N(1′)	170.9(4)	N(3′)–Cr′–N(1′)	93.4(3)

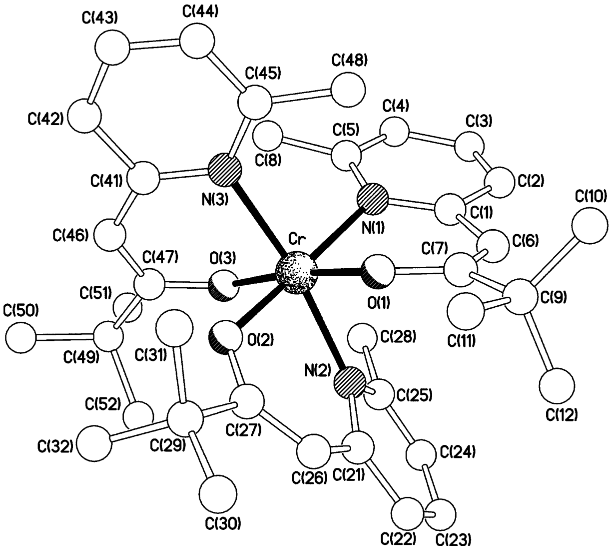

Fig. 3 The molecular structure of **3**.

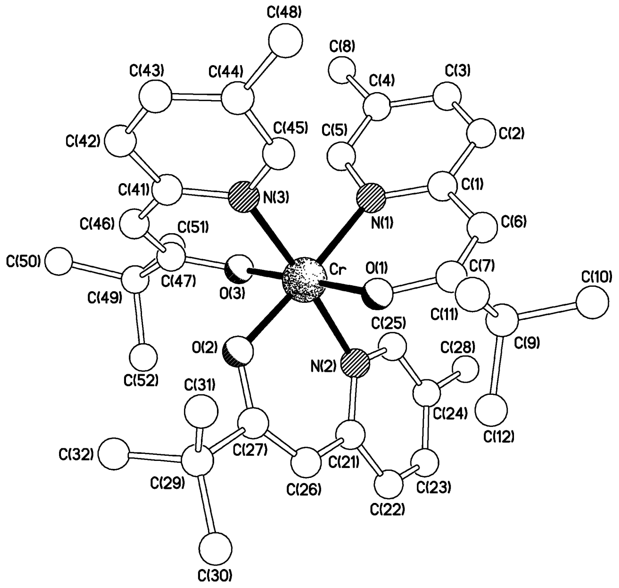

Fig. 4 The molecular structure of **6**.

nitrogen are distinctly longer than those to oxygen. A similar pattern of delocalisation of the C=C bonds into their adjacent C–O bonds to that seen in **1** is also observed here. The folds in the six-membered chelate rings are again substantial, ranging between 30 and 38°, though not as large as seen in **1**. An interesting intramolecular stabilising feature present in both independent molecules is a short C–H $\cdots$ π contact between one of the C(28) hydrogen atoms and the N(1) containing pyridyl ring; the H $\cdots$ π distances (Å) and C–H $\cdots$ π angles (°) are 2.49 and 148, and 2.30 and 169 in the two independent molecules, respectively (the orientations of these methyl groups were refined). There are no intermolecular interactions of note.

With the intent of modifying the steric attributes of the resultant pyridyl-enolate ligands we set about examining the reaction of [CrCl$_2$(THF)] with the sodium salts of a series of bis(methylpyridine)-substituted alcohols. Specifically, the methyl group substitution pattern of the pyridyl moiety in HOC(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-*x*)$_2$, was varied to include *meta* (*x* = 3, 5) or *para* (*x* = 4) substituents, *viz.* HOC(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-5)$_2$, HOC(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-4)$_2$ and HOC(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-3)$_2$. However, under similar reaction conditions as those employed to make **1**, only the octahedral tris(pyridyl-enolate) complexes [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-*x*)}$_3$] [*x* = 3 (**4**), 4 (**5**), 5 (**6**)] were isolated (Scheme 1). All the complexes have been characterised by mass spectrometry, microanalysis and by magnetic measurements. In addition, a crystal of **6** has been the subject of an X-ray diffraction study.

The structure of **6** is very similar to that of **3**, with the three bidentate ligands arranged in a *mer* configuration (Fig. 4). Unlike in **3**, though, here the Cr–O and Cr–N distances exhibit small differences at the margin of significance (Table 4) suggesting the presence of only a very slight *trans* influence (the Cr–O bonds *trans* to nitrogen are shorter than those *trans* to oxygen, and the Cr–N bonds *trans* to oxygen are longer than those *trans* to nitrogen). These differences are 'observed' here whereas they were not in **3** presumably merely due to improvements in the standard deviations of the bond lengths in **6**.

The ^{1}H NMR spectra of all the tris(pyridyl-enolate) complexes (**3**–**6**) are broad and uninformative. The magnetic susceptibilty measurements reveal magnetic moments of between 3.9–4.1 BM (Evans Balance at ambient temperature) which are consistent with three unpaired electrons (d^3). This is further supported by the X-band EPR spectra of **3**–**6** in toluene at room temperature that show sharp signals with *g*-values of 2.0, which is typical of chromium(III); there is no observable hyperfine splitting in any of the spectra. Microanalytical and mass spectrometric data for **3**–**6** are consistent with their formulations.

From these results it would seem likely that a bis(pyridyl-enolate) complex is an intermediate in the formation of the tris-chelated complexes **3**–**6**. Indeed it has been shown that under forcing conditions **1** can be converted to **3**. The steric protection of the *ortho*-methyl group imparted on the metal centre in **1**, although relatively minor as evidenced from the X-ray structure (Fig. 2 and 3), would seem sufficient to prevent, under milder conditions, the approach of another pyridyl-enolate ligand and subsequent oxidation to give **3**. This of course raises the

Table 4 Selected bond lengths [Å] and angles [°] for complex **6**

Cr–O(1)	1.919(4)	Cr–O(2)	1.898(4)	Cr–O(3)	1.931(4)
Cr–N(1)	2.093(5)	Cr–N(2)	2.078(4)	Cr–N(3)	2.059(4)
O(1)–C(7)	1.304(6)	O(2)–C(27)	1.296(6)	O(3)–C(47)	1.299(6)
C(6)–C(7)	1.356(8)	C(26)–C(27)	1.340(7)	C(46)–C(47)	1.375(8)
O(2)–Cr–O(1)	90.0(2)	O(2)–Cr–O(3)	90.2(2)	O(1)–Cr–O(3)	178.2(2)
O(2)–Cr–N(3)	86.4(2)	O(1)–Cr–N(3)	93.4(2)	O(3)–Cr–N(3)	88.4(2)
O(2)–Cr–N(2)	89.8(2)	O(1)–Cr–N(2)	88.7(2)	O(3)–Cr–N(2)	89.6(2)
N(3)–Cr–N(2)	175.7(2)	O(2)–Cr–N(1)	175.0(2)	O(1)–Cr–N(1)	89.0(2)
O(3)–Cr–N(1)	90.9(2)	N(3)–Cr–N(1)	88.8(2)	N(2)–Cr–N(1)	95.1(2)

Table 5 Selected bond lengths [Å] and angles [°] for complex **7**

Cr(1)–O(1)	2.014(3)	Cr(1)–O(2)	1.981(3)	Cr(1)–N(1)	2.163(4)
Cr(1)–N(3)	2.134(4)	Cr(1)–Cl(1)	2.813(2)	Cr(1)–Cr(2)	2.9185(12)
Cr(2)–O(1)	2.035(4)	Cr(2)–O(2)	2.037(3)	Cr(2)–N(2)	2.171(5)
Cr(2)–Cl(2)	2.361(2)	Cr(2)–Cl(1)	2.829(2)	O(1)–C(7)	1.426(7)
O(2)–C(27)	1.414(6)	C(6)–C(7)	1.562(9)	C(7)–C(8)	1.563(8)
C(26)–C(27)	1.568(7)	C(27)–C(28)	1.535(6)		
O(2)–Cr(1)–O(1)	79.93(14)	O(2)–Cr(1)–N(3)	87.2(2)	O(1)–Cr(1)–N(3)	165.9(2)
O(2)–Cr(1)–N(1)	157.5(2)	O(1)–Cr(1)–N(1)	91.4(2)	N(3)–Cr(1)–N(1)	102.7(2)
O(2)–Cr(1)–Cl(1)	83.08(11)	O(1)–Cr(1)–Cl(1)	81.23(11)	N(3)–Cr(1)–Cl(1)	91.54(12)
N(1)–Cr(1)–Cl(1)	116.35(14)	O(1)–Cr(2)–O(2)	78.15(13)	O(1)–Cr(2)–N(2)	90.7(2)
O(2)–Cr(2)–N(2)	160.8(2)	O(1)–Cr(2)–Cl(2)	174.44(11)	O(2)–Cr(2)–Cl(2)	99.07(10)
N(2)–Cr(2)–Cl(2)	93.29(14)	O(1)–Cr(2)–Cl(1)	80.50(11)	O(2)–Cr(2)–Cl(1)	81.73(11)
N(2)–Cr(2)–Cl(1)	112.0(2)	Cl(2)–Cr(2)–Cl(1)	94.37(6)	Cr(1)–Cl(1)–Cr(2)	62.30(4)
Cr(1)–O(1)–Cr(2)	92.24(13)	Cr(1)–O(2)–Cr(2)	93.1(2)		

possibility that smaller organic molecules could approach the cavity created by the outward pointing methyl groups in **1**. However, in the presence of ethylene (1 atm) no activity for ethylene polymerisation was observed. Notably, treatment of **1** with diethylaluminium chloride (30 equiv.) afforded a moderately active catalyst for ethylene polymerisation, yielding solid polyethylene with an activity of 35 g mmol^{-1} h^{-1} bar^{-1}.[6b]

In an attempt to form a pyridyl-enolate chromium(II) complex bound by an acetylene ligand, we carried out the reaction of [CrCl$_2$(THF)] with the sodium salt of HOC(Bu^t)(2-CH$_2$-NC$_5$H$_3$Me-6)$_2$ in the presence of diphenylacetylene. However, after refluxing the reaction mixture in tetrahydrofuran in a sealed ampoule for a period of one week, the only product isolated was the bimetallic chromium(II) complex [ClCr{(μ-OC-(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-6)$_2$}CrCl] (**7**). Complex **7** has been characterised by mass spectrometry, EPR and by microanalysis. In addition, and X-ray structural determination has been performed on **7**.

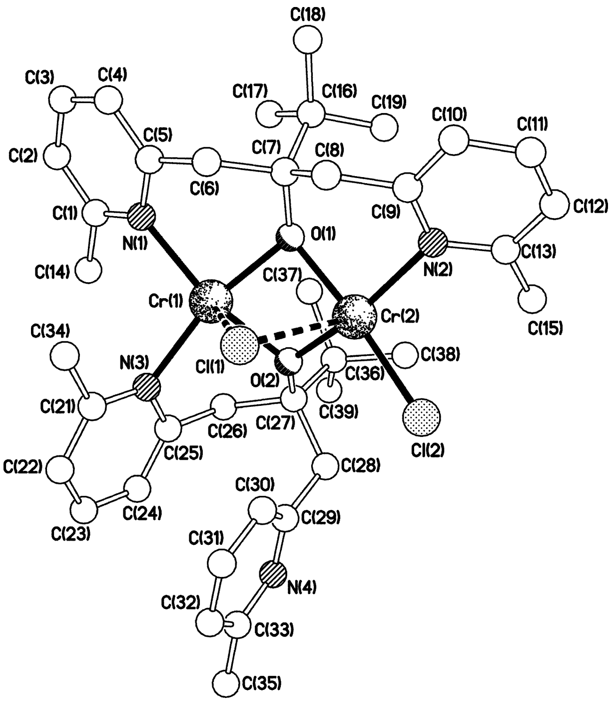

Fig. 5 The molecular structure of **7**.

Blue/green crystals of **7** suitable for an X-ray crystal structure determination were grown from the prolonged standing of a saturated acetonitrile solution. The molecular structure is shown in Fig. 5; selected bond lengths and angles are listed in Table 5. The structure shows a binuclear complex wherein there are both bidentate and tridentate alkoxide ligands. The former utilises a pyridyl nitrogen and the alkoxide oxygen (the other pyridyl nitrogen being non-coordinating) in a bidentate, binucleating mode whereas the latter makes use of all three donor atoms with the two pyridyl nitrogen atoms coordinating to different chromium centres. In both cases the alkoxide oxygen atom bridges the two chromium atoms, forming a folded Cr$_2$O$_2$ ring. Thus, one chromium centre [Cr(1)] is bonded to two *cis* pyridyl nitrogens and two *cis* alkoxide oxygen atoms, whilst the other [Cr(2)] is coordinated to the same pair of *cis* alkoxide oxygen atoms, a single pyridyl nitrogen and a chloride ion, each in a square planar geometry; the *cis* angles at Cr(1) and Cr(2) are in the ranges 79.9(1) to 102.7(2)° and 78.2(1) to 99.1(1)°, respectively. The two coordination planes are inclined by *ca.* 2° to each other and are approached by a second chloride ion in an approximately apical/bridging position (Fig. 6). The Cr–Cl(1) distances are both very long at 2.813(2) and 2.829(2) Å for Cr(1) and Cr(2), respectively, distances similar to those observed in, for example, *trans*-CrCl$_2$(H$_2$O)$_2$(py)$_2$ [2.767(1) Å] and in the related *trans*-CrCl$_2$(py)$_4$ [2.803(1) Å] complexes.[17] In these latter two structures these long Cr–Cl distances were attributed to the Jahn–Teller effect, even though they would be considered at the margin of what would be regarded as a bonding interaction. The pattern of bonding of the two chromium centres to the alkoxide ligands is somewhat anomalous, with all of the ‘equivalent’ bonds to Cr(1) being noticeably shorter than their counterparts to Cr(2)—there are not the expected variations due to the different natures of the *trans* substituents. The non-coordinating pyridyl ring is folded back such that it overlays its coordinated counterpart, entering into a π–π stacking interaction; the ring centroid ··· ring centroid separation is 3.56 Å, the two rings being inclined by 17°. There are no intermolecular interactions of note. The Cr–Cr separation of 2.9185(12) Å is marginally shorter than in related alkoxide-

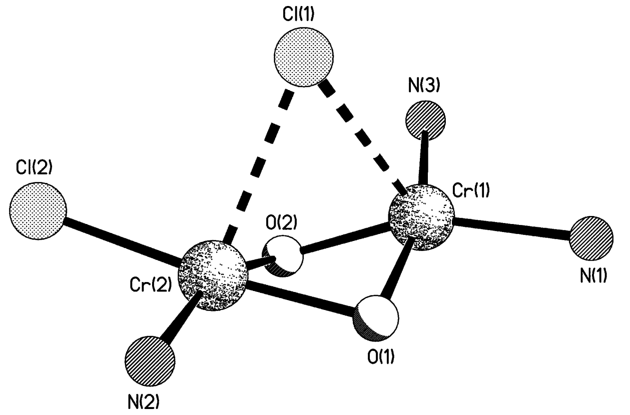

Fig. 6 The inner coordination spheres of the two chromium centres in the structure of **7**, showing the long approach of the second chloride ion [Cl(1)] and the consequent pseudo-square pyramidal coordination geometries.

bridged bimetallic chromium(II) complexes, but is slightly longer than that normally associated with a Cr–Cr single bond.[18,19] The explanation as to why a complex resulting from ligand fragmentation (*viz.* **1**) is not isolated during the formation of **7** is unclear. Nevertheless, complex **7** represents a rare example of a bimetallic complex containing a bis(methylpyridine)substituted alkoxide ligand.[20]

Complex **7** is paramagnetic exhibiting a magnetic moment of 2.25 BM per chromium centre (by the Evans NMR method) (consistent with an $S = 1$ ground state). As expected no EPR spectra are observed in acetonitrile at either 298 or 180 K [Cr(II), $S = 1$]. Microanalysis is consistent with the formulation given.

In conclusion, a series of homoleptic chromium(II) and (III) complexes bearing pyridyl-enolate ligands have been prepared *via* a ligand fragmentation route. The intermediacy of the bis(pyridyl-enolate)Cr complex in the formation of the tris(pyridyl-enolate)Cr complex has been demonstrated. Unexpectedly, the presence of diphenylacetylene prevents the ligand fragmentation from occurring. Further investigations of the transition metal coordination chemistry of these *N,O* pyridyl-enolates and of the parent bis(methylpyridine)-substituted alcohols will be published subsequently.

Experimental

General

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Imperial College. Mass spectra were obtained using either fast atom bombardment (FAB) or electron impact (EI). Magnetic susceptibility studies were performed using an Evans Balance (Johnson Matthey) at room temperature or by using the Evans NMR method (solvent, CD$_2$Cl$_2$; reference, cyclohexane).[21] The magnetic moment was calculated following standard methods[22] and corrections for underlying diamagnetism were applied to data.[23]

The complex [CrCl$_2$(THF)] was prepared as described in the literature.[24] The ligands HOC(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-x)$_2$ (x = 3–6) were prepared by the previously published procedure using the respective lutidine.[14a] All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparation of 1 and 2

Compound HOC(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-6)$_2$ (0.92 g, 3.0 mmol) and NaH (0.08 g, 3.3 mmol) in THF (30 cm^3) were refluxed for 12 h. On cooling to room temperature, solid [CrCl$_2$(THF)] (0.59 g, 3.0 mmol) was added and stirring continued for 12 h. After removal of volatiles under reduced pressure, the solid residue was extracted into warm MeCN (2 × 25 cm^3). Blue/green prisms of [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-6)$_2$}] (**1**) formed on prolonged standing (1–2 days) at ambient temperature. Yield: 0.42 g (65%). Further crops were obtained from the mother-liquor together with purple prisms of *trans*-[CrCl$_2$(2,6-dimethylpyridine)$_2$] (**2**) which were separated physically. Complex **1**: Anal. Calc. for C$_{24}$H$_{32}$CrN$_2$O$_2$: C, 66.6; H, 7.5; N, 6.5. Found: C, 66.5; H, 7.6; N, 6.9%. μ_{eff} 3.2 BM at 293 K. Complex **2**: Anal. Calc. for C$_{14}$H$_{18}$Cl$_2$CrN$_2$: C, 49.9; H, 5.4; N, 8.3. Found: C, 50.9; H, 5.7; N, 8.4%.

Preparation of 3

Complex **1** (1.00 g, 2.3 mmol) in toluene (30 cm^3) was refluxed for 48 h. On cooling to room temperature, the volatiles were removed under reduced pressure and the solid residue was extracted into warm MeCN (2 × 25 cm^3) affording [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-6)}$_3$] (**3**) as dark needles. Yield: 1.27 g (89%). Anal. Calc. for C$_{36}$H$_{48}$CrN$_3$O$_3$: C, 69.4; H, 7.8; N, 6.7%. Found: C, 68.6; H, 7.6; N, 6.7%. EI mass spectrum, *m/z* 622 [M$^+$], 432 [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-6)}$_2$], 242 [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-6)}]. μ_{eff} 4.0 BM at 293 K. EPR (toluene, 298 K): $g = 2.00$.

Preparation of 4

As for **1**, but using OC(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-5)$_2$ (0.92 g, 3.0 mmol), NaH (0.08 g, 3.3 mmol) and [CrCl$_2$(THF)] (0.59 g, 3.0 mmol) gave [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-3)}$_3$] (**4**) as golden-brown blocks. Yield: 1.04 g (73%). Anal. Calc. for C$_{36}$H$_{48}$CrN$_3$O$_3$: C, 69.4; H, 7.8; N, 6.7. Found C, 68.7; H, 7.8; N, 6.7%. EI mass spectrum, *m/z* 623 [MH$^+$]. μ_{eff} 3.9 BM at 293 K. EPR (toluene, 298 K): $g = 2.00$.

Preparation of 5

As for **1**, but using OC(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-4)$_2$ (0.92 g, 3.0 mmol), NaH (0.08 g, 3.3 mmol) and [CrCl$_2$(THF)] (0.59 g, 3.0 mmol) gave [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-4)}$_3$] (**5**) as golden-brown blocks. Yield: 1.22 g (85%). Anal. Calc. for C$_{36}$H$_{48}$CrN$_3$O$_3$: C, 69.4; H, 7.8; N, 6.7. Found C, 68.7; H, 7.7; N, 6.8%. EI mass spectrum, *m/z* 622 [M$^+$], 432 [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-4)}$_2$], 242 [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-4)}]. μ_{eff} 3.9 BM. EPR (toluene, 298 K): $g = 2.00$.

Preparation of 6

As for **1**, but using OC(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-3)$_2$ (0.92 g, 3.0 mmol), NaH (0.08 g, 3.3 mmol) and [CrCl$_2$(THF)] (0.59 g, 3.0 mmol) gave [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-5)}$_3$] (**6**) as golden-brown blocks. Yield: 0.43 g (30%). Anal. Calc. for C$_{36}$H$_{48}$CrN$_3$O$_3$: C, 69.4; H, 7.8; N, 6.7. Found C, 68.9; H, 7.8; N, 6.7%. EI mass spectrum, *m/z* 622 [M$^+$], 432 [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-5)}2], 242 [Cr{OC(Bu^t)(=2-CHNC$_5$H$_3$Me-5)}]. μ_{eff} 4.0 BM at 293 K. EPR (toluene, 298 K): $g = 2.00$.

Preparation of 7

Compound OC(Bu^t)(=2-CHNC$_5$H$_3$Me-6)$_2$ (1.00 g, 3.26 mmol) and NaH (0.08 g, 3.3 mmol) in THF (30 cm^3) were refluxed for 12 h. On cooling, the solution formed was transferred to an ampoule containing a mixture of [CrCl$_2$(THF)] (0.62 g, 3.2 mmol) and PhC≡CPh (0.57 g, 3.2 mmol) in CH$_2$Cl$_2$. Following refluxing for one week in a sealed ampoule, the volatiles were removed under reduced pressure and the residue was extracted into hot CH$_3$CN (*ca.* 40 cm^3). Standing at ambient temperature (1–2 days) afforded [ClCr{(μ-OC(Bu^t)(2-CH$_2$NC$_5$H$_3$Me-6)$_2$}CrCl] (**7**) as blue/green dichroic crystals. Yield: 0.90 g (69%). Anal. Calc. for C$_{40}$H$_{53}$Cr$_2$Cl$_2$N$_5$O$_2$.CH$_3$CN: C,

Table 6 Crystal data, data collection and refinement parameters for compounds **1**, **2**, **3**, **6** and **7**[a]

Data	**1**	**2**	**3**	**6**	**7**·MeCN
Formula	$C_{24}H_{32}N_2O_2Cr$	$C_{14}H_{18}N_2Cl_2Cr$	$C_{36}H_{48}N_3O_3Cr$	$C_{36}H_{48}N_3O_3Cr$	$C_{38}H_{50}N_4O_2Cl_2Cr_2$
Formula weight	432.5	337.2	622.8	622.8	810.8
Temperature/K	183	203	293	203	293
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	P_n (no. 7)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	19.883(4)	7.712(2)	10.957(2)	11.419(2)	16.147(2)
b/Å	10.235(1)	7.889(1)	18.642(3)	19.285(4)	11.936(2)
c/Å	11.578(2)	8.040(1)	16.593(3)	16.146(3)	21.325(4)
α/°	—	116.84(1)	—	—	—
β/°	93.89(2)	112.57(1)	90.94(2)	97.64(1)	92.90(2)
γ/°	—	93.81(1)	—	—	—
V/Å^3	2350.7(6)	385.5(1)	3389(1)	3524(1)	4105(1)
Z	4[b]	1[c]	4[d]	4	4
μ/mm^{-1}	0.51	1.08	3.07	2.95	0.70
Reflns measured	2045	1267	5298	5177	7147
Reflns obs., $\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$	1733	1114	4237	3100	3907
R_1, wR_2[e]	0.053, 0.142	0.027, 0.070	0.088, 0.217	0.065, 0.142	0.062, 0.116

[a] Details in common: graphite monochromated radiation, refinement based on F^2. [b] The molecule has crystallographic C_2 symmetry. [c] The molecule has crystallographic C_i symmetry. [d] There are two crystallographically independent molecules in the asymmetric unit. [e] $R_1 = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

59.2; H, 6.5; N, 8.6. Found: C, 58.5; H, 6.5; N, 8.6%. μ_{eff} 2.25 BM per Cr centre at 293 K. EPR (MeCN, 298 and 180 K): silent.

X-ray crystallographic studies

Table 6 provides a summary of the crystallographic data for compounds **1**, **2**, **3**, **6** and **7**. Data were collected on Siemens/Bruker P4 diffractometers using ω-scans, and the structures were refined based on F^2 using the SHELXTL program system.[25] The absolute structure of **3** was determined by a combination of R-factor tests and by use of the Flack parameter [$R_1^+ = 0.0881$, $R_1^- = 0.1024$, $x^+ = 0.00(2)$, $x^- = +1.00(2)$].

CCDC reference numbers 216348–216352.

See http://www.rsc.org/suppdata/dt/b3/b308881m/ for crystallographic data in CIF or other electronic format.

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