

Synthesis and structure determination of $[\text{Cp}^*_4\text{Cr}_4(\mu\text{-F})_5\text{Cl}_2]\text{PF}_6$. A tetranuclear chromium complex formed by fluoride abstraction from hexafluorophosphate

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Abstract

Abstraction of chloride from the binuclear chromium alkyl $[\text{Cp}^*\text{Cr}(\text{Me})\text{Cl}]_2$ yields the substitutionally labile complex $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+\text{PF}_6^-$. This compound catalyzes the polymerization of ethylene, but it slowly decomposes by abstraction of fluoride from hexafluorophosphate and chloride from CH_2Cl_2 . The crystal structure of the tetranuclear chromium complex $[\text{Cp}^*_4\text{Cr}_4(\mu\text{-F})_5\text{Cl}_2]^+\text{PF}_6^-$ was determined. Fast atom bombardment mass spectrometry of the decomposition product revealed it to be a mixture of fluoride containing compounds. Magnetic susceptibility measurements indicated strong antiferromagnetic coupling of the $S = 3/2$ ions via the fluoride bridges.

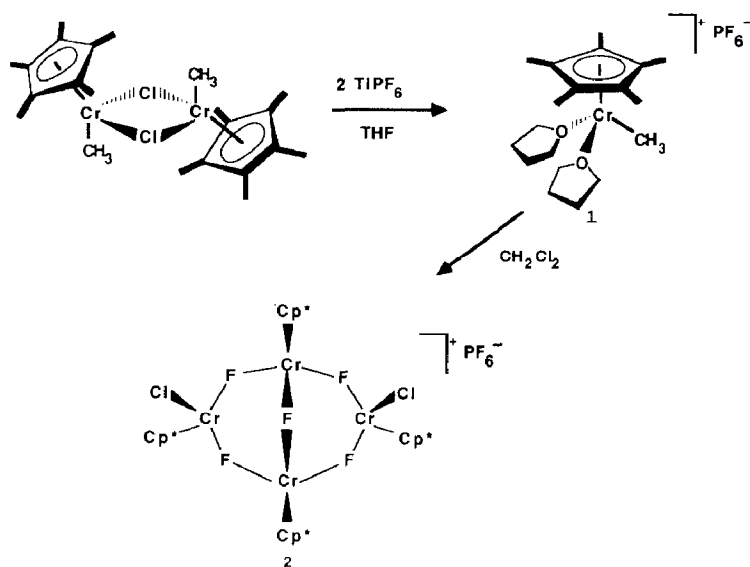
Introduction

The preparation of metal complexes with open coordination sites or easily displaced ligands has been one of the central objectives of organometallic chemistry. Such molecules facilitate the first step of any catalytic reaction cycle, i.e. substrate binding. However, the would be tailor of novel catalysts is sometimes frustrated by the ease of competitive catalyst deactivation reactions brought on by the high reactivity of his/her own creation. We have been studying the reactivity of a class of paramagnetic chromium alkyls in the belief that such metallaradicals model reactive intermediates in catalytic cycles. [1] Herein we report on an unusual product of the deactivation of a homogeneous olefin polymerization catalyst.

Results and discussion

Reaction of the dimeric chromium(III) alkyl $[\text{Cp}^*\text{Cr}(\text{Me})\text{Cl}]_2$ [1b] with 2.0 equivalents of TIPF_6 in THF followed by conventional work up yielded black needles of analytically pure $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+ \text{PF}_6^-$ (**1**) in 54% isolated yield (Scheme 1). **1** is a representative of a class of cationic half sandwich complexes of chromium under study in our laboratory [2]. It catalyzes the polymerization of ethylene but exhibits a short lifetime. Although stable in the solid state, solutions of **1** in THF or CH_2Cl_2 decomposed over the course of several days. During this time the color of the solutions changed from purple to blue. Attempts to isolate the decomposition product afforded a crystalline blue material in high yield. This material was no longer an olefin polymerization catalyst. The infrared spectrum of these crystals indicated the presence of the pentamethylcyclopentadienyl ligand as well as hexafluorophosphate anions. The ^1H NMR exhibited only one broad resonance at -64.4 ppm and the ^{19}F and ^{31}P NMR spectra showed the resonances characteristic for PF_6^- . [3] Because we felt the identification of this decomposition product might aid us in designing more stable catalysts, a crystal isolated from a decomposition reaction of **1** in CH_2Cl_2 was selected for an X-ray structure determination.

Figures 1 and 2 show the result of this analysis (see Table 1 for atomic coordinates and Table 2 and 3 for interatomic distances and angles). The molecule is a cationic tetranuclear chromium complex held together by five bridging fluoride ligands. The four chromium atoms form a butterfly core with Cr–Cr distances ranging from 3.61 Å (head to tail, Cr(1)–Cr(3)) to 5.53 Å (wingtip to wingtip, Cr(2)–Cr(4)). These distances are well outside the range of documented chromium–chromium single bonds (2.65–3.34 Å). [4] Other structurally characterized tetranuclear complexes of chromium(III) include the planar $[\text{Cr}\{(\text{OH})_2\text{-Cr}(\text{en})_2\}_3]^{6+}$ ion [5] and the cubane complex $\text{Cp}_4\text{Cr}_4\text{O}_4$ [6]. Each chromium atom of



Scheme 1

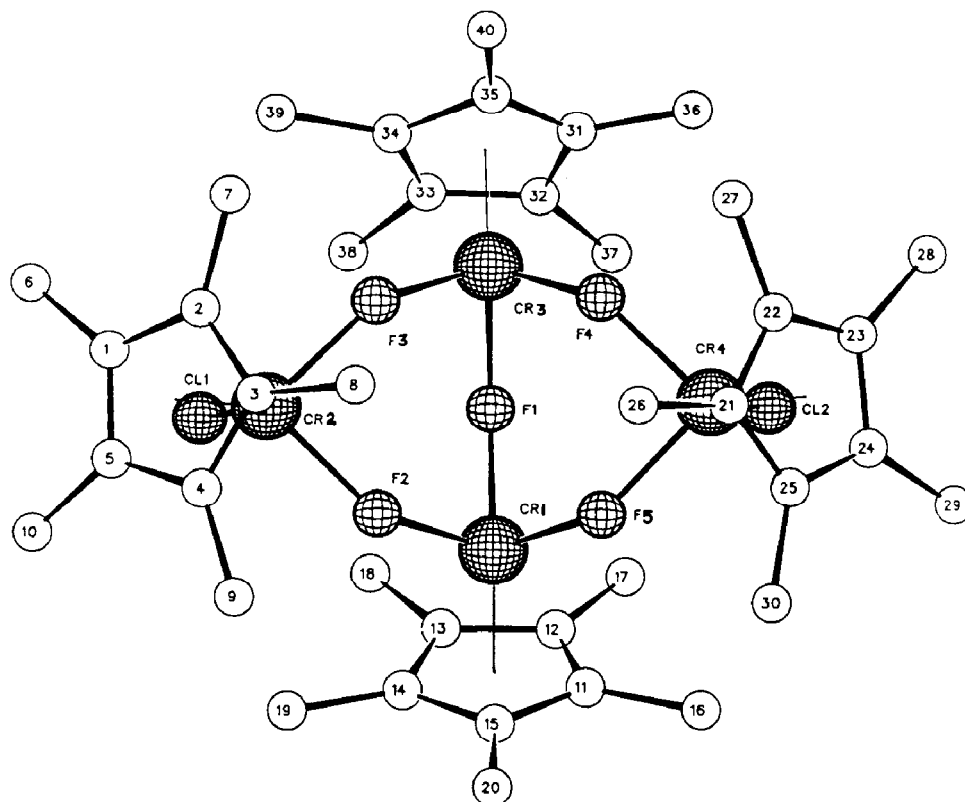


Fig. 1. Molecular structure of the $[\text{Cp}^*_4\text{Cr}_4(\mu\text{-F})_5\text{Cl}_2]^+$ cation with the atom numbering scheme. Hydrogen atoms and the hexafluorophosphate anion are omitted for clarity.

2 is bound to a pentamethylcyclopentadienyl ligand and three halogen atoms to afford the pseudooctahedral coordination environment of a three legged piano stool. Whereas Cr(2) and Cr(4) are connected to three fluoride ligands, each of which bridge two metal atoms, Cr(2) and Cr(4) feature one terminal chloride ligand each. The PF_6^- counterion adopts the expected regular octahedral structure and is well separated from the chromium complex. The molecule bears witness to the lability of

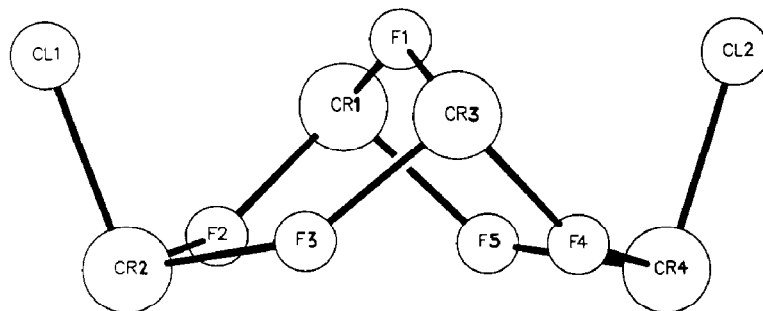


Fig. 2. Sideview of the tetranuclear core of **2**, emphasizing the butterfly geometry. Pentamethylcyclopentadienyl rings are omitted for clarity. Metal–metal distances: Cr(1)–Cr(2), 3.68 Å; Cr(1)–Cr(3), 3.61 Å; Cr(1)–Cr(4), 3.64 Å; Cr(2)–Cr(3), 3.67 Å; Cr(2)–Cr(4), 5.53 Å; Cr(3)–Cr(4), 3.66 Å.

Table 1

Fractional coordinates and thermal parameters for the non-hydrogen atoms of **2**

Estimated standard deviations of the least significant figures are given in parentheses. The isotropic equivalent thermal parameter is given for anisotropic atoms (denoted by an asterisk).

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cr(1)	0.3841(1)	0.1616(1)	0.1278(1)
Cr(2)	0.3713(1)	0.3365(1)	0.1139(1)
Cr(3)	0.4776(1)	0.2443(1)	0.0116(1)
Cr(4)	0.5577(1)	0.1500(1)	0.1320(1)
Cl(1)	0.2958(1)	0.3091(1)	0.0429(1)
Cl(2)	0.5344(1)	0.0713(2)	0.0627(1)
P	0.6724(1)	0.0548(1)	0.6354(2)
F(1)	0.4156(2)	0.1855(2)	0.0459(2)
F(2)	0.3759(2)	0.2515(2)	0.1527(2)
F(3)	0.4458(2)	0.3133(2)	0.0636(2)
F(4)	0.5409(2)	0.2197(2)	0.0734(2)
F(5)	0.4698(2)	0.1589(2)	0.1639(2)
F(6)	0.6166(4)	0.0086(4)	0.6472(4)
F(7)	0.7138(3)	0.0150(3)	0.6830(3)
F(8)	0.6480(4)	0.0945(4)	0.6893(4)
F(9)	0.6978(6)	0.0150(5)	0.5841(4)
F(10)	0.7267(4)	0.1033(4)	0.6273(4)
F(11)	0.6318(4)	0.0956(4)	0.5899(4)
C(1)	0.3455(5)	0.4404(4)	0.1141(4)
C(2)	0.4124(4)	0.4332(5)	0.1289(5)
C(3)	0.4169(4)	0.3976(5)	0.1841(4)
C(4)	0.3549(5)	0.3830(4)	0.2054(4)
C(5)	0.3104(4)	0.4093(4)	0.1615(4)
C(6)	0.3181(6)	0.4738(5)	0.0590(6)
C(7)	0.4661(5)	0.4599(5)	0.0911(5)
C(8)	0.4790(5)	0.3795(6)	0.2143(5)
C(9)	0.3376(6)	0.3455(6)	0.2619(5)
C(10)	0.2382(5)	0.4050(6)	0.1647(6)
C(11)	0.3610(4)	0.0644(4)	0.1628(4)
C(12)	0.3436(4)	0.0676(4)	0.0989(4)
C(13)	0.2857(4)	0.1160(4)	0.0929(4)
C(14)	0.2834(4)	0.1420(4)	0.1534(4)
C(15)	0.3249(4)	0.1109(4)	0.1958(4)
C(16)	0.4108(5)	0.0203(5)	0.1899(5)
C(17)	0.3700(5)	0.0275(5)	0.0477(5)
C(18)	0.2644(5)	0.1364(5)	0.0332(5)
C(19)	0.2367(4)	0.1926(5)	0.1687(5)
C(20)	0.3287(5)	0.1255(5)	0.2647(5)
C(21)	0.6104(4)	0.1942(5)	0.2100(4)
C(22)	0.6526(4)	0.1922(4)	0.1569(5)
C(23)	0.6608(4)	0.1271(5)	0.1409(4)
C(24)	0.6256(4)	0.0893(5)	0.1849(4)
C(25)	0.5958(4)	0.1303(5)	0.2259(4)
C(26)	0.5927(6)	0.2546(6)	0.2415(7)
C(27)	0.6805(5)	0.2482(5)	0.1220(6)
C(28)	0.7001(5)	0.1029(5)	0.0875(5)
C(29)	0.6252(5)	0.0170(5)	0.1856(6)
C(30)	0.5557(6)	0.1127(7)	0.2796(5)
C(31)	0.5432(4)	0.2264(5)	−0.0663(4)
C(32)	0.4849(5)	0.1974(4)	−0.0797(4)
C(33)	0.4382(4)	0.2464(5)	−0.0830(4)
C(34)	0.4679(4)	0.3054(4)	−0.0716(4)

Table 1 (continued)

Atom	x	y	z
Cr(35)	0.5341(4)	0.2930(5)	-0.0594(4)
Cr(36)	0.6059(5)	0.1909(6)	-0.0588(5)
Cr(37)	0.4729(6)	0.1265(5)	-0.0885(5)
Cr(38)	0.3674(5)	0.2388(5)	-0.0985(5)
Cr(39)	0.4355(5)	0.3694(4)	-0.0710(4)
Cr(40)	0.5832(5)	0.3415(5)	-0.0426(5)

Table 2

Interatomic distances for **2**

An estimated standard deviation of the least significant figures for each distance is given in parentheses.

Cr(1)-F(1)	1.943(5)	Cr(1)-F(2)	1.962(5)	Cr(1)-F(5)	1.956(5)
Cr(1)-C(11)	2.222(9)	Cr(1)-C(12)	2.229(9)	Cr(1)-C(13)	2.213(9)
Cr(1)-C(14)	2.219(8)	Cr(1)-C(15)	2.190(9)	Cr(2)-Cl(1)	2.270(3)
Cr(2)-F(2)	1.965(5)	Cr(2)-F(3)	1.958(5)	Cr(2)-C(1)	2.239(9)
Cr(2)-C(2)	2.222(10)	Cr(2)-Cr(3)	2.195(9)	Cr(2)-C(4)	2.219(9)
Cr(2)-C(5)	2.233(9)	Cr(3)-F(1)	1.935(5)	Cr(3)-F(3)	1.943(5)
Cr(3)-F(4)	1.945(5)	Cr(3)-C(31)	2.196(9)	Cr(3)-C(32)	2.197(9)
Cr(3)-C(33)	2.193(9)	Cr(3)-C(34)	2.204(9)	Cr(3)-C(35)	2.181(10)
Cr(4)-Cl(2)	2.272(3)	Cr(4)-F(4)	1.958(5)	Cr(4)-F(5)	1.972(5)
Cr(4)-C(21)	2.207(10)	Cr(4)-C(22)	2.238(9)	Cr(4)-C(23)	2.219(9)
Cr(4)-C(24)	2.219(9)	Cr(4)-C(25)	2.206(9)	P-F(6)	1.537(8)
P-F(7)	1.579(7)	P-F(8)	1.513(9)	P-F(9)	1.480(10)
P-F(10)	1.533(9)	P-F(11)	1.549(9)	C(1)-C(2)	1.444(14)
C(1)-C(5)	1.413(13)	C(1)-C(6)	1.489(15)	C(2)-C(3)	1.402(13)
C(2)-C(7)	1.494(14)	C(3)-C(4)	1.409(13)	C(3)-C(8)	1.501(14)
C(4)-C(5)	1.436(13)	C(4)-C(9)	1.489(15)	C(5)-C(10)	1.516(13)
C(11)-C(12)	1.423(13)	C(11)-C(15)	1.420(13)	C(11)-C(16)	1.508(13)
C(12)-C(13)	1.430(13)	C(12)-C(17)	1.490(14)	C(13)-C(14)	1.432(13)
C(13)-C(18)	1.502(14)	C(14)-C(15)	1.416(13)	C(14)-C(19)	1.478(13)
C(15)-C(20)	1.513(14)	C(21)-C(22)	1.443(13)	C(21)-C(25)	1.412(15)
C(21)-C(26)	1.481(17)	C(22)-C(23)	1.414(13)	C(22)-C(27)	1.507(15)
C(23)-C(24)	1.437(13)	C(23)-C(28)	1.498(14)	C(24)-C(25)	1.378(14)
C(24)-C(29)	1.511(14)	C(25)-C(30)	1.475(15)	C(31)-C(32)	1.391(13)
C(31)-C(35)	1.414(14)	C(31)-C(36)	1.517(15)	C(32)-C(33)	1.418(13)
C(32)-C(37)	1.514(14)	C(33)-C(34)	1.403(13)	C(33)-C(38)	1.515(14)
C(34)-C(35)	1.433(13)	C(34)-C(39)	1.500(13)	C(35)-C(40)	1.488(14)

its precursor **1**. Neither methyl groups nor any of the coordinated THF ligands remain in the decomposition product **2**. Instead, the chromium has abstracted fluoride from the 'noncoordinating' PF₆⁻ anion and chloride from the solvent methylene chloride. Both of these processes are indeed precedented [7*] and our observation merely underscores the need for avoiding the presence of potential halide donors around highly Lewis acidic early transition metal centers.

* Reference number with asterisk indicates a note in the list of references.

Table 3

Interatomic angles for **2**

An estimated standard deviation of the least significant figures for each angle is given in parentheses.

F(1)–Cr(1)–F(2)	91.8(2)	F(1)–Cr(1)–F(5)	93.2(2)
F(2)–Cr(1)–F(5)	90.0(2)	Cl(1)–Cr(2)–F(2)	95.2(2)
Cl(1)–Cr(2)–F(3)	97.0(2)	F(2)–Cr(2)–F(3)	88.3(2)
F(1)–Cr(3)–F(3)	91.3(2)	F(1)–Cr(3)–F(4)	91.6(2)
F(3)–Cr(3)–F(4)	92.1(2)	Cl(2)–Cr(4)–F(4)	94.5(2)
Cl(2)–Cr(4)–F(5)	95.4(2)	F(4)–Cr(4)–F(5)	89.1(2)
F(6)–P–F(7)	88.8(4)	F(6)–P–F(8)	87.8(5)
F(6)–P–F(9)	92.5(6)	F(6)–P–F(10)	176.3(5)
F(6)–P–F(11)	92.0(5)	F(7)–P–F(8)	88.8(4)
F(7)–P–F(9)	89.2(5)	F(7)–P–F(10)	90.9(4)
F(7)–P–F(11)	178.3(4)	F(8)–P–F(9)	178.0(6)
F(8)–P–F(10)	88.5(5)	F(8)–P–F(11)	89.7(5)
F(9)–P–F(10)	91.2(6)	F(9)–P–F(11)	92.2(5)
F(10)–P–F(11)	88.3(5)	Cr(1)–F(1)–Cr(3)	137.3(3)
Cr(1)–F(2)–Cr(2)	139.0(3)	Cr(2)–F(3)–Cr(3)	140.8(3)
Cr(3)–F(4)–Cr(4)	139.4(3)	Cr(1)–F(5)–Cr(4)	136.1(3)

The highly selective formation of **2** in so catastrophic a reaction as the breakdown of **1** into **2** seemed rather unusual. In addition the decomposition of **1** in the chloride free solvent dimethoxyethane yielded a product which was spectroscopically indistinguishable from the material obtained from CH_2Cl_2 . We were also unable to reconcile the elemental analysis of the blue material obtained from CH_2Cl_2 with the molecular formula of **2**. This led us to wonder whether **2** might only be one component of a mixture of possible decomposition products of **1**. Mass spectral analysis of the crystalline material obtained from CH_2Cl_2 supported this notion. The mass spectrum was obtained by fast atom bombardment of a sulfolane solution of that sample. The molecular ion of the cationic Cr_4 complex of **2** is observed at m/e 913 (with two ^{35}Cl). However, the spectrum features various other peaks (m/e 881, 952, 1042, 1087, 1177). Of these the one at m/e 881 is easily assigned to $\text{Cp}^*\text{Cr}_4\text{F}_7^+$, obtained by substitution of the two chloride ligands in **2** with fluoride. Several other peaks may be assigned to complexes of higher nuclearity and fragments thereof (i.e. 881, $\text{Cp}^*\text{Cr}_4\text{F}_7^+$; 952, $\text{Cp}^*\text{Cr}_3\text{F}_8^+$; 1042, $\text{Cp}^*\text{Cr}_6\text{F}_{10}^+$; 1087, $\text{Cp}^*\text{Cr}_5\text{F}_8^+$; 1177, $\text{Cp}^*\text{Cr}_6\text{F}_{10}^+$). Proof that this spectrum reflected the composition of the sample rather than scrambling in the mass spectrometer was obtained by subjecting the single crystal used for the X-ray structure determination to the same analysis. In this case the spectrum (see Fig. 3) showed only the molecular ion of **2** at m/e 913. Thus it was clear that the decomposition of **1** actually yielded a mixture of compounds. Presumably **2** formed the best crystals and one of these was chosen for the diffraction study.

Polynuclear transition metal complexes with bridging fluorides are relatively rare [8]. The only rational approach to this class of compounds is the decomposition of transition metal tetrafluoroborates in the presence of suitable ligands, a method pioneered by Reedijk et al. [9]. One motivation for preparing these molecules is the study of their magnetic properties. With one notable exception [10], all molecular compounds studied to date exhibited very small antiferromagnetic interactions transmitted by the fluoride bridges [11]. We were thus surprised, when the chro-

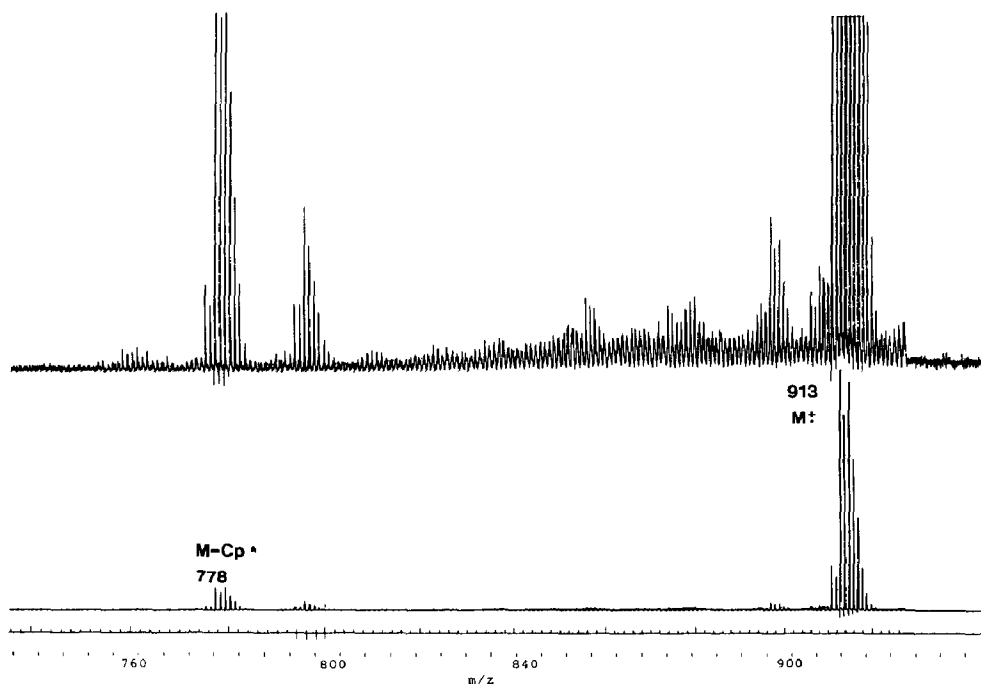


Fig. 3. FABMS (fast atom bombardment mass spectrum) of the single crystal of **2** used for the X-ray diffraction study. The spectrum represents a single scan; the top trace has a signal intensity of 45 mV full scale while the bottom trace measures 500 mV full scale.

mium tetramer described herein showed very strong antiferromagnetic coupling [12] between the four $S = 3/2$ ions. The magnetic susceptibility of the blue material derived from **1** in CH_2Cl_2 was measured in the temperature interval 3–300 K. We have demonstrated (see above), that this material is a mixture of related complexes and consequently no attempt was made to model the exchange interaction quantitatively. However, the unusually low magnetic susceptibility of the sample indicated extensive spin pairing of chromium(III) centers. For the purposes of comparison only, the data were interpreted as being characteristic of pure **2**, and a room temperature effective moment of $\mu_{\text{eff}} = 1.16 \mu_{\text{B}}$ was calculated. This may be compared to the room temperature value of $\mu_{\text{eff}} = 6.8 \mu_{\text{B}}$ for the structurally related tetranuclear chromium complex $[\text{Cr}_4(\text{OH})_6(\text{en})_6]^{6+}$, which features six bridging hydroxides [13]. Clearly the fluoride bridges in **2** are very efficient transmitters of the exchange interactions between the Cr^{III} centers.

Conclusion

Paramagnetic alkyl chromium(III) compounds with labile ligands are catalytically active, but they also decompose by atom abstraction from halide sources. A tetranuclear chromium complex with five bridging fluorides has been prepared by attack on the hexafluorophosphate anion. The complex was characterized by FAB-MS, a crystal structure determination, and magnetic susceptibility measurements. The chromium(III) centers exhibit strong antiferromagnetic coupling mediated by the fluoride bridges.

Experimental

General comments. NMR spectra were recorded on Varian XL 200, or Bruker WM 300 spectrometers. IR spectra were obtained on a Mattson Instruments Alpha Centauri spectrometer. All manipulations involving air sensitive organometallic compounds were carried out in a Vacuum Atmospheres inert atmosphere box under N_2 or on a Schlenk line using Ar. Solvents (with the exception of CH_2Cl_2) were distilled under N_2 from purple benzophenone ketyl. CH_2Cl_2 was distilled under N_2 from CaH_2 . $[Cp^*Cr(Me)Cl]_2$ was prepared as previously described [1b]. $TiPF_6$ was purchased from Strem Chemicals and used as received. Elemental analyses were carried out by Chemical Analytical Services, Berkeley, CA.

*(η^5 -Pentamethylcyclopentadienyl)(methyl)bis(tetrahydrofuran)chromium(III)hexafluorophosphate, $[Cp^*Cr(THF)_2Me]^+PF_6^-$, (1).* 1.084 g $TiPF_6$ (3.10 mmol) was added all at once to a stirred solution of 0.700 g $[Cp^*Cr(Me)Cl]_2$ (1.47 mmol) in 20 ml THF. Over the course of several hours the solution turned reddish purple and a gray precipitate formed. After 10 hours the solution was filtered and the solvent evaporated under vacuum. The solid residue was washed with Et_2O . The material so obtained was recrystallized from THF/ Et_2O to yield black needles of **1** (778 mg, 54%). 1H NMR (CD_2Cl_2): δ 8.98 (br, 4H), 8.00 (br, 4H), -25.6 (br, 15H) ppm; IR (nujol): 1250(w), 1172(w), 1120(m), 1040(w), 1012(s), 891(w), 838(vs), 726(w), 642(w), 555(s) cm^{-1} ; m.p.: 115-120 °C (dec). Anal. Calcd. for $C_{19}H_{34}CrO_2PF_6$: C, 46.44; H, 6.97. Found: C, 46.54; H, 7.05.

*Tetrakis(η^5 -pentamethylcyclopentadienyl)bis(chloro)pentakis(μ -fluoro)tetrachromium(III) hexafluorophosphate, $[Cp^*_4Cr_4Cl_2(\mu-F)_5]^+PF_6^-$, (2).* Circa 25 ml CH_2Cl_2 were vacuum transferred into a flask containing 197 mg **1** (0.4 mmol). The mixture was warmed to room temperature and stirred for 2 days. During this time the initially red-purple solution turned bright blue. The solvent was evaporated and the residue was recrystallized from CH_3CN/Et_2O to afford 100 mg of blue crystals. 1H NMR (CD_2Cl_2): δ -64.4 (br) ppm; ^{19}F NMR (CD_2Cl_2 , trifluoroacetic acid capillary reference): δ -73.3 (d, $J(PF)$ 660 Hz) ppm; ^{31}P NMR (CD_2Cl_2 , PCl_3 capillary reference): δ -143 (septet); IR (KBr): 2932(s), 2925(s), 1485(s), 1450(s), 1383(s), 1076(m), 1025(m), 844(vs), 807(m), 797(m), 601(m), 557(vs), 537(vs) cm^{-1} . **2** did not melt below 310 °C. Anal. Found: C, 42.42; H, 5.66. $C_{40}H_{60}Cl_2Cr_4F_{11}P$ calcd: C, 45.33; H, 5.71%. (see Results and discussion).

Crystal structure determination of 2. A single crystal of **2** was sealed in a glass capillary under N_2 . The capillary was mounted on a Syntex P2₁ diffractometer. Crystal data and a summary of parameters pertinent to the data collection are given in Table 4. Lattice constants were determined by a least squares fit of 15 diffractometer-measured 2θ values. The chromium atoms were located using direct methods (MULTAN). All other non-hydrogen atoms were located by subsequent difference Fourier maps. Hydrogen atom parameters were generated from assumed geometries and were not refined. At the end of the isotropic refinement an empirical absorption correction [14] was applied. The minimal, maximal and average absorption corrections were 0.752, 1.837, and 0.983. Block diagonal least squares anisotropic refinement of all non-hydrogen atoms was carried out with the program CRYSTALS. The highest peak in the final difference map measured 1.01 $e/\text{\AA}^3$. All crystallographic calculations were performed on a Prime 9950 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were: RANTAN 80

Table 4

Crystal data for $[\text{Cp}^*_4\text{Cr}_4(\mu\text{-F})_5\text{Cl}_2]^+ \text{PF}_6^-$

Formula	$\text{C}_{40}\text{H}_{60}\text{Cl}_2\text{Cr}_4\text{F}_{11}\text{P}$
Formula Weight	1059.8
Crystal System	orthorhombic
Space Group	<i>Pbca</i>
Z	8
<i>a</i> , Å	20.936(8)
<i>b</i> , Å	20.909(7)
<i>c</i> , Å	21.474(8)
<i>V</i> , Å ³	9401(6)
<i>d</i> _{calc} , g/cm ³	1.498
Crystal dimensions, mm	0.2 × 0.3 × 0.5
Radiation	Cu- <i>K</i> _α (λ 1.5418 Å)
Temperature	25 °C
Scan method	$\theta - 2\theta$
2θ range, deg	0–57
Scan rate, deg/min	variable (1° scans)
Number of data collected	7279
Number of unique data > 3σ	3232
Number of parameters refined	523
Absorption coefficient	96.1
<i>R</i>	0.052
<i>R</i> _w	0.061

and MULTAN 78 (locally modified to perform all Fourier calculations) by P. Main, S.E. Hull, L. Lessinger, G. Germain, J.P. Declercq, and M.M. Woolfson, University of York, England, 1980; BLS 78A, by K. Hirotsu and E. Arnold, Cornell University, 1980; CRYSTALS, by D.J. Watkin and J.R. Carruthers, Oxford University, 1981; REDUCE and UNIQUE, data reduction programs, by M.E. Lewonowicz, Cornell University, 1978; PL1PLOT, by G. VanDuyne, Cornell University, 1984; and TABLES, by G. VanDuyne, Cornell University, 1986.

Mass spectrometric analyses. Fast Atom Bombardment Mass Spectrometry (FABMS) was performed on a Kratos MS-50 double focussing instrument. Xenon was used as the bombarding gas with a voltage of 8 kV and 1.5 mA current. Resolution was measured at 1/2000 with a bandwidth filter of 30 kHz and 6 kV accelerating voltage. Samples were dissolved in anhydrous sulfolane under Ar in a dry box and transferred to the mass spectrometer using a glove bag positioned around the probe entrance port.

Magnetic measurements. The magnetic susceptibility of the material obtained after decomposition of **1** in CH₂Cl₂ was measured on a polycrystalline sample using a Faraday balance. Variable temperature control (3–300 K) was obtained using a helium flow cryostat. The sample was loaded into a high purity quartz bucket in a dry box and transferred to the cryostat in an O-ring sealed container. The diamagnetic force due to the sample holder was subtracted over the entire temperature range. The susceptibility was measured at 100 and 70% of full field to check for ferromagnetic impurities. Calibration was performed with HgCo(SCN)₄ (16.44 × 10⁻⁶ emu/g at 298 K). The data were corrected for diamagnetism using Pascal constants [15] (–540 × 10⁻⁶ emu/mol).

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