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Chromium(II) complexes bearing 2,6-substituted *N*,*N′*-diarylformamidinate ligands

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The synthesis, isolation and characterisation of several new chromium(II) complexes of the *N*,*N′*-bis(2,6-xylyl)-formamidinate ligand (DXylF) has been undertaken. The structure of three such complexes, namely Cr(DXylF)$_2$, **1**, Cr$_2$(μ-Cl)$_2$(DXylF)$_2$(THF)$_2$, **2**, and Cr$_2$(Ac)$_2$(DXylF)$_2$(THF)$_2$, **3**, have been determined by X-ray crystallography. It has been shown that the steric demands of the 2,6-xylyl group effectively discourage the formation of the homoleptic paddlewheel structure Cr$_2$(DXylF)$_4$: instead, the mononuclear (but stoichiometrically equivalent) complex Cr(DXylF)$_2$, **1** was obtained. It is likely that the unusual dichromium dichloride-bridged intermediate **2** also owes its stability to the presence of such bulky substituents. Although this complex does not possess a significant metal–metal bonding interaction [Cr–Cr = 2.612(1) Å], it has however, proven to be a useful starting material for the preparation of the novel quadruply bonded dichromium mixed acetate–formamidinate complex **3** [Cr–Cr (avg) = 2.339(7) Å]. In both **2** and **3**, the 2,6-xylyl groups force the formamidinate ligands to oppose one another contrary to the *trans* effect. In addition, it was found that compound **3** can be accessed from the chromium acetate starting material and, for comparison, an attempt was also made to prepare the *N*,*N′*-bis(*o*-anisyl)formamidinate (DPh$^{\mathrm{OMe}}$F) analogue. With the formamidinates occupying positions *cis* to one another and with the absence of axially coordinated THF ligands, the molecular structure of the resultant Cr$_2$(Ac)$_2$(DPh$^{\mathrm{OMe}}$F)$_2$, **4** [Cr–Cr = 2.037(1) Å], is different from that of **3**.

Introduction

The complexation of chromium(II) by amidinates typically results in the assembly of four bridging ligands about a quadruply bonded Cr$_2^{4+}$ core.[1] Such a construction brings these ligands and the substituents that they bear into very close proximity. One might anticipate that it should be possible to take advantage of steric interactions to hinder or even prohibit the formation of such paddlewheel species. Indeed, several studies exploring similar ideas can already be found in the literature.[2–5]

In 1977, it was shown that despite the utility of the reaction between Mo(CO)$_6$ and HDArF (*N*,*N′*-diarylformamidine, Ar = phenyl, *p*-tolyl, *m*-tolyl, *o*-tolyl, *p*-chlorophenyl and 3,5-xylyl) to form Mo$_2$(DArF)$_4$ compounds, no identifiable product could be obtained in the analogous reaction with the 2,6-xylyl derivative.[2] Predictably, a later study in 1998 using the 'super-amidine' ligand *N*,*N′*-bis(2,6-diisopropylphenyl)acetamidine (HDIPhA) also failed to produce the Mo$_2$(DIPhA)$_4$ compound, with (*N*-HDIPhA)Mo(CO)$_5$ and (η^6-HDIPhA)Mo(CO)$_3$ being isolated instead.[3]

In 1993, it was also shown that whereas the *N*,*N′*-bis-(cyclohexyl)formamidinate ligand (DCyF) reacts with CrCl$_2$ to form the familiar dinuclear complex Cr$_2$(DCyF)$_4$; the *N*,*N′*-bis(cyclohexyl)acetamidinate ligand (DCyA) reacts to form only the mononuclear rectangular-planar complex Cr(D-CyA)$_2$.[4] This result shows clearly how even a subtle change in the balance of *intra*-molecular steric interactions (by the introduction of a methyl group at the seemingly innocent amidinate carbon atom) can dramatically change the complexation behaviour of the ligand. Furthermore, the steric bulk of the amidinate can be increased to such an extent that even the rectangular planar complex is destabilised, as in the reaction of *N*,*N′*-bis(trimethylsilyl)benzamidinate ligand (DTMSB) with CrCl$_2$ for example, where a mononuclear flattened tetrahedral complex Cr(DTMSB)$_2$ is obtained instead.[5]

Recently in this laboratory, we have found that certain DArF ligands (Ar = *o*-chlorophenyl[6,7] and *o*-bromophenyl[7]) hinder but do not prevent the formation of the complex Cr$_2$(DArF)$_4$. In these cases, the intermediate complex Cr$_2$(μ-Cl)(DArF)$_3$ could be isolated *en route* to the *tetra*-formamidinate. This type of compound was unprecedented;[6] these Cr$_2$(μ-Cl)(DArF)$_3$ compounds are the first examples of A-frame complexes possessing quadruply bonded M$_2^{4+}$ moieties. Their isolation can possibly be attributed to the unique combination of both steric bulk and axial coordination provided by the formamidinate's *o*-chlorophenyl or *o*-bromophenyl substituents.[6,7]

Since there are six substituents for only two axial positions within the Cr$_2$Cl(DArF)$_3$ motif, four of the aromatic groups must locate a proton in the vicinity of the axial positions rather than a halide atom.[6,7] Thus, we wondered about the effects of giving the phenyl groups no choice about their orientation; *i.e.* to see how the substitution of all four *ortho* protons of the *N*,*N′*-diarylformamidinate ligand modifies its coordination chemistry. We report here some of our results obtained using the *N*,*N′*-bis(2,6-xylyl)formamidinate ligand (DXylF). The significant compounds described in this paper are summarised in Fig. 1.

Results and discussion

The reaction of two equivalents of LiDXylF with one equivalent of CrCl$_2$ in THF or toluene affords the red complex Cr(DXylF)$_2$, **1**. The molecular structure of compound **1** was determined by single-crystal X-ray diffraction and is illustrated in Fig. 2. Selected bond lengths and angles are listed in Table 1 while crystallographic data are shown in Table 2. The molecule resides on a centre of inversion. Rather than a dichromium *tetra*-formamidinate paddlewheel complex, a mononuclear planar complex of the same stoichiometry is the product of the

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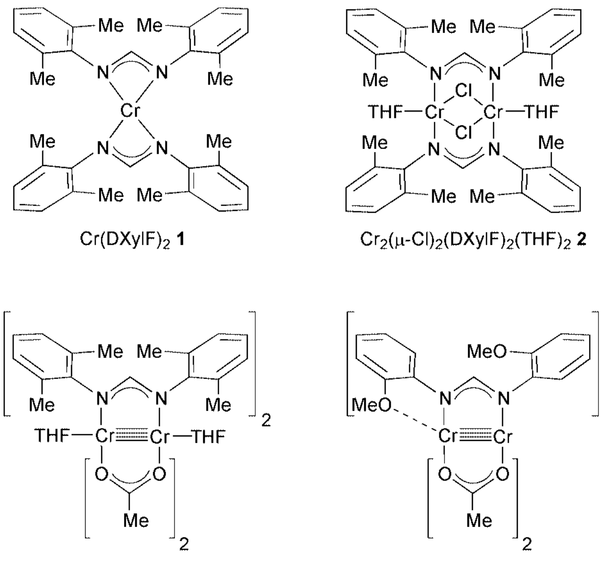
reaction. Fig. 2 clearly indicates that the complex is heavily distorted from the ideal square geometry. For example, the N(1)–N(2a) *inter*-ligand distance is much longer than the N(1)–N(2) *intra*-ligand (*cf.* 3.472(3) and 2.219(3) Å, respectively). Accordingly, the N(1)–Cr–N(2) angle is relatively acute at 65.2(1)°. Thus, the metal geometry is best described as rectangular rather than square. It is of note that the planes of the 2,6-xylyl groups do not lie perpendicular to the rectangular plane, but are inclined at 50.8(1)° [calculated from the intersection of the C(2)–C(6)–C(7) and the N(1)–Cr–N(2) planes].

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1**–**4**

1			
Cr–N(1)	2.075(2)	N(1)–Cr–N(2)	65.17(7)
Cr–N(2)	2.045(2)	N(1)–C(9)–N(2)	113.9(2)
		C(8)–N(1)–C(9)	125.2(2)
		C(9)–N(2)–C(10)	124.4(2)
2			
Cr(1)–Cr(1′)	2.612(1)	N(1)–Cr–N(2)	172.4(1)
Cr(1)–N(1)	2.078(2)	Cr(1)–Cl(1)–Cr(1′)	62.59(2)
Cr(1)–N(2)	2.072(2)	Cl(1)–Cr(1)–Cl(1′)	116.73(2)
Cr(1)–Cl(1)	2.370(1)	Cl(1)–Cr(1)–O(1)	149.36(6)
Cr(1)–Cl(1′)	2.596(1)	Cl(1′)–Cr(1)–O(1)	93.91(6)
Cr(1)–O(1)	2.124(2)	C(8)–N(1)–C(9′)	116.1(2)
		C(9)–N(2)–C(10)	116.0(2)
3			
Cr(A)–Cr(AA)	2.342(1)	N–Cr–O (avg)	90(3)
Cr(A)–Cr(BA)	2.342(1)	Cr–Cr–O_{axial} (avg)	178.9(9)
Cr(C)–Cr(CA)	2.329(1)	O–Cr–O (avg)	176.8(2)
Cr(D)–Cr(DA)	2.344(1)	N–Cr–N (avg)	179.3(3)
Cr–Cr (avg)	2.339(7)		
Cr–O (avg)	2.016(5)		
Cr–N (avg)	2.091(3)		
Cr···O_{axial} (avg)	2.31(1)		
4			
Cr(1)–Cr(2)	2.037(1)	N(1)–Cr(1)–O(5)	172.2(1)
Cr(1)–N(1)	2.023(4)	N(2)–Cr(2)–O(6)	176.4(1)
Cr(1)–N(3)	2.027(4)	N(3)–Cr(1)–O(7)	176.6(1)
Cr(2)–N(2)	2.035(3)	N(4)–Cr(2)–O(8)	171.6(1)
Cr(2)–N(4)	2.020(3)	Cr(1)–Cr(2)···O(4)	167.1(1)
Cr(1)–O(1)	2.353(3)	O(1)···Cr(1)–Cr(2)	166.4(1)
Cr(1)–O(5)	2.003(3)	C(7)–N(1)–C(8)	120.0(4)
Cr(1)–O(7)	2.017(3)	C(8)–N(2)–C(9)	116.8(4)
Cr(2)–O(4)	2.337(3)	C(22)–N(3)–C(23)	117.1(4)
Cr(2)–O(6)	2.016(3)	C(23)–N(4)–C(24)	121.6(4)
Cr(2)–O(8)	2.010(3)	N(1)–C(8)–N(2)	118.2(4)
		N(3)–C(23)–N(4)	118.6(4)
		O(5)–C(31)–O(6)	122.1(4)
		O(7)–C(33)–O(8)	122.6(4)



$Cr(DXylF)_2$ **1**

$Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$ **2**

trans-$Cr_2(DXylF)_2(Ac)_2(THF)_2$ **3**

cis-$Cr_2(DPh^{OMe}F)_2(Ac)_2$ **4**

Fig. 1 Schematic drawings of the compounds described in this paper.

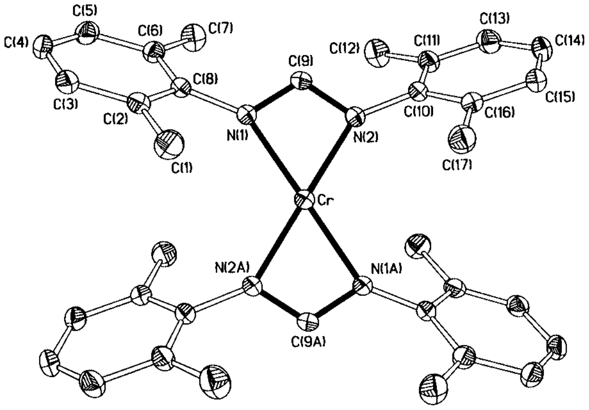


Fig. 2 The molecular structure of $Cr(DXylF)_2$, **1**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

Table 2 Crystallographic data for complexes **1**–**4**

	1	**2**	**3**·$0.5C_6H_5Me$	**4**·$2C_6H_5Me$
Formula	$C_{34}H_{38}CrN_4$	$C_{42}H_{54}Cl_2Cr_2N_4O_2$	$C_{49.5}H_{64}Cr_2N_4O_6$	$C_{48}H_{52}Cr_2N_4O_8$
M	554.68	821.79	915.05	916.94
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	8.529(1)	8.1949(2)	16.074(1)	18.424(4)
b/Å	8.890(1)	11.191(1)	17.903(2)	13.020(3)
c/Å	10.375(1)	11.708(1)	18.791(2)	20.308(4)
α/°	78.187(2)	88.543(4)	112.427(1)	90
β/°	81.956(2)	79.794(5)	98.266(2)	112.19(3)
γ/°	82.329(2)	71.665(6)	93.240(2)	90
V/Å^3	757.9(2)	1002.6(2)	4909.8(7)	4511(2)
ρ_{calc}/g cm^{-3}	1.215	1.361	1.238	1.350
μ/mm^{-1}	0.405	0.716	0.492	0.539
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073	0.71073
T/K	213(2)	213(2)	213(2)	213(2)
Z	1	1	4	4
$R1^1$, $R1^{2\,a}$	0.053, 0.144	0.037, 0.043	0.062, 0.171	0.067, 0.133
$wR2^1$, $wR2^{2\,a}$	0.068, 0.158	0.091, 0.096	0.098, 0.198	0.157, 0.160
GOF	1.036	1.087	1.091	1.005

[a] Superscript 1 denotes the value of the residual considering only the reflections for which $I > 2\sigma(I)$. Superscript 2 denotes the value of the residual for all reflections.

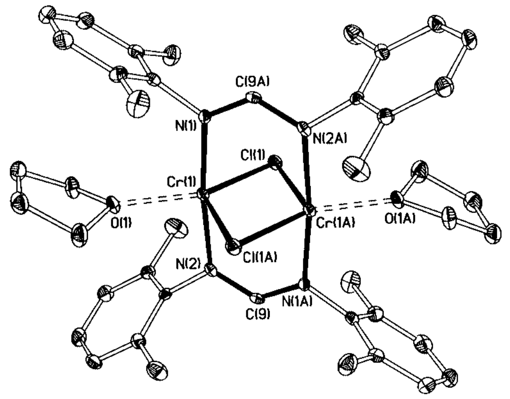


Fig. 3 The molecular structure of $Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$, **2**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

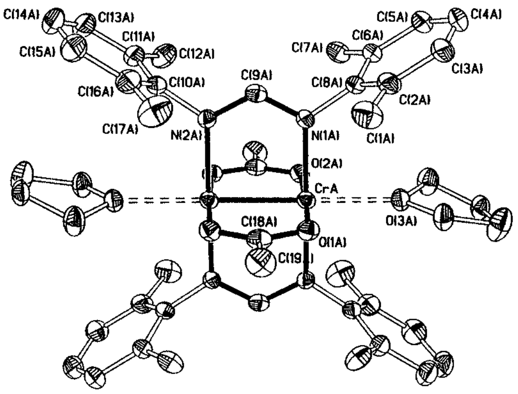


Fig. 4 The molecular structure of $Cr_2(Ac)_2(DXylF)_2(THF)_2$, **3**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

Presumably this twisting is attributable to crystal packing effects. Although the 2,6-xylyl groups are located at the periphery of the complex, it is apparent they have a profound effect upon the nature of the chromium environment. Clearly, the presence of the 2,6-xylyl groups prevents the construction of a paddlewheel structure since sixteen methyl groups cannot be accommodated over the two axial positions. Furthermore, the steric bulk provided by the 2,6-xylyl groups prevents the association of molecules of **1** into a non-bridged quadruply bonded species analogous to $Li_4[Cr_2(C_4H_8)_4]$, for example.[8] Compound **1** is obviously analogous to the *N*,*N′*-bis(cyclohexyl)acetamidinate complex $Cr(DCyA)_2$ discussed in the introductory remarks.[4]

In contrast, the reaction of equimolar amounts of LiDXylF and $CrCl_2$ in THF affords the blue complex $Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$, **2**. The analogous reaction in toluene does not result in an unsolvated version of compound **2**, rather the complex $Cr(DXylF)_2$, **1**, is obtained with half of the $CrCl_2$ remaining unreacted. The molecular structure of compound **2** was determined by single-crystal X-ray diffraction and is illustrated in Fig. 3. Selected bond lengths and angles are listed in Table 1 while crystallographic data are shown in Table 2. The unit cell contains a single molecule of **2** that resides on a centre of inversion. Compound **2** contains two chromium ions which are separated by 2.612(1) Å. This distance precludes the presence of significant metal–metal bonding interactions and accordingly compound **2** is found to be paramagnetic ($\mu_{eff} = 3.25\ \mu_B$ per metal atom perhaps indicating two unpaired electrons; *cf.* $\mu_{eff} = 4.77\ \mu_B$ per high-spin d^4 metal atom in **1**). Presumably, the proximity of the metal ions is enforced by the two bridging formamidinate and two bridging chloride ligands. The formamidinate ligands are found to be *trans* to one another presumably for steric reasons. As in compound **1**, the 2,6-xylyl groups in compound **2** are twisted, making an angle of 73.3(3)° to the Cr_2N_4 plane. The remainder of the coordination sphere is occupied by two THF molecules. These solvate ligands do not merely act as weak ‘axial’ donors: with a Cr–O separation of 2.124(2) Å, they are in fact tightly bound. Although it might appear that each chromium atom occupies a trigonal bipyramidal environment (as illustrated in Fig. 3), compound **2** is actually far less symmetrical than it seems. In particular, the Cr–Cl distances fall into two distinct long and short pairs at 2.370(1) and 2.596(1) Å, with each chromium atom possessing a contact of each type. The long Cr–Cl distances are found to be in the positions *cis* to the Cr–O bond while the short Cr–Cl distances are *trans*. It is interesting to compare these relationships with those observed in the paramagnetic and seemingly analogous dimethylphosphinomethane (DMPM) compound $Cr_2(\mu\text{-}Cl)_2(DMPM)_2Cl_2$.[9] In this latter compound, the trend is reversed with the long Cr–Cl distances [2.595(1) Å] at the positions *trans* to the terminal Cr–Cl bond while the short Cr–Cl distances [2.379(1) Å] are *cis*. It is unclear why two apparently similar compounds, $Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$, **2**, and $Cr_2(\mu\text{-}Cl)_2(DMPM)_2Cl_2$ are actually so dissimilar. This is perhaps a consequence of the metal–metal separation [2.612(1) and 3.237(1) Å, respectively] and Cl–Cr–Cl angle [116.73(2) and 98.92(4)°]. Both of these parameters are a function of the donor atom separation within the bidentate ligands [*cf.* N–N = 2.345(3) and P–P = 3.132(3) Å].

From a structural viewpoint the isolation of compound **2** was not what we sought. Our objective was to obtain a quadruply-bonded dichromium compound with just two bridging bidentate ligands. Although such a quadruply bridged compound might be obtained by the removal of the THF ligands from $Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$, **2**, by heating or by applying a vacuum, our efforts to date have not met with success: when compound **2** was heated under nitrogen, under reduced pressure, or in refluxing toluene, a green intractable material was obtained consistently. This material has not yet been identified.

Compound **2** has, however, already proven to be a useful starting material for another novel quadruply bonded species. The reaction of $Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$, **2**, with two equivalents of sodium acetate in THF affords the orange complex $Cr_2(Ac)_2(DXylF)_2(THF)_2$, **3**. The molecular structure of compound **3** was determined by single-crystal X-ray diffraction and is shown in Fig. 4. Selected bond lengths and angles are listed in Table 1 while crystallographic data are shown in Table 2. The structure is comprised of four independent but chemically equivalent molecules of **3** in addition to two toluene solvent molecules (one of which is disordered). Each of the four molecules of **3** resides on an inversion centre. The molecular structure of **3** consists of two chromium atoms [avg. Cr–Cr = 2.339(7) Å] which are spanned by two *trans* bridging formamidinate ligands and two *trans* bridging acetate ligands. The metal–metal bond is elongated owing to the presence of two axially coordinated THF ligands. With an average $Cr\cdots O_{axial}$ distance of 2.31(1) Å, the THF ligands in **3** are much less tightly coordinated than in $Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$, **2** [*cf.* 2.124(2) Å]. Two carbon atoms in each of the THF ligands were found to be disordered. Each disorder was modelled over two sites with equal occupancy.

Compound **3** is of significance because it is the first mixed formamidinate–acetate dichromium paddlewheel species. Moreover, all of the dimolybdenum analogues possess the *cis* conformation, with the exception of the acetamidinate compound $Mo_2(Ac)_2(DXylA)_2(THF)_2$ which appeared in the literature almost twenty years ago.[10]

Unfortunately a similar outcome could not be observed for the reactions of $Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$, **2**, and two equivalents of LiDXylF, lithium *N*,*N′*-bis(*o*-anisyl)formamidinate ($LiDPh^{OMe}F$) or lithium *N*,*N′*-bis(*o*-tolyl)formamidinate ($LiDPh^{Me}F$). The reaction with LiDXylF lead to mononuclear $Cr(DXylF)_2$, **1**, while the latter anisyl and tolyl derivatives gave

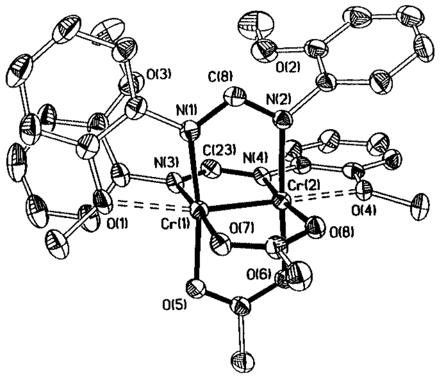


Fig. 5 The molecular structure of $Cr_2(Ac)_2(DPh^{OMe}F)_2$, **4**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

the homoleptic $Cr_2(DPh^{OMe}F)_4$ and $Cr_2(DPh^{Me}F)_4$ paddlewheel compounds along with $Cr(DXylF)_2$ in a 1 : 2 ratio. In the latter cases a disproportionation of the ligands occurred and the anticipated *trans* mixed formamidinate paddlewheel compounds were not obtained.

Since $Mo_2(Ac)_2(DXylA)_2(THF)_2$ was prepared from the reaction of LiDXylA and $Mo_2(Ac)_4$,[10] we decided to see whether the analogous reaction between LiDXylF and $Cr_2(Ac)_4$ in THF would also take place to afford the complex $Cr_2(Ac)_2(DXylF)_2(THF)_2$, **3**. Indeed it did and in higher yield (*cf.* 77% with 41% starting from **2**). For comparison, we also attempted the reaction of $LiDPh^{OMe}F$ and $Cr_2(Ac)_4$ in THF and obtained the compound $Cr_2(Ac)_2(DPh^{OMe}F)_2$, **4**. The molecular structure of **4** was determined by single-crystal X-ray diffraction and is shown in Fig. 5. Selected bond lengths and angles are listed in Table 1 while crystallographic data are shown in Table 2. The structure is comprised of one molecule of **4** along with two toluene solvent molecules. The complex consists of two quadruply bonded chromium atoms at a separation of 2.037(1) Å. The molecular structure of compound **4** differs from that of compound **3** in two major ways: firstly, the bridging formamidinate and acetate ligands have a cisoid relationship in **4**. Secondly, the THF ligands which considerably elongated the metal–metal bond in **3** are displaced by two of the four *o*-methoxyphenyl groups of the formamidinate [$Cr \cdots O =$ 2.337(3) and 2.353(3) Å; *cf.* 2.31(1) Å for **3**]. It is of note that the methoxyphenyl groups do not elongate the metal–metal bond as strongly as axial THF molecules. This is because the methoxyphenyl group is not as strong a σ donor as a THF molecule and also because the oxygen atom sits directly over the metal–metal axis in compound **3** whereas it is pulled off to one side by the formamidinate ligand in **4** [*cf.* $Cr–Cr \cdots O$ (avg) = 178.9(9) for **3** and 166.7(5)° for **4**]. The ^1H-NMR spectrum of **4** in C_6D_6 shows only a sharp singlet for the MeO protons ($\delta = 3.04$) illustrating that this conformation is not retained in C_6D_6 solution at room temperature. It is also of note that in the tetra-*N*,*N′*-bis(*o*-anisyl)formamidinate complex $Cr_2(DPh^{OMe}F)_4$ the Cr–Cr distance is 2.140(2) Å, almost 0.1 Å longer than in **4**.[8] In $Cr_2(DPh^{OMe}F)_4$, the metal–metal bond is elongated by two axial interactions between two *trans* formamidinate ligands. At 2.402(2) and 2.635(2) Å, the $Cr \cdots O$ contact distances in $Cr_2(DPh^{OMe}F)_4$ are surprisingly longer than in compound **4**. Since it is unlikely that the metal–metal bond length is dependent on whether the *cis* or the *trans* ligands provide the oxygen donors it may then be concluded that the acetate ligand actually has a slight shortening effect over the formamidinate.

Conclusions

It has been shown that the DXylF ligand forms a mononuclear complex $Cr(DXylF)_2$, **1**, with $CrCl_2$ rather than a dinuclear one containing a quadruply-bonded Cr_2^{4+} moiety presumably for steric reasons. However, this inhibition does not prevent the formation of other dinuclear species since the non-metal–metal bonded complex $Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$, **2**, is isolable, although it is still unclear why this molecule does not adopt a structure with a quadruple bond: Only compounds with three or four bridging bidentate ligands (with the exception of the non-bridged alkyls) have been observed with a dichromium quadruple bond. Compound **2**, however, does react with sodium acetate to form the mixed acetate–formamidinate complex *trans*-$Cr_2(Ac)_2(DXylF)_2(THF)_2$, **3**, which possesses a quadruple bond, but the related mixed formamidinate–formamidinate compounds do not appear to be accessible. Compound **3** can also be prepared from the chromium acetate starting material. With the preparation of *cis*-$Cr_2(Ac)_2(DPh^{OMe}F)_2(THF)_2$, **4**, this reaction has been established as a more general synthesis to novel mixed acetate–formamidinate species.

Experimental

Methods and materials

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk and drybox techniques unless otherwise stated. Solvents were purified by conventional methods from Na/K. The formamidines were prepared by the thermolysis at 130 °C of triethyl orthoformate in the presence of two equivalents of the appropriate aniline over 4 h. The white solids obtained were washed with large amounts of pentane before use. Other chemicals were purchased from Aldrich and used as received. Infrared spectra were recorded in the range 4000–1000 cm^{-1} on a Perkin-Elmer 16PC FTIR spectrometer using KBr pellets; NMR spectra were recorded on a Varian XL-200, spectrometer; while magnetic measurements were made using a Johnson Matthey magnetic susceptibility balance. Elemental analyses were satisfactory for all compounds.

Syntheses

$Cr(DXylF)_2$, 1. In a typical reaction, MeLi (1.02 cm^3, 1.6 M in diethyl ether, 1.63 mmol) was added dropwise to a suspension of anhydrous $CrCl_2$ (100 mg, 813 µmol) and HDXylF (410 mg, 1.63 mmol) in THF (20 cm^3). The light blue suspension changed gradually to a turbid red solution. After 6 h, the THF was then removed under vacuum and the solid red-purple residue washed with ice-cold hexanes (4 × 5 cm^3) before extraction into benzene (30 cm^3). After the benzene solution was filtered through Celite to ensure the removal of LiCl, the solvent was removed under vacuum to reveal a red powdery solid of $Cr(DXylF)_2$, **1**. Yield: 177 mg, 319 µmol, 39%. The analogous reaction in toluene required 18 h for completion.

$Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$, 2. MeLi (0.51 cm^3, 1.6 M in diethyl ether, 813 µmol) was added dropwise to a suspension of anhydrous $CrCl_2$ (100 mg, 813 µmol) and HDXylF (205 mg, 813 µmol) in THF (20 cm^3). The light blue suspension changed gradually to a dark blue solution. After 3 h, the THF was then removed under vacuum and the solid dark blue residue washed with ice-cold hexanes (4 × 5 cm^3) before extraction into benzene (30 cm^3). After the benzene solution was filtered through Celite to ensure the removal of LiCl, the solvent was removed under vacuum to reveal a dark blue powdery solid of $Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$, **2**. Yield: 139 mg, 169 µmol, 42%.

$Cr_2(Ac)_2(DXylF)_2(THF)_2$ 3. *From* 2. Anhydrous sodium acetate (67 mg, 813 µmol) in THF (20 cm^3) was added dropwise to $Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$ **2** (334 mg, 407 µmol) in THF (20 cm^3) by cannula transfer. The dark blue solution changed gradually to orange. After 4 h, the THF was removed under vacuum and the solid orange residue redissolved in benzene (30 cm^3).

After the benzene solution was filtered through Celite to ensure the removal of both LiCl and any unreacted sodium acetate, the solvent was removed under vacuum to reveal an orange polycrystalline solid of $Cr_2(Ac)_2(DXylF)_2(THF)_2$, **3**. Yield: 146 mg, 168 µmol, 41%.

From chromium acetate. In a typical reaction, MeLi (0.51 cm^3, 1.6 M in diethyl ether, 813 µmol) was added dropwise to a suspension of HDXylF (208 mg, 813 µmol) in THF (20 cm^3). This yellow solution was added in turn to a suspension of anhydrous chromium acetate (138 mg, 407 µmol) in THF (20 cm^3) by cannula transfer. The brown suspension turned gradually to orange. After 4 h, the product was isolated as described in the reaction of $Cr_2(\mu\text{-}Cl)_2(DXylF)_2(THF)_2$, **2**, and sodium acetate to reveal $Cr_2(Ac)_2(DXylF)_2(THF)_2$, **3**, an orange polycrytalline solid, yield: 272 mg, 313 µmol, 77%.

An analogous procedure using $DPh^{OMe}F$ (205 mg, 813 µmol) gave the complex $Cr_2(Ac)_2(DPh^{OMe}F)_2$, **4** (orange, yield: 247 mg, 337 µmol, 83%).

Spectroscopic data

1. +FABMS: $m/z = 554$ (M^+ calc. 554.9) with 304 ($M^+ -$ DXylF) and 253 ($DXylF^+$) observed. IR (KBr disk): $\nu/cm^{-1} =$ 1640 (m), 1605 (s), 1509 (s), 1373 (sh), 1362 (sh), 1290 (w), 1256 (w), 1245 (m) 1207 (s), 1185 (s), 1139 (w) and 1020 (s). Magnetic measurement: χ_{mol} (corrected molar susceptibility)/10^3 cgs = 9.726 and $\mu_{eff}/\mu_B = 4.77$. Calc. for $C_{34}H_{38}CrN_4$: C, 73.6; H, 6.9; N, 10.1%. Found: C, 73.8; H, 7.0; N, 10.0%.

2. +FABMS: $m/z = 412$ (M^{2+} calc. 410.9) with 253 ($DXylF^+$) observed. IR (KBr disk): $\nu/cm^{-1} = 1650$ (s), 1605 (s), 1570 (s), 1536 (s), 1405 (w), 1354 (m), 1264 (w), 1249 (w), 1236 (m) 1200 (w), 1177 (m) and 1034 (s). Magnetic measurement: χ_{mol} (corrected molar susceptibility)/10^3 cgs = 8.945 and $\mu_{eff}/\mu_B = 4.59$ (3.25 per chromium atom). Calc. for $C_{42}H_{54}Cl_2Cr_2N_4O_2$: C, 61.4; H, 6.6; N, 6.8%. Found: C, 60.9; H, 6.2; N, 7.2%.

3. +FABMS: $m/z = 868$ (M^+ calc. 869.0) with 726 ($M^+ -$ 2THF, largest intensity ion peak) and 363 ($M^{2+} -$ 2THF) observed. IR (KBr disk): $\nu/cm^{-1} = 1629$ (s), 1607 (vs), 1560 (s), 1545 (s), 1486 (s), 1475 (s), 1441 (s), 1347 (vs), 1340 (sh), 1327 (s), 1319 (s), 1282 (m), 1267 (s), 1170 (s), 1158 (s), 1104 (m), 1060 (m), 1043 (sh), 1032 (s) and 1017 (s). ^{1}H-NMR (C_6D_6): δ 8.65 (s, 2H, form), 6.96 (d, 8H, Ar, $J = 7.6$ Hz), 6.19 (t, 4H, Ar, $J = 7.6$ Hz), 3.41 (br s, 8H, THF), 2.46 (s, 6H, Ac), 2.29 (s, 24H, Me) and 1.13 (br s, 8H, THF). Calc. for $C_{46}H_{60}Cr_2N_4O_6 \cdot 0.5C_6H_5Me$: C, 65.0; H, 7.1; N, 6.1%. Found: C, 64.4; H, 6.6; N, 6.5%.

4. +FABMS: $m/z = 732$ (M^+ calc. 732.9) with 673 ($M^+ -$ Ac) and 477 ($M^+ -$ DXylF) observed. IR (KBr disk): $\nu/cm^{-1} =$ 1634 (m), 1605 (s), 1558 (s), 1539 (s), 1486 (s), 1440 (s), 1347 (vs), 1322 (vs), 1280 (m), 1242 (s), 1199 (s), 1176 (s), 1111 (m), 1043 (m), 1022 (s). ^{1}H-NMR (C_6D_6): δ 9.01 (s, 2H, form), 6.98–6.87 (m, 12H, Ar), 6.69 (t, 4H, Ar, $J = 7.7$ Hz), 3.04 (s, 12H, OMe) and 2.39 (s, 6H, Ac). Calc. for $C_{34}H_{36}Cr_2N_4O_8 \cdot 2C_6H_5Me$: C, 62.9; H, 5.7; N, 6.1%. Found: C, 62.3; H, 5.4; N, 6.4%.

Crystallographic studies

Single crystals suitable for X-ray diffraction measurements were obtained from concentrated toluene solutions at −20 °C. Crystallographic data for complexes **1**, **3**$\cdot 0.5C_6H_5Me$ and **4**$\cdot 2C_6H_5Me$ were collected on a Bruker SMART 1000 diffractometer, and for **2** on a Nonius FAST diffractometer. Both machines are equipped with a low temperature device. Crystallographic details are given in Table 2.

Structure solution and refinement. The positions of the metal atoms and their first coordination spheres were determined by direct methods and refined against F^2 using SHELXL-93.[11] All non-hydrogen atoms were found by successive iterations of least-squares refinement. Hydrogen atoms were added in calculated positions and allowed to ride on their parent atoms unless they appeared in difference maps. For crystalline **1**, **2** and **4**$\cdot 2C_6H_5Me$, all of the non-hydrogen atoms were refined anisotropically. For crystalline **3**$\cdot 0.5C_6H_5Me$ toluene, however, this was with the exception of several carbon atoms belonging to the disordered THF ligands and the disordered toluene solvate; each disorder was modelled over two sites and the atoms refined at half occupancy.

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