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Quadruply Bonded Dichromium Complexes with Variously Fluorinated Formamidinate Ligands

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Complexes of chromium with various amidinate anions of *N*,*N*′-di(biphenyl)formamidine (DbiPhF), *N*,*N*′-di(pentafluorophenyl)formamidine ($DPh^{F_5}F$), *N*,*N*′-di(*p*-fluorophenyl)formamidine ($DPh^{p-F}F$), *N*,*N*′-di(*o*-fluorophenyl)formamidine ($DPh^{o-F}F$), *N*,*N*′-di(3,5-fluorophenyl)formamidine ($DPh^{3,5-F}F$), and *N*,*N*′-di(*m*-fluorophenyl)formamidine ($DPh^{m-F}F$) have been synthesized and structurally characterized to study the response of the M−M multiple bond to the donor capacity of the ligand by varying the substituents of the aromatic rings. All six of these dinuclear fluorinated amidinate derivatives of the chromium(II) compounds have the paddlewheel configuration. The synthetic route involves the reaction of $CrCl_2$ with the corresponding lithium salt of the ligands, LiDArF (where Ar = *o*-C_6H_4F, *m*-C_6H_4F, *p*-C_6H_4F, *p*-$C_6H_4C_6H_5$, C_6F_5, or 3,5-$C_6H_3F_2$). Compounds $[Cr_2(DPh^{p-F}F)_4]$ (**1**), $[Cr_2(DPh^{m-F}F)_4]$ (**2**), $[Cr_2(DPh^{3,5-F}F)_4]\cdot C_6H_{14}$ (**3**$\cdot C_6H_{14}$), and $[Cr_2(DbiPhF)_4]\cdot 0.7CH_2Cl_2$ (**4**$\cdot 0.7CH_2Cl_2$) show no variation in the Cr−Cr quadruple bond length, even though the ligands have very different basicities. In the solid state, $[Cr_2(DPh^{F_5}F)_4]$ (**5**) shows close axial contacts between the *o*-F atoms and the chromium metal centers. The ^{19}F NMR show an unresolved and broad signal for all *o*-F atoms that cannot be resolved even at very low temperature. To assess the efficiency of the contacts, $[Cr_2(DPh^{o-F}F)_4]$ (**6**) was prepared. The crystal structure shows the same kind of Cr···F interactions as in **5**, and an elongation of the Cr−Cr quadruple bond, compared with the values for the complexes **1**, **2**, **3**, and **4**. These new complexes reveal that the electronic contribution of the ligand basicity to the M−M bond is smaller and less important than the axial interactions of the chromium centers. Crystal data: for **1**, orthorhombic, space group *Fddd* with $a = 25.25(7)$ Å, $b = 26.752(12)$ Å, $c = 28.57(4)$ Å, $\alpha = \beta = \gamma = 90°$, and $Z = 16$; for **2**, triclinic, space group $P\bar{1}$ with $a = 9.606(12)$ Å, $b = 9.727(10)$ Å, $c = 13.249(11)$ Å, $\alpha = 69.24(1)°$, $\beta = 73.84(2)°$, $\gamma = 84.24(2)°$, and $Z = 1$; for **3**$\cdot C_6H_{14}$, triclinic, $P\bar{1}$ with $a = 10.8274(10)$ Å, $b = 13.739(2)$ Å, $c = 18.152(4)$ Å, $\alpha = 83.25(1)°$, $\beta = 75.61(2)°$, $\gamma = 70.246(10)°$, and $Z = 2$; for **4**$\cdot 0.7CH_2Cl_2$, triclinic $P1$ with $a = 9.689(2)$ Å, $b = 13.7088(3)$ Å, $c = 16.844(3)$ Å, $\alpha = 69.90(3)°$, $\beta = 87.10(3)°$, $\gamma = 70.13(3)°$, and $Z = 1$; for **5**, monoclinic, $C2/c$ with $a = 19.114(3)$ Å, $b = 18.957(3)$ Å, $c = 29.923(6)$ Å, $\beta = 97.27(1)°$, and $Z = 4$; for **6**, triclinic, $P\bar{1}$ with $a = 10.225(2)$ Å, $b = 11.312(2)$ Å, $c = 11.797(3)$ Å, $\alpha = 117.08(1)°$, $\beta = 96.432(2)°$, $\gamma = 107.52(2)°$, and $Z = 1$.

Introduction

Complexes containing Cr_2^{4+} moieties have been the focus of attention of many studies in the area of multiply bonded compounds;[1] they are still a source of many surprises.[2] For the lantern-type complexes, the Cr−Cr distances vary over a range of more than 0.7 Å. The shortest is 1.828(2) Å for Cr_2(2-oxyphenyl)$_4$ whereas distances of 2.4 Å or more are commonly found in dichromium tetracarboxylates of the type $Cr_2(O_2CR)_4\cdot L_2$. Generally, Cr−Cr distances of less than 2.0 Å are known as “supershort”.

Axial ligation typically increases the metal-to-metal bond length. For example, compounds of the type $[Cr_2((2\text{-xylyl})NCMeO)_4]L'L$[3] have been prepared for L′ = L = no ligand; L = THF, L′ = no ligand; L = L′ = THF and L = L′ = pyridine. The Cr−Cr distances are 1.937(2), 2.023(1), 2.221(3), and 2.354 Å, respectively. Thus, the presence of more axial ligands or stronger donors in axial positions significantly lengthens the Cr−Cr bonds.

However, more subtle variations in the Cr−Cr bonds have been the subject of much speculation. Several attempts to design experiments to probe such effects have failed. In a series of related compounds of Cr_2L_4, L = 2-methylhydroxy-6-pyridinate, methylaminopyridinate, and dimethylhydroxypyridine, the Cr−Cr distances are 1.889(1), 1.870(3), and 1.903(3) Å, respectively. However, when L = chlorohydroxypyridinate the Cr−Cr distance of 1.955(2) Å is distinctly longer. Two hypotheses have been considered to explain such elongation in the bond. One is that lone pairs on the chlorine atoms may interact weakly with the metal atom orbitals, perhaps placing some electron density into the π^* orbital, thus weakening the Cr−Cr bond. The other is that the electron-withdrawing effect of the Cl atoms weakens the donor strength of the ring nitrogen atoms and that this, in a manner not completely clear, weakens the Cr−Cr bond.

At the time a seemingly straightforward experiment was tried by preparing the analogous compound with fluorine instead of

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(1) Cotton, F. A.; Walton, R. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, 1993; Chapter 4.

(2) See, for example: Cotton, F. A.; Murillo, C. A.; Pascual, I. *Inorg. Chem. Commun.* **1999**, *2*, 101.

(3) Cotton, F. A.; Ilsley, W. H.; Kaim, W. J. *Am. Chem. Soc.* **1980**, *102,* 3464.

10.1021/ic990007l CCC: $18.00

Table 1. Crystallographic Data for Complexes **1**−**6**

	1	**2**	**3**·C_6H_{14}	**4**·0.7CH_2Cl_2	**5**	**6**
formula	$Cr_2F_8C_{40}H_{24}N_{12}$	$Cr_2F_8C_{52}H_{40}N_8$	$Cr_2F_{16}C_{55.5}H_{28}N_{12}$	$Cr_2C_{100.82}H_{76}Cl_{1.65}N_8$	$Cr_2F_{40}C_{52}H_4N_8$	$Cr_2F_8C_{52}H_{40}N_8$
fw	1030.31	1020.82	1214.86	1562.03	1604.63	1030.31
space group	*Fddd*	$P\bar{1}$	$P\bar{1}$	*P*1	*C*2/*c*	$P\bar{1}$
a, Å	25.25(7)	9.606(12)	10.8274(10)	9.689(2)	19.114(3)	10.225(2)
b, Å	26.752(12)	9.727(10)	13.739(2)	13.708(3)	18.957(3)	11.312(2)
c, Å	28.57(4)	13.249(11)	18.152(4)	16.844(3)	29.923(6)	11.797(3)
α, deg	90	69.24(1)	83.25(1)	69.90(3)	90	117.08(1)
β, deg	90	73.84(2)	75.61(2)	87.10(3)	97.27(1)	96.432(2)
γ, deg	90	84.24(2)	70.426(10)	70.13(3)	90	107.52(2)
V, Å^3	19 298(58)	1141.9(2)	2462.7(7)	1970.3(7)	10 755(4)	1107.5(4)
D_{calc} g cm^{-3}	1.417	1.484	1.638	1.316	1.982	1.543
μ, mm^{-1}	0.526	0.556	0.552	0.388	0.593	0.573
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp (°C)	−60	−60	−60	−60	−60	−60
Z	16	1	2	1	4	1
R1^1, R1^2 [a,b]	0.094, 0.105	0.119, 0.147	0.044, 0.050	0.095, 0.126	0.050, 0.068	0.073, 0.0601
wR2^1, wR2^2 [b,c]	0.247, 0.259	0.318, 0.350	0.108, 0.114	0.220, 0.255	0.119, 0.135	0.1628, 0.1450

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] Superscript 1 denotes value of the residual considering only the reflections for which $I > 2^{\sigma}(I)$. Superscript 2 denotes value of the residual for all reflections. [c] $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o2)^2]]^{1/2}$.

Table 2. Selected Bond Distances (Å) for Compounds **1**−**6**, $[Cr_2(DArF)_4]$

compd	ligand	Cr−Cr	Cr−N	Cr−N	Cr−F
1[a]	$DPh^{p-F}F$	1.917(6)	2.043(6)		
			2.083(6)		
		1.915(5)	2.054(6)		
			2.057(5)		
2	$DPh^{3,5-F}F$	1.9057(7)	2.038(3)	2.035(3)	
			2.043(3)	2.046(3)	
			2.065(3)	2.073(3)	
			2.084(3)	2.100(3)	
3	$DPh^{m-F}F$	1.916(2)	2.062(7)		
			2.054(6)		
			2.066(6)		
			2.054(6)		
4	DbiPhF	1.928(2)	2.041(11)	2.063(12)	
			2.056(11)	2.063(11)	
			2.064(11)	2.070(12)	
			2.084(11)	2.072(10)	
5	$DPh^{F_5}F$	2.0121(11)	2.061(4)	2.048(4)	2.465(4)
			2.064(4)	2.082(4)	2.498(3)
			2.078(4)	2.090(4)	
			2.109(4)		
6	$DPh^{o-F}F$	1.968(2)	2.058(5)		2.651(5)
			2.062(5)		
			2.065(5)		
			2.085(5)		

[a] Two independent molecules.

chlorine atoms. However, the structure of the fluorine derivative differed from that of the chlorine derivative in several ways, including the presence of an axial ligand. These differences eliminated the possibility of making an informative comparison.

We now know that formamidinate complexes of the type $Cr_2(ArNC(H)NAr)_4$ are easily made, and thus, various aryl groups can be used to probe the effect of the substituents on the Cr−Cr distance. By designing appropriate formamidinates we have engineered lantern complexes with ligands having different electronic donating or withdrawing ability; some contain weak axial interactions; others do not. Our objective was to shed more light on the question of which effect has a higher impact on the Cr−Cr distance: weak axial ligation or the basicity of the bridging ligands? The results presented in this paper will be seen to favor the former.

Experimental Section

Methods and Materials. All operations were carried out under a nitrogen atmosphere using standard Schlenk or drybox techniques unless otherwise stated. Solvents were purified by conventional methods and distilled under nitrogen from CaH_2 or Na/K, as appropriate. The formamidine $HDPh^{F_5}F$ was prepared following a published procedure[4] but with several modifications: triethyl *o*-formate and pentafluoroaniline were mixed in stoichoimetric ratio at room temperature; to the mixture was added concentrated HCl until there was no further precipitation. The white precipitate was then filtered and recrystallized from $CHCl_3$/hexanes. This method increased the yield by up to 20% above that reported in the literature; $HDPh^{o-F}F$, $HDPh^{3,5-F}F$, $HDPh^{m-F}F$, and $HDPh^{p-F}F$ were prepared following similar procedures. Other chemicals were purchased from Aldrich and used as received. Infrared spectra were recorded in the range 4000−400 cm^{-1} on a Perkin-Elmer 16PC spectrophotometer using KBr pellets. Nuclear magnetic resonance spectra were recorded on a Bruker 200 at 200 MHz or on a Unity Plus 300 spectrometer at 300 MHz for ^1H and 282 MHz for ^{19}F. Reference standards were as follows: ^1H, CH_2Cl_2 (internal, 5.34 ppm); ^{19}F, CCl_3F (external, 0.0 ppm). Values for the C, H, and N analyses on all the samples were satisfactory; these analyses were performed by Canadian Microanalytical Service.

Preparation of $[Cr_2(DPh^{p-F}F)_4]$ (1). A freshly prepared suspension of $LiDPh^{p-F}F$ (0.36 g of $HDPh^{p-F}F$ and 1.65 mL of MeLi 1 M in 15 mL of THF) was added dropwise to 0.10 g of $CrCl_2$ in THF. The gray solid immediately reacted to give a yellow-green solution, but it was stirred for an additional 2 h. The solvent was then removed under reduced pressure, and, to eliminate the LiCl, the residue was extracted with warm toluene, filtered, and layered with hexanes. The yellow product was partially soluble in CH_2Cl_2, toluene, benzene, and pyridine. Yield (in crystals): 72% (0.305 g). ^1H NMR (300 MHz, CD_2Cl_2, rt) (ppm): 8.63 (C−H, 1); 6.72 (*m*-H, 2); 6.17 (*o*-H, 2). ^{19}F: −121.07 (*p*−F). IR (cm^{-1}): 1607 (m), 1569 (s), 1496 (vs), 1329 (m), 1314 (s), 1210 (vs), 1155 (m), 1095 (w), 962 (m), 938 (m), 833 (m), 775 (m), 581 (w), 511 (w), 464 (w), 447 (w).

Preparation of $[Cr_2(DPh^{m-F}F)_4]$ (2). It was prepared similarly to **1** (0.10 g of $CrCl_2$, 0.36 g of $HDPh^{m-F}F$, 1.6 mL of MeLi, 1 M). The yellow-orange product was more soluble in organic solvents at room temperature than the *o*-F derivative. Yield (in crystals): 67% (0.15 g). ^1H NMR (300 MHz, CD_2Cl_2, rt) (ppm): 8.798 (s, 1, C−H methine), 7.005 (q, 2, H^{meta}), 6.73 (t, 2, H_p), 6.08 (m, 4, H^{ortho}). ^{19}F: −113.2 ppm (F^{meta}). IR (cm^{-1}): 1572 (s), 1560 (s), 1331 (m), 1263 (m), 1171 (m), 1149 (m), 11369 (w), 951 (m), 774 (m), 688 (m), 520 (w), 443 (e), 420 (w).

Preparation of $[Cr_2(DPh^{3,5-F}F)_4]$ (3·C_6H_{14}). It was prepared similarly to **1** (0.1 g of $CrCl_2$, 0.43 g of $HDPh^{3,5-F}F$, 1.6 mL of MeLi, 1 M). The yellow-orange product was less soluble in organic solvents, at room temperature, than the *p*-F and *o*-F derivatives. Yield: 63% (0.29 g). ^1H NMR (300 MHz, CD_2Cl_2, rt) (ppm): 8.81 (C−H, 1), 6.52 (*p*-H, 1), 5.77 (*o*-H, 2). ^{19}F NMR (282 MHz, CD_2Cl_2, rt) (ppm):

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(4) Saeed, A. A. H.; Selman, S. A. *Can. J. Spectrosc.* **1982**, *27*, 123.

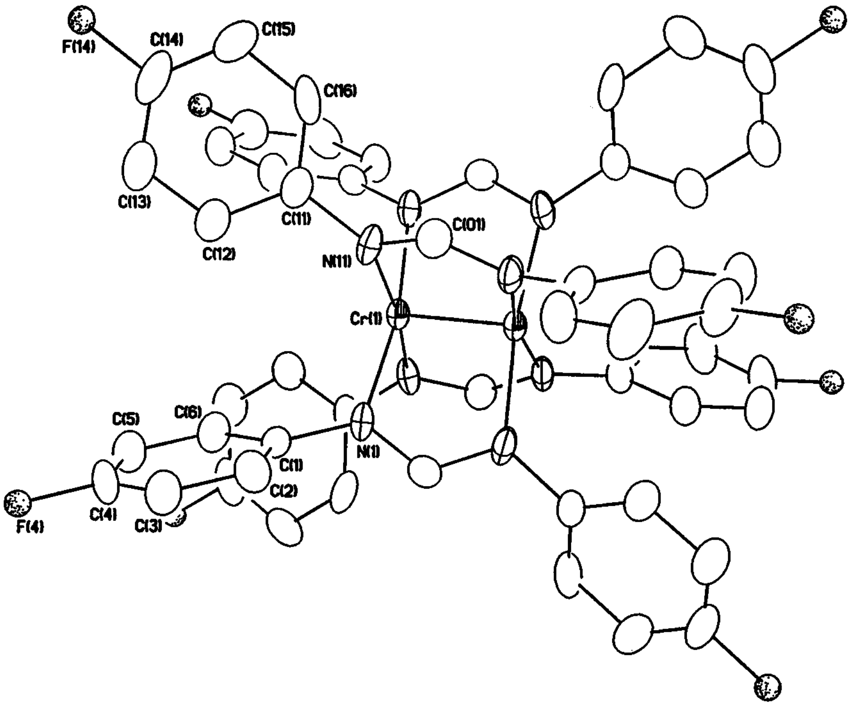

Figure 1. Drawing of the molecular structure of $[\mathrm{Cr_2(DPh^{p-F}F)_4}]$ (**1**). Displacement ellipsoids are drawn at their 50% probability level. Hydrogen atoms have been omitted for clarity.

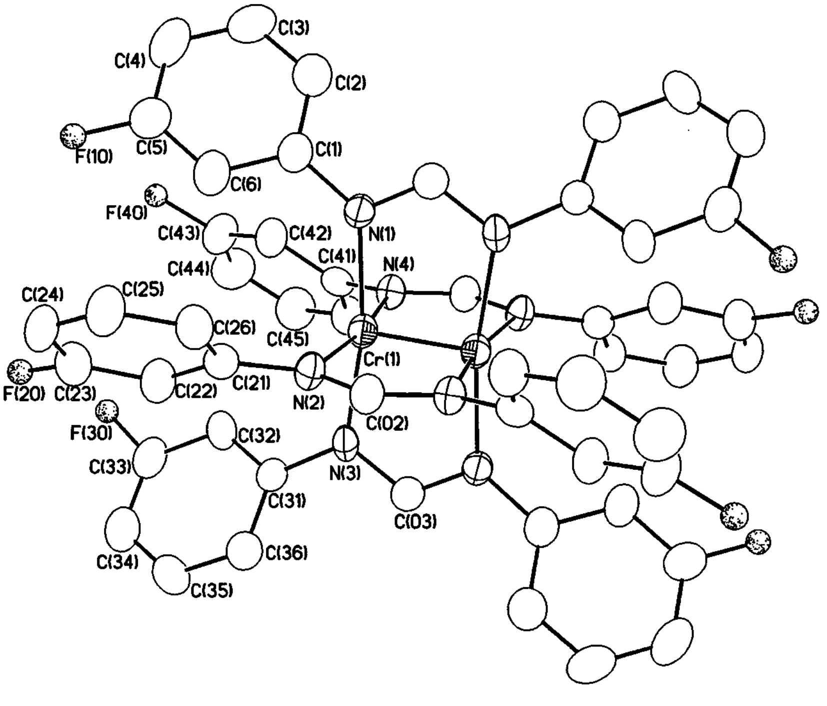

Figure 2. Displacement ellipsoid plot of $[\mathrm{Cr_2(DPh^{m-F}F)_4}]$ (**2**). Displacement ellipsoids are drawn at their 50% probability level. Fluorine atoms are disordered over both meta positions; only one is shown.

−109.62 (F^{meta}). IR (cm^{-1}): 1619 (m), 1593 (s), 1543 (m), 1525 (w), 1509 (w), 1459 (m), 1320 (w), 1161 (m), 1118 (s), 1032 (m), 991 (m), 834 (m), 670 (m).

Preparation of $[\mathrm{Cr_2(DbiPhF)_4}]$ ($4\cdot CH_2Cl_2$). It was prepared similarly to **1** (0.1 g of $CrCl_2$, 0.57 g of HD(biPh)F), 1.6 mL MeLi, 1 M). The orange-red product is very soluble at room temperature in nonpolar organic solvents. Yield: 74% (0.60 g). ^{1}H NMR (200 MHz, CD_2Cl_2, rt) (ppm): 9.07 (s, 1, C−H amidine), 7.47 (H^{meta}, 4) 7.36 (H^{meta} second ring, tt, 4), 7.32 (H^{para}, dt, 2), 7.26 (H^{ortho}, 4, dt), 6.52 (d, H^{ortho}, 4). IR (cm^{-1}): 1560 (vs), 1515 (s), 1482 (vs), 1320 (br, s), 1227 (s), 1190 (m), 1006 (w), 966 (w), 936 (w), 830 (m), 764 (s), 738 (m), 695 (s), 450 (w).

Preparation of $[\mathrm{Cr_2(DPh^{F_5}F)_4}]$ (5). Freshly distilled toluene (ca. 10 mL) was added to 0.05 g of $CrCl_2$ (0.4 mmol). To this suspension was added $\mathrm{LiDPh^{F_5}F}$, prepared in 8 mL of toluene from 0.30 g of $\mathrm{HDPh^{F_5}F}$ and 0.81 mL of 1 M MeLi in THF/cumene. The mixture was stirred for 3 h at room temperature; the solution became greenish; it was allowed to react for an additional 6 h and was filtered under nitrogen. The solvent was pumped off and the residue extracted with CH_2Cl_2, yielding a clear light green-yellowish solution, which was then layered with hexanes. Block-shaped, orange crystals formed within a few days at room temperature. The product, green-yellowish when powdered, is also soluble in THF, in which it forms dark mauve solutions, probably due to the coordination of the solvent to the axial

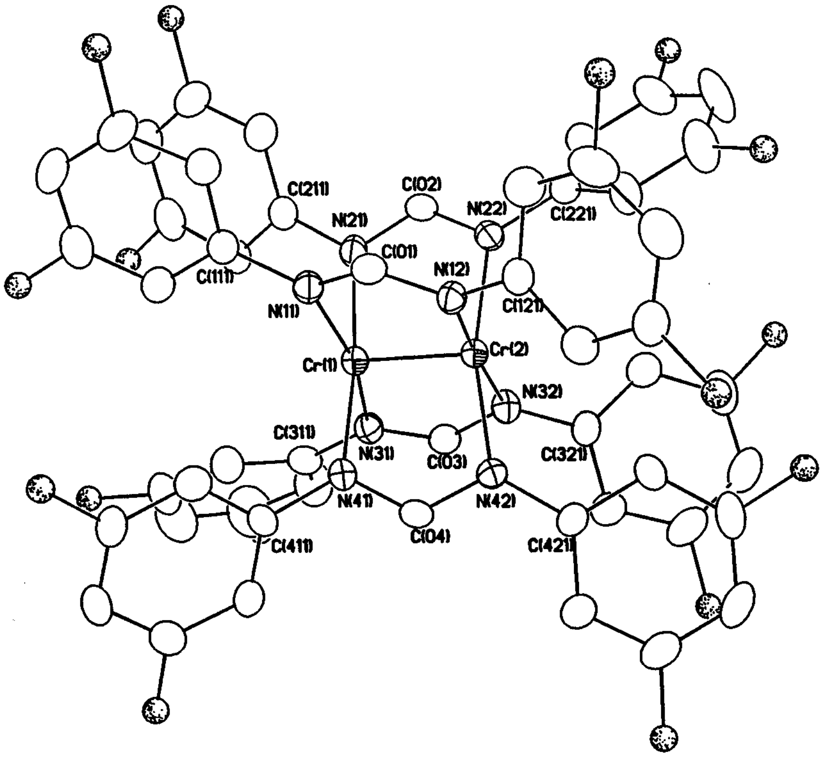

Figure 3. Molecular structure of $[Cr_2(DPh^{3,5-F}F)_4]$ in **3**·C_6H_{14}. Displacement ellipsoids are drawn at their 50% probability level. Hydrogen atoms have been omitted for clarity. Fluorine atoms are represented by their equivalent isotropic displacement thermal parameter.

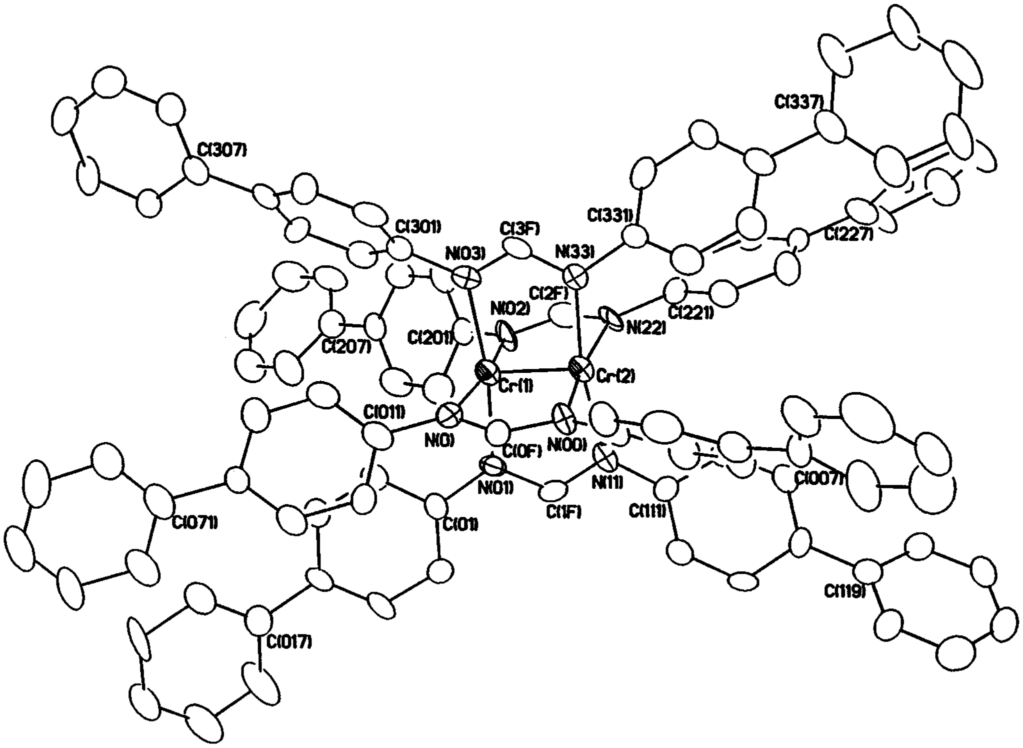

Figure 4. Plot of $[Cr_2(DbiPhF)_4]$ in **4**·0.7CH_2Cl_2. Displacement ellipsoids are drawn at their 50% probability level. Hydrogen atoms have been omitted for clarity.

position. ^1H NMR (300 MHz, CD_2Cl_2) (ppm): 7.94 (C−H, s). ^{19}F: −155.42 (F^{ortho}), −162.41 (F^{para}), −165.40 (F^{meta}).

Preparation of $[Cr_2(DPh^{o-F}F)_4]$ (6). Anhydrous chromium dichloride (0.05 g, 0.4 mmol) was suspended in 10 mL of freshly distilled toluene. A stoichiometric amount of $LiDPh^{o-F}F$ (mole ratio 1:2) prepared in situ at room temperature in 10 mL of toluene was added to the gray suspension. The mixture was allowed to reach room temperature and was stirred for 18 h. The color changed from gray to green and finally to canary yellow. Lithium chloride was filtered off, and the solution was layered with hexanes. After 10 days at room temperature, block-shaped yellow crystals formed. Yield: 0.13 g (62%). IR (cm^{-1}): 1619 (m), 1611 (m), 1587 (s), 1569 (s), 1493 (s), 1455 (m), 1336 (s), 1293 (w), 1247 (s), 1230 (m), 1194 (w), 1150 (w), 1100 (m), 1032 (m), 970 (m), 942 (w), 865 (w), 852 (w), 802 (m), 763 (m), 766 (m), 745 (s), 561 (m), 443 (m). ^1H NMR (200 MHz, CD_2Cl_2) (ppm): 6.744 (H^{meta}), 6.542 (H^{para}), 3.69 (C−H)

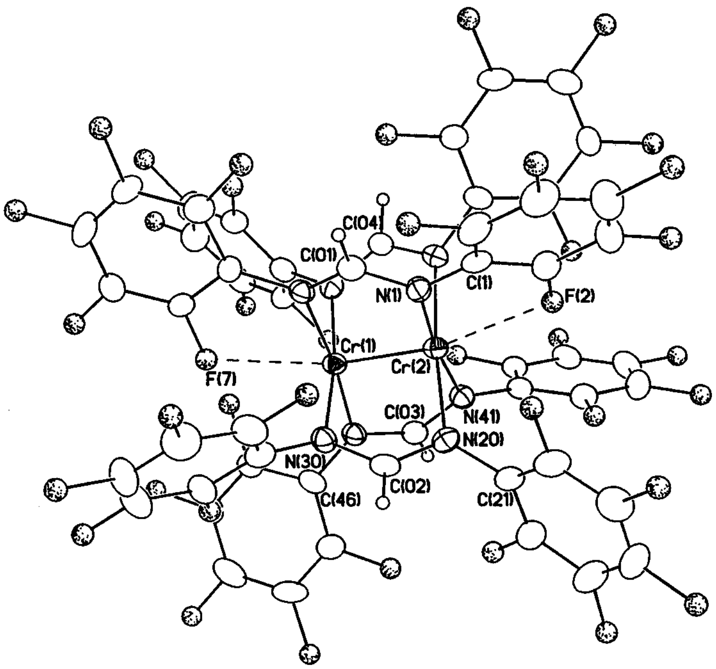

Figure 5. Drawing of $[Cr_2(DPh^{F_5}F)_4]$ (**5**) showing two Cr···F interactions. Displacement ellipsoids are drawn at their 50% probability level. Hydrogen atoms have been omitted for clarity.

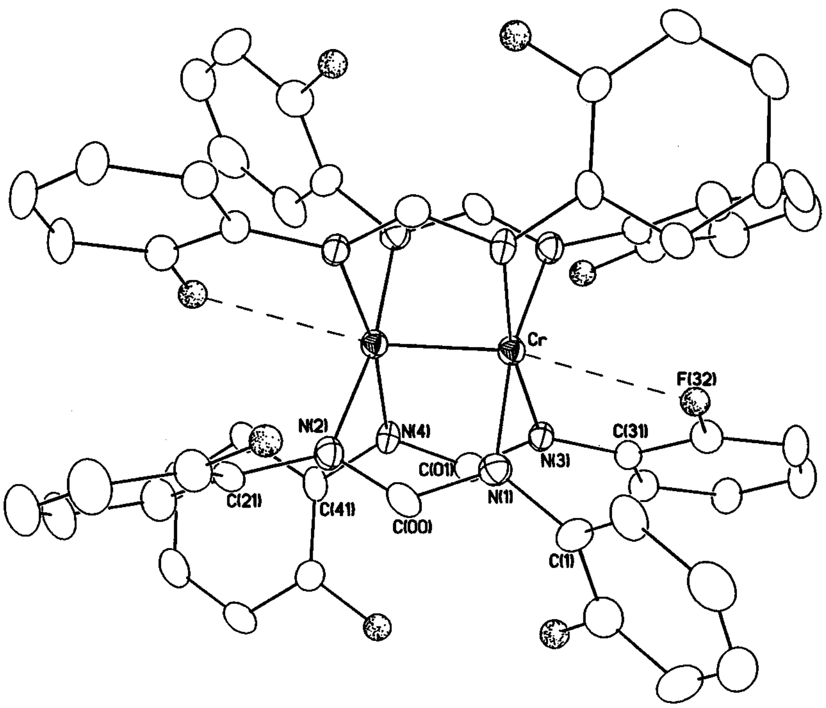

Figure 6. Drawing of the molecular structure of $[Cr_2(DPh^{o-F}F)_4]$ (**6**). Ellipsoids are drawn at their 50% probability level. Hydrogen atoms have been omitted for clarity. The Cr···F axial interactions are also observable in **5**.

Crystallographic Studies. Crystallographic data for complexes **1**−**6** were collected in a Nonius FAST diffractometer equipped with a low-temperature device operating at −60 °C. Crystals were attached with grease at the tips of quartz fibers. Cell parameters, Laue group, cell type, and mosaic spread for each crystal were determined using at least 150 reflections obtained by scanning over 110° in ω with tilt on ω of 0.3° per scan frame. Data collection was performed in three different regions, over more than one hemisphere of the reflection sphere. Frames were collected at different exposure times for each crystal, depending on the diffracting power of the crystal. Data sets were reduced with the MADNES subroutine that accounted for Lorentzian and polarization corrections. Absorption corrections were applied for **4**. All the structures were solved by direct methods. Non-hydrogen atoms were found on Fourier maps after successive least-squares refinement cycles. Hydrogen atoms were found in difference maps, but some of these were restrained to ride on geometric positions of the parent atoms to increase the data-to-parameter ratio. All the structures were refined using Shelx92 software packages.

Crystallographic data for **1**−**6** are given in Table 1. In contrast to the isomorphic chromium amidinate series recently reported,[5] in which most of the complexes crystallized in space group $P\bar{1}$, these compounds crystallize in various space groups and lattice types, even though they were crystallized under similar conditions. Compound **4**, [Cr2-

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(5) Carlson-Day, K. M.; Eglin, J. L.; Lin, C.; Smith, L. T.; Staples, R. J.; Wipf, D. O. *Polyhedron*, in press.

(DbiPhF)$_4$], crystallizes in the noncentrosymmetric space group *P*1, with 0.7 molecule of interstitial CH_2Cl_2. The two enantiomers ($\delta\delta\delta\delta$ and $\lambda\lambda\lambda\lambda$) cocrystallize in an 80:20 ratio. Complex **1**, $[Cr_2(DPh^{p-F}F)_4]$, crystallizes solvent-free and packs in a high-symmetry arrangement, in space group *Fddd*. Compounds **3**, $[Cr_2(DPh^{3,5-F}F)_4]$, **2**, $[Cr_2(DPh^{m-F}F)_4]$·hexane, and **6**, $[Cr_2(DPh^{o-F}F)_4]$, pack in the solid state in the centrosymmetric arrangement of space group $P\bar{1}$, with a whole molecule per asymmetric unit. Complex **5**, $[Cr_2(DPh^{F_5}F)_4]$, crystallizes in space group *C*2/*c*. Selected interatomic distances for all compounds are provided in Table 2.

Results

The reaction of anhydrous $CrCl_2$ with LiDArF, as described in eq 1, leads to crystalline yellow to orange materials, which were characterized by elemental analysis, NMR spectroscopy, and single-crystal X-ray diffraction as the paddlewheel structures $[Cr_2(DArF)_4]$.

$$2CrCl_2 + 4LiDArF \xrightarrow{THF} Cr_2(DArF)_4 + 4LiCl \qquad (1)$$

Spectroscopic Results. All complexes are diamagnetic, as shown by NMR. ^1H NMR data for all complexes are consistent with their solid state structures. The ^{19}F spectrum of **5** recorded at room temperature has three sets of signals: a sharp triplet centered at 32.16 ppm assigned to the *p*-F atoms, a broad doublet at 29.17 ppm attributed to the F in the meta position, and a nonresolved broad signal around 39.08 ppm, due to the F atoms in the ortho position. The ^{19}F NMR spectra at −20, −40, and −60 °C show no significant changes in the *o*-F NMR signals. We believe that, in solution, the Cr−F interactions are probably involved in a dynamic equilibrium, with rotation of the phenyl ring.

Structures. Figures 1−6 present thermal ellipsoid plots for compounds **1**−**6**, respectively. Table 2 summarizes the critical distances that we wish to compare for these six molecules.

All six molecules have the expected paddlewheel structure with short Cr−Cr bonds, and the Cr−N distances, which range from 2.035 to 2.108 Å, have average values that are not significantly different from one compound to another. However, there is one conspicuous discontinuity apparent in Table 2, namely, that in compounds **1**−**4** the Cr−Cr distances are all in a narrow range, 1.906(1)−1.928(2) Å, whereas in compounds **5** and **6** they are well outside of this range, with values of 2.012(1) and 1.968(2) Å, respectively.

Discussion

We focus here on the bimodal distribution of the Cr−Cr distances found in the six new compounds reported here. The one thing that distinguishes the two compounds with the longer Cr−Cr bonds is that they both have ortho fluorine atoms, while the other ones do not. To strengthen this distinction, we also cite the Cr−Cr distances in five other $Cr_2(DArF)_4$ compounds that also do not have ortho fluorine atoms. These compounds and their Cr−Cr distances are those with the following Ar groups:

p-MeC_6H_4	1.930(2) Å[6a]
m-$MeOC_6H_4$	1.918(1) Å[5]
p-ClC_6H_4	1.907(1) Å[5]
3,5-$Cl_2C_6H_3$	1.916(1) Å[5]
m-$CF_3C_6H_4$	1.902(1) Å[5]

It seems clear that the presence of flourine atoms at one or both ortho positions leads to elongation of the Cr−Cr bond. The question is why.

The answer seems to be that *o*-F atoms are in a position to interact axially with the chromium atoms, and they do so, as can be seen in Figures 5 and 6. Moreover, in the *o*-FC_6H_4 case, compound **6**, there are only two such interactions with, Cr···F distances of 2.651 Å, while in the C_6F_5 case, compound **5**, there are four Cr···F interactions, with distances of 2.465 and 2.488 Å, in accord with the fact that in **6** the lengthening (to 1.97 Å) is not as great as that in **5** (to 2.01 Å).

It has been recognized that Cr−Cr quadruple bond lengths are very sensitive to the influence of axial ligands,[1] but these results reinforce the message. One would not expect that these axial Cr···F interactions could be very strong, but nonetheless they result in easily measurable lengthening of the Cr−Cr bond. On the other hand, over the nine other compounds that have been mentioned here the variation of Cr−Cr bond distances is very small and there is no discernible relationship with the inductive effect of the Ar groups in weakening the basicity of the formamidinate ligands.

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Supporting Information Available: Complete listing of crystallographic data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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