Chromium(II) complexes bearing 2-substituted \(N,N'-\)diarylformamidinate ligands

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A study regarding the interaction of several \(\text{o}r\text{tho}\) ring-substituted \(N,N'-\)diarylformamidinate ligands (DPh\(^X\)F, \(X = \text{Me}, \text{OMe}, \text{Cl} \text{and Br}\)) with the Cr\(^{2+}\) 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\(_2(DPh^X)F_4\), \(I [X = \text{Me}, \text{OMe}, \text{Cl} \text{and Br}; \text{Cr} - \text{Cr} = 1.925(1), 2.140(2), 2.208(2) \text{and} 2.272(2) \text{Å, respectively}], \) 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\(_2(\mu-\text{Cl})(DPh^F)\), \(2 [X = \text{Cl} \text{and Br}; \text{Cr} - \text{Cr} = 1.940(1) \text{and} 1.940(2) \text{Å, respectively}]\). 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 \(\text{ortho}\) substituents and the Cr\(^{2+}\) moiety.

Introduction

Amidinate complexes of Cr(II) are now well known.\(^1-8\) Most prevalent are those compounds that possess a quadruply bonded Cr\(^{2+}\) 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.\(^8\) Although the earliest dichromium \(\text{tetra-amidinate}\) complex to be structurally characterised was that of the \(N,N'-\)diphenylacetamidinate ligand (R\(^N\)NCR\(^\text{N}R\)'\(^H\), \(R'^{1} = \text{Me} \text{and} R'^{2} = \text{Ph}\)),\(^8\) the formamidinate ligands (R\(^N\)H) have found much greater application. This is because the synthetic methods available allow a wider variation in the substituent R\(^N\) of the formamidinate ligand. For example, formamidinate paddlewheel complexes bearing p-tolyl,\(^3\) cyclohexyl,\(^3\) \(m\)-MeO\(C\)\(H_3\),\(^3\) \(p\)-Cl\(C\)\(H_3\),\(^3\) 3,5-Cl\(_2\)\(C\)\(H_3\),\(^3\) and 3,5-Me\(_2\)\(C\)\(H_3\),\(^6\) 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 \(\text{ortho}\) fluoro substituents are present in the aromatic groups of an \(N,N'-\)diarylformamidinate ligand (DPh\(^F\)), there is a significant lengthening of the metal–metal bond.\(^3\) For example, in the \(\text{tetra-formamidinate}\) paddlewheel complexes Cr\(_2(DPh^F)\), \(R'^{1} = \text{H} \text{and} R'^{2} = \text{o}-\text{fluorophenyl} \text{and} \text{Cr}_2(DPh^{\text{flu}}F)_4 \text{[R}'^1 = \text{H} \text{and} R'^{2} = \text{pentafluorophenyl}] \text{the Cr–Cr distances were found to be} 1.968(2) \text{and} 2.012(1) \text{Å, respectively}.\(^3\) 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 \(\pi^*\) or \(\sigma^*\) character or both. Our parallel work with the 2,6-bis(phenylimino)peripinidinate ligand (DPhiP), however, showed that intramolecular \(\pi^*\) 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.\(^9\)

![Fig. 1 Schematic representations of the paddlewheel 1 and the A-frame 2 structures discussed in this paper. The chromium atoms are quadruply bonded.](image)

When we extended our study to \(N,N'-\)diarylformamidinate ligands bearing \(\text{ortho}\) chloro substituents instead, our (initial) findings were quite unexpected.\(^8\) We observed that three equivalents of LiDPhiP reacted with two equivalents of CrCl\(_2\), to afford the unprecedented A-frame complex Cr\(_3(\mu-\text{Cl})(DPhiP)\), \(2c \text{[R}'^1 = \text{H} \text{and} R'^{2} = \alpha-\text{C}_6\text{H}_4\text{Cl}]\). This was unusually interesting.
because it was the only example of an A-frame complex possessing a quadruply bonded $M_4^+$ moiety. All other known A-frame complexes have long metal-metal separations. At first, we believed that the stabilization 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 DPhF ligand across the dichromium unit. Our further work involving the DPhF ligand, however, has shown that the tetraformamidinate $\text{Cr}_2(\text{DPhF})_4$ 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 complexion behaviour of ortho ring substituted $N,N'$-difunctional formamidinate ligands (DPhF; $X = \text{Me, OMe, Cl, and Br}$) toward $\text{Cr}(II)$. 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 $\text{LiDPhF}_4$, the reaction of three equivalents of $\text{LiDPhF}_4$ with two equivalents of $\text{CrCl}_2$ in THF affords the green complex $\text{Cr}_2(\mu-$Cl-$\text{DPhF})_2$, 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 $\text{Cr}_2(\mu-$Cl-$\text{DPhF})_4$, 2e. The Cr–Cr distance of 1.940(2) Å [cf. 1.940(1) Å for 2e] 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 2.84(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 2e]. 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. $\text{Cr}--\text{N} \approx 2.02(1)$ and $\text{Cr}--\text{N} \approx 2.06(1)$ Å]. It is of note that 2e 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.

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*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.*

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>1a</th>
<th>1b</th>
<th>1c</th>
<th>1d</th>
<th>2d</th>
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<tr>
<td>$\text{Cr}_2(\text{DPhF})_4$</td>
<td>$\text{Cr}_2(\text{DPhF})_4$</td>
<td>$\text{Cr}_2(\text{DPhF})_4$</td>
<td>$\text{Cr}_2(\text{DPhF})_4$</td>
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**Table 2** Crystallographic data for complexes 1a–1d and 2d.

<table>
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<tr>
<th>Formula</th>
<th>$M$ (g mol$^{-1}$)</th>
<th>Space group</th>
<th>$a$ Å</th>
<th>$b$ Å</th>
<th>$c$ Å</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\rho_{\text{calc}}$ g cm$^{-3}$</th>
<th>$\mu$ mm$^{-1}$</th>
<th>$\lambda$(Mo-K$\alpha$) Å</th>
<th>$T/K$</th>
<th>$Z$</th>
<th>$R_1$, $R_1^{\text{w}}$, $wR_2^{\text{w}}$</th>
<th>GOF</th>
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<td>$\text{C}_9\text{H}_8\text{Cr}_2\text{N}_4$</td>
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<td>$P1$</td>
<td>10.743(2)</td>
<td>10.900(2)</td>
<td>18.073(4)</td>
<td>90</td>
<td>90</td>
<td>1.281</td>
<td>0.648</td>
<td>0.71073</td>
<td>158(2)</td>
<td>2</td>
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<td>1.071</td>
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<td>$\text{C}_9\text{H}_8\text{Cr}_2\text{N}_4\text{O}_4$</td>
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<td>$P2_1$</td>
<td>14.242(3)</td>
<td>20.524(4)</td>
<td>12.330(3)</td>
<td>110.48(2)</td>
<td>90</td>
<td>1.599</td>
<td>1.559</td>
<td>1.357</td>
<td>138(2)</td>
<td>1</td>
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<td>9.523(2)</td>
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<td>1.940(2)</td>
<td>1.218</td>
<td>0.458</td>
<td>0.919</td>
<td>0.123, 0.253</td>
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<td>$P2_1$</td>
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<td>2753(1)</td>
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<td>110.48(2)</td>
<td>90</td>
<td>1.940(2)</td>
<td>1.218</td>
<td>0.458</td>
<td>0.919</td>
<td>0.123, 0.253</td>
<td>1.071</td>
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</table>

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*Fig. 1* A drawing of the molecular structure of $\text{Cr}_2(\mu-$Cl-$\text{DPhF})_2$, 2d. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

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**Fig. 2** A drawing of the molecular structure of $\text{Cr}_2(\mu-$Cl-$\text{DPhF})_2$, 2d. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms omitted for clarity.
There is a clear distinction in the $^1$H-NMR spectrum of compound 2d (in C$_6$D$_6$ 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 methylene resonances of the cis and trans ligands in 2c appear at $\delta$ 8.55 and 8.49, respectively, whereas in 2d they are observed at $\delta$ 8.45 and 8.82, respectively.

The reaction of three equivalents of LiDPh$_6^\text{Me}$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$_6^\text{Me}$-F)$_6$, 1a, is obtained even at $-78$ °C. This compound is, however, best prepared by the reaction of two equivalents of LiDPh$_6^\text{Me}$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 $D_4h$ symmetry with all of the methyl groups oriented away from the $C_2$ 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$_6^\text{F}$ with two of CrCl$_2$ in THF gave Cr$_4$(μ-Cl)(DPh$_6^\text{F}$)$_2$, 2c, but since the chlorine atom is of comparable size to a methyl group we wondered if the reaction of four LiDPh$_6^\text{F}$ molecules with two of CrCl$_2$ could proceed to form Cr$_4$(DPh$_6^\text{F}$)$_4$, 1c. Secondly, an inspection of the space-filling representation of Cr$_2$(DPh$_6^\text{Me}$-F)$_6$, 1a (see Fig. 4), shows that it is unlikely that a paddlewheel structure can be formed using an $N,N'$-diarylfomamidinate 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.  

It was found that the reaction of two equivalents of the lithiated cis ring-substituted formamidinates LiDPh$_6^{\text{OMe}}$F, LiDPh$_6^{\text{F}}$F and LiDPh$_6^{\text{Me}}$F with one equivalent of CrCl$_2$ in THF or benzene affords the corresponding paddlewheel complex Cr$_2$(DPh$_6^{\text{F}}$F)$_2$, 1b, in each case.

The molecular structure of Cr$_2$(DPh$_6^{\text{OMe}}$F)$_6$, 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$_6^{\text{OMe}}$F)$_6$, 1b, is almost 0.2 Å longer than that in Cr$_2$(DPh$_6^{\text{Me}}$F)$_6$, 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$_2$Ac$_2$(H$_2$O)$_2$. The $^1$H-NMR spectrum in C$_6$D$_6$ shows only a sharp singlet at $\delta$ 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 around the o-anisyl rings.

The structures of Cr₂(DPh₃F)₄, 1c, and Cr₂(DPh₅F)₄, 1d, were determined by single-crystal X-ray diffraction. Although they do not form isomorphous crystals, the molecular structures of Cr₂(DPh₃F)₄, 1c, and Cr₂(DPh₅F)₄, 1d, (C2c and P1, 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)···Cl(2A) = 2.766(2) Å; and Cr(1)···Br(1A) = 2.890(3) Å and Cr(2)···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 Cr₂(DPh₅F)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 Cr₂(µ-Cl)(DPh₃F)₄, 2c, and Cr₂(µ-Cl)(DPh₅F)₄, 2d, counteract the Cr–Cr lengthening effect of axial ligation observed in Cr₂(DPh₃F)₄, 1c, and Cr₂(DPh₅F)₄, 1d.

In analogy to LiDPh₅[Cl], it was found that the reaction of three equivalents of LiDPh₅F or LiDPh₅OMe with two of CrCl₂ in THF or benzene does not afford the appropriate chloride-bridged species even at ~78 °C. Again only a tetraformamidinate species could be isolated. It is unclear why A-frame type complexes for the ligands DPh₅F (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 Cr₂(DPh₅F)₄, 1c. This is not the case for the A-frame compounds Cr₂(µ-Cl)(DPh₃F)₄, 2c, and Cr₂(µ-Cl)(DPh₅F)₄, 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 Cr₂(DPh₅FOMe)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 orthoformaldehyde 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 cm³, 1.6 M in diethyl ether, 1.63 mmol) was added dropwise to a suspension of anhydrous CrCl₂ (100 mg, 813 µmol)
through Celite to ensure the removal of LiCl, the solvent was removed under vacuum to leave an orange polycrystalline solid, Cr$_2$(DPhMeF)$_4$, 1a. Yield: 219 mg, 220 µmol, 54%. Analogous procedures using HDPPh$_3$(OMe) (417 mg, 1.63 mmol), HDPPh$_2$(Me) (432 mg, 1.63 mmol) or HDPPh$_3$(F) (577 mg, 1.63 mmol) gave the complexes Cr$_2$(DPh$_3$(OMe)), 1b (orange, yield: 271 mg, 241 µmol, 59%), Cr$_2$(DPh$_2$(Me)) 1e (orange, yield: 187 mg, 161 µmol, 40%) or Cr$_2$(DPh$_3$(F))$_2$, 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, 1.12 mmol) was added dropwise to a suspension of anhydrous CrCl$_3$ (100 mg, 813 µmol) and HDPPh$_3$(F) (323 mg, 1.22 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 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 a green polycrystalline solid, Cr$_2$(µ-Cl)(DPh$_3$(F))$_2$, 2e. This is a modification of the published procedure. Yield: 143 mg, 154 µmol, 38%. An analogous procedure using HDPPh$_3$(OMe) (431 mg, 1.22 mmol) gave the complex [Cr$_2$(µ-Cl)(HDPPh$_3$(OMe))]$_2$ 2d (green, yield: 234 mg, 195 µmol, 48%).

**Spectroscopic data**

[Cr$_2$(DPh$_3$(OMe))]$_2$. 1a. + FABMS: m/z = 996 (M$^+$ calc. 997.1) and 498 (M$^+$ observed). IR (KBr disk): ν/cm$^{-1}$ = 1631(s), 1612(s), 1590(m), 1507(s), 1424(m), 1393(m), 1263(w), 1203(w), 1185(w), 1139(m) and 1039(m). δ/µmol 1.4 h, 1.3 a, 1.2 c. For crystalline 1c. 1d, and 2d the calculations on a Nonius CAD4 diffractometer equipped with a low temperature device. Crystallographic data for complex 1e were collected on a Nonius FAST diffractometer equipped with a low temperature device. Crystallographic data for the 1d 2C$_2$H$_5$Br$_2$Cl$_2$CrN$_2$C$_2$. 39: 1: 2. 3: 4. 5. 6. 7. 8. 9. 10. 11. 12. Found: C, 61.1; H, 5.3; N, 10.2%.

[Cr$_2$(DPh$_3$(F))]$_2$. 1a. + FABMS: m/z = 1124 (M$^+$ calc. 1125.2), 869 (M$^+$ - DPh$_3$(OMe)) and 562 (M$^+$ observed). IR (KBr disk): ν/cm$^{-1}$ = 1624(s), 1606(s), 1584(s), 1599(s), 1444(m), 1428(w), 1376(m), 1331(m), 1263(w), 1243(s), 1199(w), 1110(m) and 1019(w). δ/µmol 1.4 h, 1.3 a, 1.2 c. For crystalline 1c. 1d, and 2d the calculations on a Nonius CAD4 diffractometer equipped with a low temperature device. Crystallographic data for complex 1e were collected on a Bruker SMART 100 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 SHELXL93. For crystalline 1a, 1b and 2d all but 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 7.8 or 9.1 occupancy. For crystalline 1d 2C$_2$H$_5$Br$_2$Cl$_2$CrN$_2$C$_2$. 39: 1: 2. 3: 4. 5. 6. 7. 8. 9. 10. 11. 12. Found: C, 61.1; H, 5.3; N, 10.2%.

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**References**
