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

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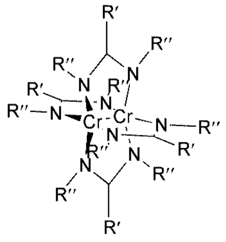
A study regarding the interaction of several *ortho* ring-substituted *N*,*N*′-diarylformamidinate ligands (DPh^{X}F, X = Me, OMe, Cl and Br) with the Cr_2^{4+} moiety has been undertaken. X-Ray diffraction and spectroscopic data have shown that while all of these ligands form the well-known paddlewheel type complex $Cr_2(DPh^XF)_4$, **1** [X = Me, OMe, Cl and Br; Cr–Cr = 1.925(1), 2.140(2), 2.208(2) and 2.272(2) Å, respectively], two of them form highly unusual A-frame type complexes with short Cr–Cr bonds, and the smallest M–X–M angle ever reported in an A-frame structure. These are $Cr_2(\mu\text{-}Cl)(DPh^XF)_3$, **2** [X = Cl and Br; Cr–Cr = 1.940(1) and 1.940(2) Å, respectively]. For some of the paddlewheel complexes, the elongation of the metal–metal bond distance out of the 'super-short' range (Cr–Cr > 2.00 Å) has been attributed to the presence of axial interactions between two of the *ortho* substituents and the Cr_2^{4+} moiety.

Introduction

Amidinate complexes of Cr(II) are now well known.[1–8] Most prevalent are those compounds that possess a quadruply bonded Cr_2^{4+} unit surrounded by four bridging amidinate ligands.[1–7] This class of complex, shown schematically in Fig. 1, is known as the 'paddlewheel' because of its structural characteristics.[1] Although the earliest dichromium *tetra*-amidinate complex to be structurally characterised was that of the *N*,*N*′-diphenylacetamidinate ligand (R″NCR′NR″; R′ = Me and R″ = Ph),[2] the formamidinate ligands (R′ = H) have found much greater application. This is because the synthetic methods available allow a wider variation in the substituent R″ of the formamidinate ligand. For example, formamidinate paddlewheel complexes bearing *p*-tolyl,[3] cyclohexyl,[4] *m*-$MeOC_6H_4$,[5] *p*-ClC_6H_4,[5] 3,5-$Cl_2C_6H_3$[5] and 3,5-$Me_2C_6H_3$[6] groups have all been structurally characterised (to name but a few). It is of note that in all of these compounds the Cr–Cr distances do not exceed 1.93 Å. The implication is that the basicity of the formamidinate ligand has little influence upon the metal–metal separation.

More recently, however, we have shown that whenever *ortho* fluoro substituents are present in the aromatic groups of an *N*,*N*′-diarylformamidinate ligand (DPh^{X}F), there *is* a significant lengthening of the metal–metal bond.[7] For example, in the *tetra*-formamidinate paddlewheel complexes $Cr_2(DPh^FF)_4$ (R′ = H and R″ = *o*-fluorophenyl) and $Cr_2(DPh^{5F}F)_4$ (R′ = H and R″ = pentafluorophenyl) the Cr–Cr distances were found to be 1.968(2) and 2.012(1) Å, respectively.[7] The elongation of the metal–metal bond did not occur because of a reduction in ligand basicity, but rather because of the presence of Cr···F axial interactions. For these fluorinated derivatives, it was unclear whether the axial interactions were of σ* or π* character or both. Our parallel work with the 2,6-bis(phenylimino)piperidinate ligand (DPhIP), however, showed that intramolecular π* coordination alone can account for a dramatic elongation of a metal–metal bond. For example, in the complex $Cr_2(DPhIP)_4$, four off-axis Cr···N interactions elongate the Cr–Cr bond to 2.265(1) Å.[9]



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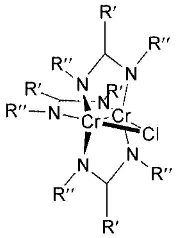
1a: R′ = H, R″ = *o*-C_6H_4Me (X = Me)
1b: R′ = H, R″ = *o*-C_6H_4OMe (X = OMe)
1c: R′ = H, R″ = *o*-C_6H_4Cl (X = Cl)
1d: R′ = H, R″ = *o*-C_6H_4Br (X = Br)



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2c: R′ = H, R″ = *o*-C_6H_4Cl (X = Cl)
2d: R′ = H, R″ = *o*-C_6H_4Br (X = Br)

Fig. 1 Schematic representations of the paddlewheel **1** and the A-frame **2** structures discussed in this paper. The chromium atoms are quadruply bonded.

When we extended our study to *N*,*N*′-diarylformamidinate ligands bearing *ortho* chloro substituents instead, our (initial) findings were quite unexpected.[8] We observed that three equivalents of LiDPh^{Cl}F reacted with two equivalents of $CrCl_2$ to afford the unprecedented A-frame complex $Cr_2(\mu\text{-}Cl)(DPh^{Cl}F)_3$, **2c**. In this compound, one chloride and three formamidinate ligands bridge a dichromium unit (see Fig. 1, R′ = H and R″ = *o*-C_6H_4Cl). This was unusually interesting

Table 1 Selected bond lengths (Å) for complexes **1a**–**1d** and **2d**. X is the substituent of the aryl group

	1a	**1b**	**1c**	**1d**	**2d**
Compound	$Cr_2(DPh^{Me}F)_4$	$Cr_2(DPh^{OMe}F)_4$	$Cr_2(DPh^{Cl}F)_4$	$Cr_2(DPh^{Br}F)_4$	$Cr_2Cl(DPh^{Br}F)_3$
Cr–Cr	1.925(1)	2.140(2)	2.208(2)	2.272(2)	1.940(2)
Cr–N	2.045(4)–2.094(4)	2.053(7)–2.104(7)	2.065(8)–2.091(8)	2.048(8)–2.099(8)	2.064(7)–2.019(7)
Cr–X	—	2.402(2), 2.635(2)	2.766(2)	2.890(3), 2.943(2)	2.865(2), 2.842(2)

Table 2 Crystallographic data for complexes **1a**–**1d** and **2d**

	1a	**1b**	**1c**	**1d**·$2C_6H_5Me$	**2d**
Formula	$C_{60}H_{60}Cr_2N_8$	$C_{60}H_{60}Cr_2N_8O_8$	$C_{52}H_{36}Cl_8Cr_2N_8$	$C_{66}H_{52}Br_8Cr_2N_8$	$C_{39}H_{27}Br_6ClCr_2N_6$
M	997.16	1125.16	1160.49	1700.44	1198.58
Space group	$P\bar{1}$	$P2_1$	$C2/c$	$P\bar{1}$	$C2/c$
a/Å	10.743(2)	10.900(2)	19.313(2)	13.051(1)	19.60(1)
b/Å	14.242(3)	20.524(4)	11.971(3)	13.716(1)	19.157(5)
c/Å	18.073(4)	12.330(3)	22.833(6)	20.714(1)	22.02(1)
α/°	76.39(3)	90	90	105.937(1)	90
β/°	74.84(3)	93.52(3)	110.48(2)	96.117(1)	100.67(3)
γ/°	81.95(3)	90	90	112.520(1)	90
V/Å^3	2585(1)	2753(1)	4945(2)	3198.3(3)	8125(6)
ρ_{calc}/g cm^{-3}	1.281	1.357	1.559	1.765	1.96
μ/mm^{-1}	0.648	0.458	0.919	5.384	6.54
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073	0.71073	0.71073
T/K	158(2)	166(2)	213(2)	213(2)	138(2)
Z	2	2	4	2	8
$R1^1$, $R1^{2a}$	0.050, 0.092	0.047, 0.082	0.120, 0.146	0.078, 0.252	0.057, 0.144
$wR2^1$, $wR2^{2a}$	0.123, 0.139	0.100, 0.113	0.230, 0.253	0.161, 0.191	0.094, 0.163
GOF	1.071	1.091	1.354	1.042	1.179

[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.

because it was the only example of an A-frame complex possessing a quadruply bonded M_2^{4+} moiety;[8] all other known A-frame complexes have long metal–metal separations.[10] At first, we believed that the stability of this compound may have been a consequence of the bulky nature of the *o*-chlorophenyl rings and that the paddlewheel complex might be inaccessible because there was insufficient space to add a fourth DPh^{Cl}F ligand across the dichromium unit. Our further work involving the DPh^{Cl}F ligand, however, has shown that the *tetra*-formamidinate $Cr_2(DPh^{Cl}F)_4$ is indeed accessible. In this paper, we wish to report this work and also some other significant results obtained during the course of our studies into the complexation behaviour of *ortho* ring substituted *N*,*N*′-di(phenyl)formamidinate ligands (DPh^{X}F; X = Me, OMe, Cl and Br) toward Cr(II). In particular, we have employed ligands that have substituents of differing sizes and electronegativities to explore the phenomenon of *intra*-molecular axial ligation. These results are summarised in Fig. 1.

Results and discussion

In analogy to the reaction involving LiDPh^{Cl}F,[8] the reaction of three equivalents of LiDPh^{Br}F with two equivalents of $CrCl_2$ in THF affords the green complex $Cr_2(\mu\text{-}Cl)(DPh^{Br}F)_3$, **2d**. The molecular structure of **2d** was determined by single-crystal X-ray diffraction and is illustrated in Fig. 2. Selected bond lengths are listed in Table 1 while crystallographic data are shown in Table 2. The molecular structure of compound **2d** was found to be isostructural with the *ortho* chloro derivative $Cr_2(\mu\text{-}Cl)(DPh^{Cl}F)_3$, **2c**.[9] The Cr–Cr distance of 1.940(2) Å [*cf.* 1.940(1) Å for **2c**] is within the normal range for a 'super-short' quadruple bond despite the presence of two weak axial Cr ··· Br interactions. The two mutually *trans* formamidinate ligands provide one bromine donor atom each at 2.865(2) and 2.842(2) Å for Cr(1) ··· Br(1) and Cr(2) ··· Br(6), respectively [*cf.* 2.741(2) and 2.778(2) Å for the analogous Cr ··· Cl distances in **2c**]. The very short intermetallic separation in **2d** makes the Cr–Cl–Cr angle very acute at 46.53(8)° [*cf.* 46.67(2)° for **2c**] and the Cr–Cl distances slightly elongated at 2.454(3) and 2.458(3) Å [*cf.* 2.441(1) and 2.440(1) Å for **2c**]. The chromium–nitrogen distances can be divided into two sets since the formamidinate ligand *trans* to the bridging chlorine atom is more tightly bound than the formamidinate groups that are *cis* [*cf.* Cr–N$_t$ ≈ 2.02(1) and Cr–N$_c$ ≈ 2.06(1) Å]. It is of note that **2c** and **2d** are exceptional compounds in that they are the only examples in which a chloride ligand bridges a quadruply bonded dimetallic unit. Because of the shortness of the M–M distance, these complexes display the most acute M–X–M angle ever seen in an A-frame structure.

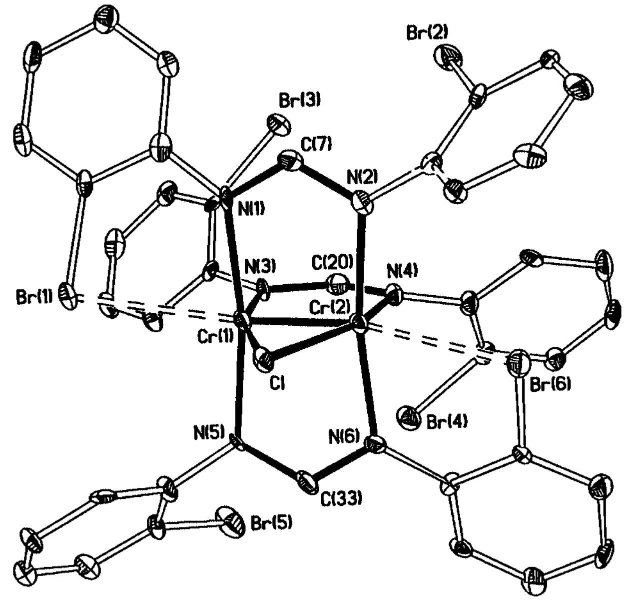

Fig. 2 A drawing of the molecular structure of $Cr_2(\mu\text{-}Cl)(DPh^{Br}F)_3$, **2d**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

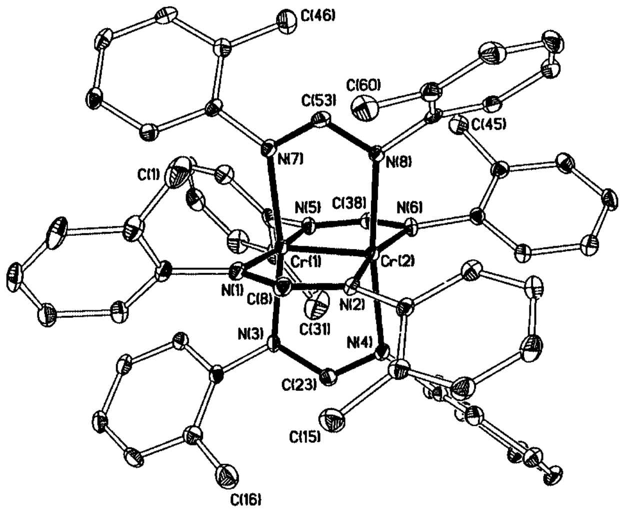

Fig. 3 A drawing of the molecular structure of $Cr_2(DPh^{Me}F)_4$, **1a**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

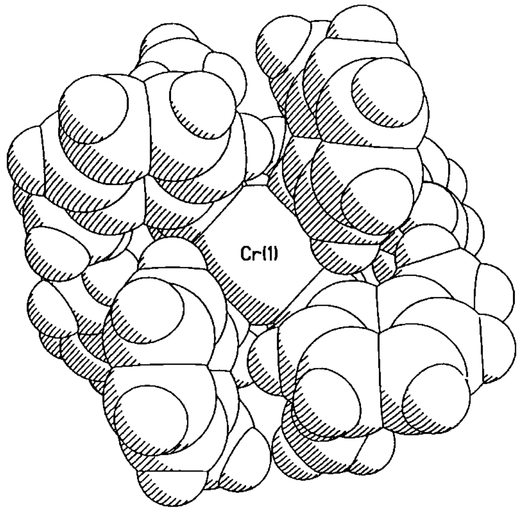

Fig. 4 A space-filling model of the molecular structure of $Cr_2(DPh^{Me}F)_4$, **1a** as viewed down the metal–metal axis.

There is a clear distinction in the ^{1}H-NMR spectrum of compound **2d** (in C_6D_6 at room temperature) between the signals arising from protons belonging to the formamidinate ligands *cis* to the bridging chlorine atom and those belonging to the formamidinate that is *trans*. The intensity ratio of the *cis* signal to the corresponding *trans* peak is 2 : 1 as in the spectrum of compound **2c** under identical conditions. However, while all of the signals attributable to the *cis* ligand appear at higher field than their *trans* counterparts for **2c**, this is not true for compound **2d**. For example, the methyne resonances of the *cis* and *trans* ligands in **2c** appear at δ 8.55 and 8.49, respectively, whereas in **2d** they are observed at δ 8.45 and 8.82, respectively.

The reaction of three equivalents of $LiDPh^{Me}F$ with two of $CrCl_2$ in THF or benzene does not afford the analogous chloride-bridged species; rather the orange complex $Cr_2(DPh^{Me}F)_4$, **1a**, is obtained even at −78 °C. This compound is, however, best prepared by the reaction of two equivalents of $LiDPh^{Me}F$ with one of $CrCl_2$. The molecular structure of compound **1a** was determined by single-crystal X-ray diffraction. Selected bond lengths and angles are listed in Table 1 while crystallographic data are shown in Table 2. From Fig. 3, it can be seen that each molecule has D_4 symmetry with all of the methyl groups oriented away from the C_4 axis (the Cr–Cr bond). Although compound **1a**, with its Cr–Cr distance of 1.925(1) Å, is a rather unremarkable example of a dichromium *tetra*-formamidinate complex, its very existence raised some interesting questions. Firstly, we had already observed that the reaction of three equivalents of $LiDPh^{Cl}F$ with two of $CrCl_2$ in THF gave $Cr_2(\mu\text{-}Cl)(DPh^{Cl}F)_3$, **2c**, but since the chlorine atom is of comparable size to a methyl group we wondered if the reaction of four $LiDPh^{Cl}F$ molecules with two of $CrCl_2$ could proceed to form $Cr_2(DPh^{Cl}F)_4$, **1c**.[9] Secondly, an inspection of the space-filling representation of $Cr_2(DPh^{Me}F)_4$, **1a** (see Fig. 4), shows that it is unlikely that a paddlewheel structure can be formed using an *N*,*N*′-diarylformamidinate ligand which has methyl groups in all four *ortho* positions. The former question will be answered here while the latter forms the subject of the following paper.[11]

It was found that the reaction of two equivalents of the lithiated *cis* ring-substituted formamidinates $LiDPh^{OMe}F$, $LiDPh^{Cl}F$ and $LiDPh^{Br}F$ with one equivalent of $CrCl_2$ in THF or benzene affords the corresponding paddlewheel complex $Cr_2(DPh^XF)_4$, **1*x***, in each case.

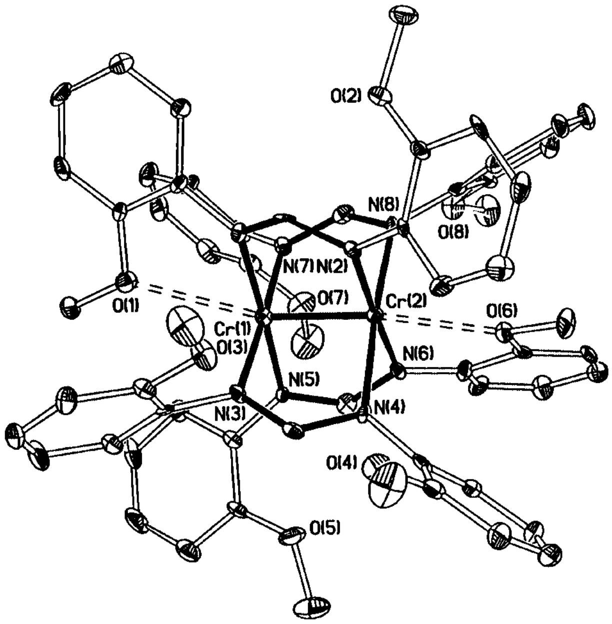

Fig. 5 A drawing of the molecular structure of $Cr_2(DPh^{OMe}F)_4$, **1b**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

The molecular structure of $Cr_2(DPh^{OMe}F)_4$, **1b**, was determined by single-crystal X-ray diffraction and is illustrated in Fig. 5. Selected bond lengths and angles are listed in Table 1 while crystallographic data are shown in Table 2. The molecules of **1b** pack in the non-centrosymmetric space group $P2_1$. At 2.140(2) Å, the Cr–Cr bond length in $Cr_2(DPh^{OMe}F)_4$, **1b**, is almost 0.2 Å longer than that in $Cr_2(DPh^{Me}F)_4$, **1a**. This elongation can be attributed to the presence of axial interactions between the oxygen donor atoms of the methoxy substituents and the dichromium unit. Only two of the eight methoxy groups (one each from a pair of mutually *trans* formamidinate ligands) are turned in over the axial sites at distances of 2.635(2) and 2.402(2) Å [Cr(1)···O(1) and Cr(2)···O(6), respectively]. It is of note that the oxygen donor atoms in compound **1b** do not sit directly over the Cr–Cr axis as in, for example, the acetate complex $Cr_2Ac_4(H_2O)_2$[12] [Cr–Cr = 2.288(2) Å]. They are pulled off to one side by the formamidinate ligands such that Cr(2)–Cr(1)···O(1) = 156.6(1)° and Cr(1)–Cr(2)···O(6) = 160.4(2)°. The ^{1}H-NMR spectrum in C_6D_6 shows only a sharp singlet at δ 3.05 for all of the methoxy groups. This is an indication that the solid state conformation is not retained in solution at room temperature. Presumably, the time-averaged equivalency of the methoxy groups arises from a rotation among the *o*-anisyl rings.

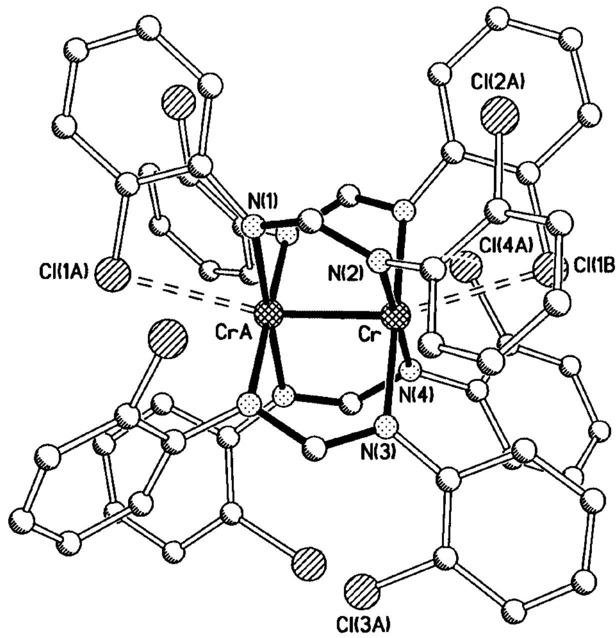

Fig. 6 A drawing of the molecular structure of $Cr_2(DPh^{Cl}F)_4$, **1c**. Only one orientation of each of the disordered *o*-chlorophenyl groups is depicted. Hydrogen atoms omitted for clarity.

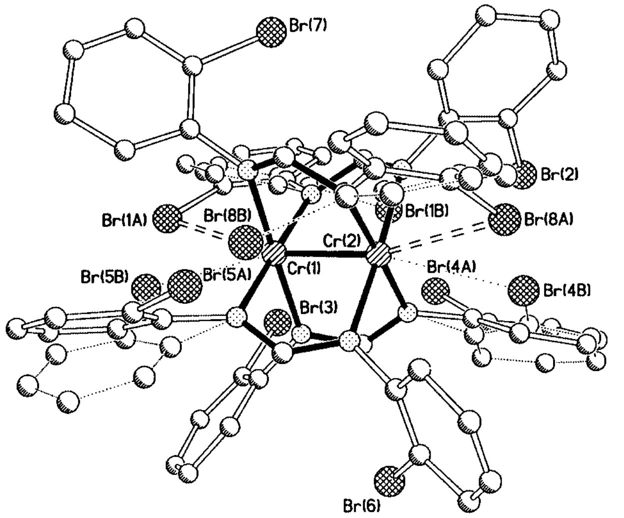

Fig. 7 A drawing of the molecular structure of $Cr_2(DPh^{Br}F)_4$, **1d**, illustrating the disorder of the *o*-bromophenyl groups. Hydrogen atoms omitted for clarity.

The structures of $Cr_2(DPh^{Cl}F)_4$, **1c**, and $Cr_2(DPh^{Br}F)_4$, **1d**, were determined by single-crystal X-ray diffraction. Although they do not form isomorphous crystals, the molecular structures of $Cr_2(DPh^{Cl}F)_4$, **1c**, and $Cr_2(DPh^{Br}F)_4$, **1d**, ($C2/c$ and $P\bar{1}$, respectively) are very similar. Selected bond lengths and angles are listed in Table 1 while crystallographic data are shown in Table 2. Molecules of **1c** reside on inversion centres, while molecules of **1d** occupy general positions. Co-crystallised along with **1d** are two equivalents of disordered toluene solvate molecules. All of the *o*-halogenophenyl groups in **1c** were found to be disordered over two orientations (see Fig. 6). In **1d**, only the *o*-halogenophenyl groups involved in axial ligation were disordered (see Fig. 7). However, it can be discerned that two of the halogen groups from a *cis* pair of formamidinate ligands interact with the dichromium moiety in both compounds [$Cr(A)\cdots Cl(2A) = 2.766(2)$ Å; and $Cr(1)\cdots Br(1A) = 2.890(3)$ and $Cr(2)\cdots Br(8A) = 2.943(2)$ Å]. As a consequence, the Cr–Cr bonds are considerably elongated to 2.208(2) and 2.272(2) Å, respectively. This means that among all the dichromium paddlewheel compounds that are supported only by bidentate nitrogen donor ligands and no direct axial coordination, the $Cr_2(DPh^{Br}F)_4$, **1d**, molecule possesses the longest metal–metal bond observed to date. Accordingly crystals of **1d** actually appear green rather than orange. It is of importance to repeat here that the bond lengths in the related A-frame compounds **2c** and **2d** are 1.940(1) and 1.940(2) Å, while for **1c** and **1d** they are 2.208(2) and 2.272(2) Å, respectively. The inference here is that the bridging chloride groups in $Cr_2(\mu\text{-}Cl)(DPh^{Cl}F)_3$, **2c**, and $Cr_2(\mu\text{-}Cl)(DPh^{Br}F)_3$, **2d**, counteract the Cr–Cr lengthening effect of axial ligation observed in $Cr_2(DPh^{Cl}F)_4$, **1c**, and $Cr_2(DPh^{Br}F)_4$, **1d**.

In analogy to $LiDPh^{Me}F$, it was found that the reaction of three equivalents of $LiDPh^{F}F$ or $LiDPh^{OMe}F$ with two of $CrCl_2$ in THF or benzene does not afford the appropriate chloride-bridged species even at −78 °C. Again only a *tetra*-formamidinate species could be isolated. It is unclear why A-frame type complexes for the ligands $DPh^{X}F$ (X = Me, OMe and F) have not yet been isolated.

Conclusions

In this paper we have shown that the presence of donor groups at the *ortho* position on the phenyl rings of an *N*,*N*′-diarylformamidinate can significantly lengthen the chromium–chromium bond in the paddlewheel type complexes $Cr_2(DPh^{X}F)_4$, **1*x***. This is not the case for the A-frame compounds $Cr_2(\mu\text{-}Cl)(DPh^{Cl}F)_3$, **2c**, and $Cr_2(\mu\text{-}Cl)(DPh^{Br}F)_3$, **2d**, in which the chromium–chromium bond remains in the ‘super-short’ range despite the presence of comparable axial interactions. These latter A-frame compounds are intermediates *en route* to the former paddlewheel compounds. It appears that the stabilisation of these intermediates is possible only for the Cl and Br derivatives among those *N*,*N*′-diarylformamidinates studied but there is no clear reason why. It is perhaps the consequence of a delicate interplay of axial ligation and steric interactions. We have also shown that three isomers are possible for the paddlewheel compounds in the solid state. These are the m-*exo* isomer (Me) where all of the substituents are turned away from the metal–metal axis; the *trans*-m-*endo* (OMe) where two of the substituents from a *trans* pair of ligands are turned in; and the *cis*-m-*endo* isomer (Cl and Br) where two of the substituents from a *cis* pair of ligands are turned in. The methoxy proton equivalency observed in the ^1H-NMR spectrum of $Cr_2(DPh^{OMe}F)_4$, **1b**, however, indicates that these conformations are probably not retained in solution at room temperature. Our research into similarly ligated dimetallic species is ongoing in an effort to rationalise our observations further.

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 while NMR spectra were recorded on a Varian XL-200 spectrometer.

Syntheses

Type 1: paddlewheel complexes. 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 HDPh^{Me}F (365 mg, 1.63 mmol) in THF (20 cm^3). The gray suspension changed gradually to a turbid orange solution. After 3 h, the THF was removed under vacuum and the solid yellow residue washed with warm hexanes (3 × 20 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 leave an orange polycrystalline solid, Cr$_2$(DPh^{Me}F)$_4$, **1a**. Yield: 219 mg, 220 µmol, 54%. Analogous procedures using HDPh^{OMe}F (417 mg, 1.63 mmol), HDPh^{Cl}F (432 mg, 1.63 mmol) or HDPh^{Br}F (577 mg, 1.63 mmol) gave the complexes Cr$_2$(DPh^{OMe}F)$_4$, **1b** (orange, yield: 271 mg, 241 µmol, 59%), Cr$_2$(DPh^{Cl}F)$_4$, **1c** (orange, yield: 187 mg, 161 µmol, 40%) or Cr$_2$(DPh^{Br}F)$_4$, **1d** (green, yield: 305 mg, 201 µmol, 49%).

Type 2: A-frame complexes. In a typical reaction, MeLi (0.76 cm^3, 1.6 M in diethyl ether, 1.22 mmol) was added dropwise to a suspension of anhydrous CrCl$_2$ (100 mg, 813 µmol) and HDPh^{Cl}F (323 mg, 1.22 mmol) in THF (20 cm^3). The gray suspension changed gradually to a turbid green solution. After 3 h, the THF was removed under vacuum and the solid green residue washed with warm hexanes (320 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 leave a green polycrystalline solid, Cr$_2$(µ-Cl)(DPh^{Cl}F)$_3$, **2c**. This is a modification of the published procedure. Yield: 143 mg, 154 µmol, 38%. An analogous procedure using HDPh^{Br}F (431 mg, 1.22 mmol) gave the complex [Cr$_2$(µ-Cl)(HDPh^{Br}F)$_3$] **2d** (green, yield: 234 mg, 195 µmol, 48%).

Spectroscopic data

[Cr$_2$(DPh^{Me}F)$_4$] 1a. +FABMS: *m*/*z* = 996 (M$^+$ calc. 997.1) and 498 (M^{2+}) observed. IR (KBr disk): *ν*/cm^{-1} = 1631(s), 1612(s), 1590(m), 1507(s), 1424(m), 1339(m), 1263(w), 1203(w), 1139(m) and 1039(m). ^{1}H-NMR (C$_6$D$_6$): *δ* 8.57 (s, 4H, form), 6.98 (d, 8H, Ar, *J* = 7.7 Hz), 6.82 (t, 8H, Ar, *J* = 7.7 Hz), 6.65 (t, 8H, Ar, *J* = 7.7 Hz), 6.07 (d, 8H, Ar, *J* = 7.7 Hz) and 2.19 (s, 24H, Me). Calc. for $C_{60}H_{60}Cr_2N_8$: C, 72.3; H, 6.1; N, 11.2. Found: C, 72.1; H, 6.0; N, 11.0%.

[Cr$_2$(DPh^{OMe}F)$_4$] 1b. +FABMS: *m*/*z* = 1124 (M$^+$ calc. 1125.2), 869 (M$^+$ − DPh^{OMe}F) and 562 (M^{2+}) observed. IR (KBr disk): *ν*/cm^{-1} = 1624(s), 1606(s), 1584(s), 1509(s), 1444(m), 1428(w), 1376(m), 1331(m), 1263(w), 1243(w), 1199(w), 1110(m) and 1019(w). ^{1}H-NMR (C$_6$D$_6$): *δ* 8.91 (s, 4H, form), 6.84–6.72 (m, 16H, Ar), 6.53 (t, 8H, Ar, *J* = 8.0 Hz), 6.18 (d, 8H, Ar, *J* = 8.0 Hz) and 3.05 (s, 24H, OMe). Calc. for $C_{60}H_{60}Cr_2N_8O_8$: C, 64.0; H, 5.4; N, 10.0. Found: C, 64.1; H, 5.3; N, 10.2%.

[Cr$_2$(DPh^{Cl}F)$_4$] 1c. +FABMS: *m*/*z* = 1160 (M$^+$ calc. 1160.5), 896 (M$^+$ − DPh^{Cl}F), 580 (M^{2+}) and 387 (M^{3+}) observed. IR (KBr disk): *ν*/cm^{-1} = 1617(m), 1613(s), 1590(m), 1571(s), 1498(s), 1457(w), 1340(m), 1260(m), 1227(m), 1194(w), 1125(w) and 1034(m). ^{1}H-NMR (C$_6$D$_6$): *δ* 8.53 (s, 4H, form), 7.50 (d, 8H, Ar, *J* = 8.1 Hz), 7.04 (m, 8H, Ar), 6.93 (m, 8H, Ar) and 6.50 (d, 8H, Ar, *J* = 7.9 Hz). Calc. for $C_{52}H_{36}Cl_8Cr_2N_8$: C, 53.8; H, 3.1; N, 9.7. Found: C, 53.5; H, 2.9; N, 9.9%.

[Cr$_2$(DPh^{Br}F)$_4$] 1d. +FABMS: *m*/*z* = 1518 (M$^+$ calc. 1516.4), 1163 (M$^+$ − DPh^{Br}F) and 759 (M^{2+}) observed. IR (KBr disk): *ν*/cm^{-1} = 1614(m), 1604(s), 1593(m), 1570(m), 1493(s), 1422(w), 1367(w), 1327(m), 1264(w), 1211(m), 1200(sh), 1192(sh) and 1022(m). ^{1}H-NMR (C$_6$D$_6$): *δ* 8.76 (s, 4H, form), 7.66 (d, 8H, Ar, *J* = 7.6 Hz), 7.02 (t, 8H, Ar, *J* = 7.6 Hz), 6.97 (t, 8H, Ar, *J* = 7.6 Hz) and 6.45 (d, 8H, Ar, *J* = 7.6 Hz). Calc. for $C_{52}H_{36}Br_8Cr_2N_8\cdot 2C_6H_5Me$: C, 46.7; H, 3.1; N, 6.6. Found: C, 46.2; H, 2.6; N, 6.9%.

[Cr$_2$Cl(DPh^{Cl}F)$_3$] 2c. +FABMS: *m*/*z* = 930 (M$^+$ calc. 931.5), 895 (M$^+$ − Cl), 664 (M$^+$ − DPh^{Cl}F) and 397 (M$^+$ − 2DPh^{Cl}F) observed. ^{1}H-NMR (C$_6$D$_6$): *δ* 8.55 (s, $2H_c$, form), 8.49 (s, $2H_t$, form), 7.44 (d, $4H_c$, Ar, *J* = 7.9 Hz), 7.02 (t, $4H_c$, Ar, *J* = 7.9 Hz), 6.89 (d, $4H_c$, Ar, *J* = 8.0 Hz), 6.79 (t, $4H_c$, Ar, *J* = 7.9 Hz), 6.61 (d, $2H_t$, Ar, *J* = 8.0 Hz), 6.54 (t, $2H_t$, Ar, *J* = 7.9 Hz), 6.49 (t, $2H_t$, Ar, *J* = 8.0 Hz) and 6.20 (t, $2H_t$, Ar, *J* = 8.0 Hz). Calc. for $C_{39}H_{27}Cl_7Cr_2N_6$: C, 50.3; H, 2.9; N, 9.0. Found: C, 50.3; H, 2.6; N, 8.9%.

[Cr$_2$Cl(DPh^{Br}F)$_3$] 2d. +FABMS: *m*/*z* = 1197 (M$^+$ calc. 1198.6), 1163 (M$^+$ − Cl) and 846 (M$^+$ − DPh^{Br}F) observed. *ν*/cm^{-1} = 1618(m), 1613 (sh), 1603(s), 1593(m), 1584(w), 1567(w), 1505(m), 1491(s), 1420(m), 1370(m), 1349(m), 1322(m), 1260(w), 1204(m), 1192 (sh), 1165(w), 1098(m) and 1018(m). ^{1}H-NMR (C$_6$D$_6$): *δ* 8.82 (s, $1H_t$, form), 8.45 (s, $2H_c$, form), 7.63 (d, $4H_c$, Ar, *J* = 7.9 Hz), 7.10 (d, $4H_c$, Ar, *J* = 7.9 Hz), 6.85 (d, $4H_t$, Ar, *J* = 8.1 Hz), 6.81 (t, $4H_c$, Ar, *J* = 7.9 Hz), 6.56 (d, $2H_t$, Ar, *J* = 8.1 Hz), 6.47 (t, $4H_c$, Ar, *J* = 7.9 Hz) and 6.15 (t, $2H_t$, Ar, *J* = 8.1 Hz). Calc. for $C_{39}H_{27}Br_6ClCr_2N_6$: C, 39.1; H, 2.3; N, 7.0. Found: C, 38.7; H, 2.0; N, 7.2%.

Crystallographic studies

Single crystals of **1a**, **1b**, **1c** and **2d** suitable for X-ray diffraction measurements were obtained by layering hexanes over a benzene solution at room temperature. Single crystals of **1d**·2C$_6$H$_5$Me were obtained from a concentrated toluene solution at −20 °C. Crystallographic data for complexes **1a**, **1b** and **2d** were collected on a Nonius CAD4 diffractometer equipped with a low temperature device. Crystallographic data for complex **1c** were collected on a Nonius FAST diffractometer equipped with a low temperature device. Crystallographic data for **1d**·2C$_6$H$_5$Me were collected on a Bruker SMART 1000 diffractometer equipped with a low temperature device.

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.[13] For crystalline **1a**, **1b** and **2d** all of the non-hydrogen atoms were refined anisotropically. For crystalline **1c**, this was also done with the exception of the carbon atoms of the disordered *o*-chlorophenyl rings; each disorder was modelled over two sites and the atoms refined at either 7 : 3 or 9 : 1 occupancy. For crystalline **1d**·2C$_6$H$_5$Me, all of the non-hydrogen atoms were refined anisotropically with the exception of the carbon atoms of the two disordered toluene molecules; each disorder was modelled over two sites and the atoms refined to almost equal occupancy. Half of the *o*-bromophenyl rings were also disordered. The half that was not disordered was refined anisotropically. Each disorder was modelled over two sites and the atoms refined at 3 : 2 occupancy.

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