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SYNTHESIS AND TRANSFORMATIONS OF CYCLOPENTADIENYL-TRIFLUOROACETATE–CHROMIUM(III) COMPLEXES

I.L. EREMENKO, A.A. PASYNSKII *, O.G. VOLKOV, O.G. ELLERT and V.T. KALINNIKOV

N.S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, Leninskii Prospekt 31, Moscow B-71 (U.S.S.R.)

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Summary

The reaction of chromocene with trifluoroacetic acid in benzene yields blue-green crystals of the paramagnetic ionic complex $[Cp_2Cr]^+[CpCr(OOCCF_3)_3]^-$ (I) ($\mu_{eff.}$ = 3.70 (297 K) to 3.41 (77 K) BM). Upon recrystallizing from THF, complex I gives blue needles of the monomer $CpCr(OOCCF_3)_2 \cdot THF$ (III) ($\mu_{eff.}$ = 3.70 BM) which under treatment with an equimolar quantity of pyridine is transformed to violet needles of $CpCr(OOCCF_3)_2 \cdot Py$ (IV) ($\mu_{eff.}$ = 3.44 BM). On the other hand, the successive action of excess trifluoroacetic acid and pyridine on complex III affords violet crystals of the octahedral monomer $(C_5H_5N)_3Cr(OOCCF_3)_3$ (V) ($\mu_{eff.}$ = 3.96 BM) which has been characterized by a complete X-ray analysis ($Cr—O_{OOCCF_3}$ (mean) 1.95(1) Å, Cr—N (mean) 2.10(1) Å). Similarly, complex V can be obtained along with $[CpCrS]_4$ from the binuclear complex $(CpCrSCMe_3)_2S$.

Introduction

The known reactions of chromocene, Cp_2Cr, with proton donor reagents lead to loss of the sandwich structure and elimination of one or both cyclopentadienyls. Thus Cp_2Cr reacting with hydrogen halides HX (X = F, Cl, Br) in water eliminates one Cp ring to give $CpCrX_3^-$ anions, isolated in the form of ammonium salts (for X = Cl, Br) [1]. On the other hand, Cp_2Cr reacts with PyH^+Br^- and $PyH^+I_3^-$ to give $CpCrX_2 \cdot Py$ (X = Br or I, respectively). On heating in tetrahydrofuran the anion $CpCrCl_3^-$ was shown to form the neutral complex $CpCrCl_2 \cdot THF$ [1]. Heating of Cp_2Cr with thio- and selenophenol as well as with tert-butylmercaptan leads to the monocyclopentadienyl complexes $[CpCr(SPh)_2]_3$, $[CpCr(SePh)_2]_2$ [2] and $(CpCrSCMe_3)_2S$ [3], respectively. Analogously, Cp_2Cr reacts with tert-butanol, and trimethyl- and triphenylsilanols giving rise to the dimers $[CpCrOR]_2$ (R = CMe_3, $SiMe_3$ and $SiPh_3$).

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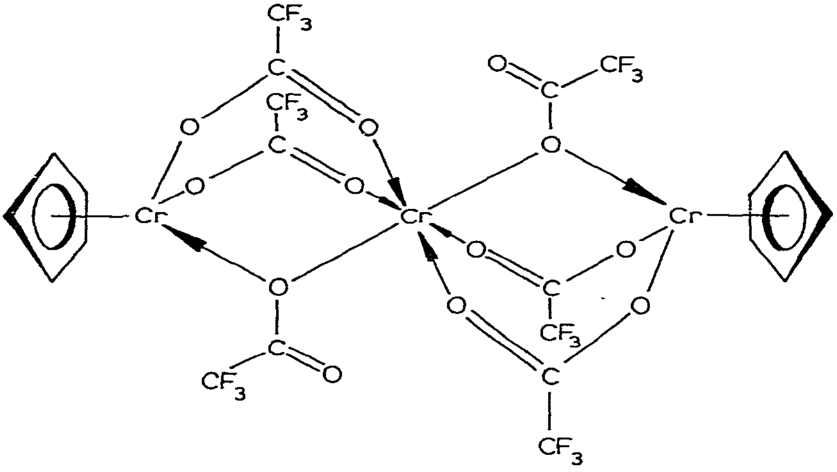
However, the less branched primary and secondary alcohols produce only the pure alcoholates $[Cr(OR)_2]_n$ [4]. In reactions of Cp_2Cr with carboxylic acids the extent of ligand substitution depends first of all on the acid strength. Thus the weak trimethylacetic acid yields only the pure carboxylate $[Me_3CCOOH \cdot Cr(OOCCMe_3)_2]_2$ [5], whereas trifluoracetic acid vapour bubbled slowly through a toluene solution of Cp_2Cr affords the mixed trinuclear complex [6]:

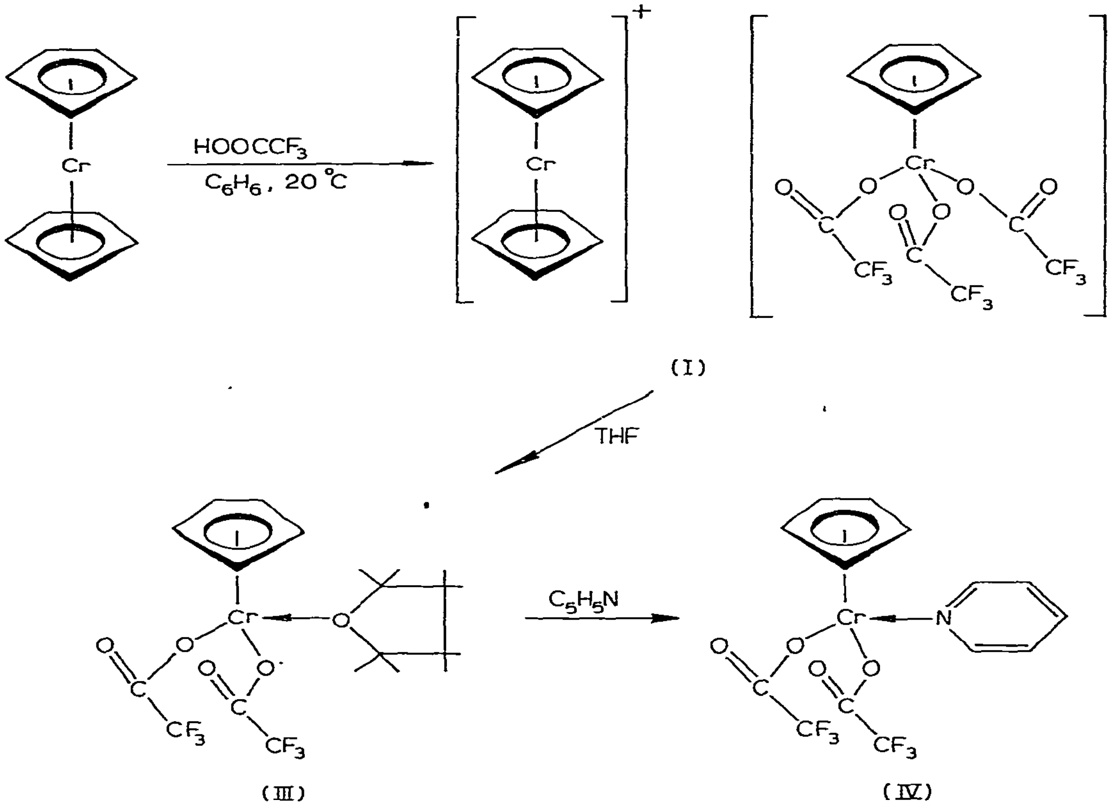


The complex is unusual due to the simultaneous presence of one fully substituted chromium and two cyclopentadienylchromium groups: two $CpCr(OOCCF_3)_2$ fragments and one $Cr(OOCCF_3)_2$ fragment. It was of interest to study in more detail the transformation of chromocene to chromium cyclopentadienyltrifluoroacetates and finally to the pure trifluoroacetates of chromium.

Results and discussion

The reaction of chromocene with F_3CCOOH solution (1 : 3 mole) in benzene gives green prisms of the ionic complex $[Cp_2Cr]^+ \cdot [CpCr(OOCCF_3)_3]^-$ (I).

The effective magnetic moment of I decreases from 3.70 to 3.41 BM in the range of 297—77 K. Complex I behaves analogously to the known $[Cp_2Cr]^+$-$[CpCrCl_3]^-$ (II), for which the total magnetic moment is 5.55 BM [1] or (3.94 BM per chromium atom). The chemical properties of II and I are also similar. When recrystallized from THF they readily give blue needles of the monomers $CpCrCl_2 \cdot THF$ [1] and $CpCr(OOCCF_3)_2 \cdot THF$ (III), respectively. The effective magnetic moment of III (3.70 BM) is close to the spin only value for Cr^{III} and is temperature independent. The presence of C_5H_5 ligands in I and III was confirmed by alkaline hydrolysis of the complexes followed by distillation of the C_5H_5 into TlOH solution and evolution of CpTl. The IR spectra of I and III (bands at 835, 1020 and 3100 cm^{-1}) shows the π-bonding nature of C_5H_5—Cr. The IR spectra of I and III also contain the bands of the symmetrical and antisymmetrical stretching modes of the trifluoroacetate (1440 and 1720 cm^{-1} for I and 1445 and 1700 cm^{-1} for III). The difference between these frequencies (280 and 255 cm^{-1}, respectively) is characteristic of terminal $OOCCF_3$ coordination [7]. The coordinated THF molecule in III has bands at 1055, 2920 and 2980 cm^{-1}.



Treatment of III with an equimolar quantity of pyridine affords violet needles of $CpCr(OOCCF_3)_2 \cdot C_5H_5N$ (IV). Its IR spectrum shows no bands of THF but contains the typical coordinated pyridine modes (728, 1078 and 3142 cm^{-1}). Analogously to III, complex IV is a monomer and its $\mu_{eff.}$ is equal to 3.44 BM and is temperature independent.

The remaining ring could not be eliminated by refluxing IV in pyridine. But when III was treated successively with an equimolar quantity of trifluoroacetic acid and excess pyridine it lost its C_5H_5, yielding $Py_3Cr(OOCCF_3)_3$ (V).

Complex V was isolated in the form of violet prisms with a magnetic moment of 3.95 BM ($\mu_{eff.}$), which is temperature independent at 295—77 K. In the region of the OCO stretching modes the IR spectrum of V shows strong bands at 1410 and 1770 cm^{-1} assigned to the symmetrical and antisymmetrical vibrations, respectively ($\Delta\nu = 360$ cm^{-1}). According to a complete X-ray analysis *, the monomer V has an usual but slightly distorted octahedral environment with two *trans*-located pyridine molecules and two *trans*-located terminal trifluoroacetate groups. The third pyridine molecule is in a *trans*-position to the third terminal $OOCCF_3$ group. The Cr—O distances are identical (mean

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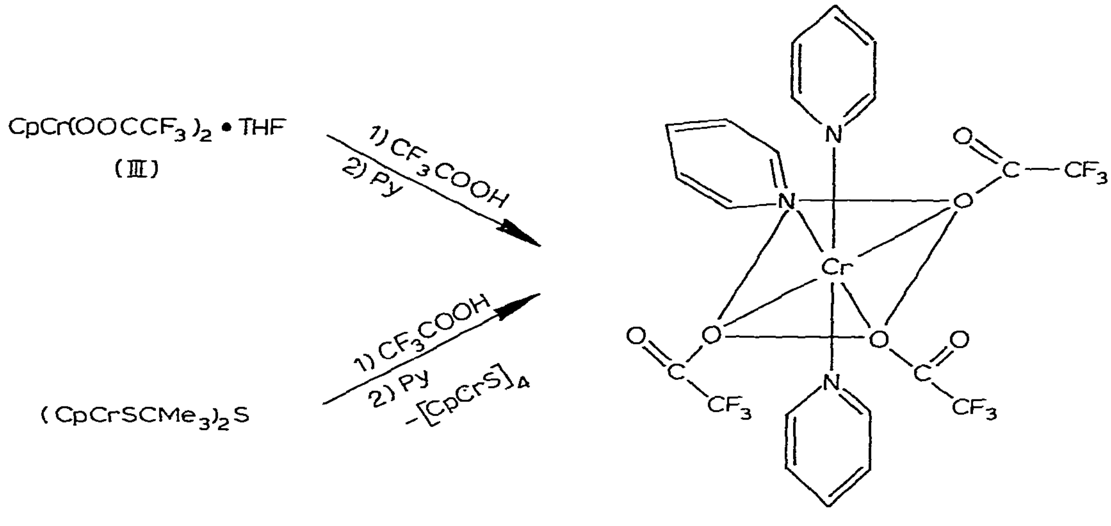
* The X-ray study was performed by A.S. Antsynshkina, L.M. Dikareva and M.A. Porai-Koshits; the detailed structure is to be published.

1.95(1) Å) and the Cr—N distances are almost equal (mean 2.10(1) Å).



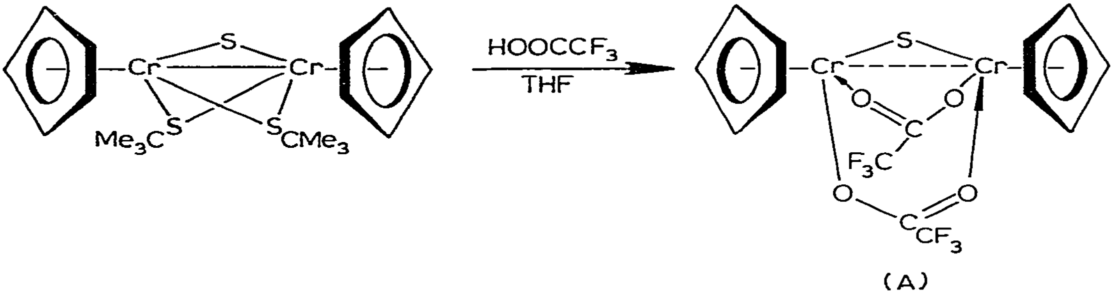
(V)

Our reaction products from Cp_2Cr and trifluoroacetic acid have the general formula $CpCr(OOCCF_3)_2 \cdot L$, here L = $OOCCF_3^-$, THF or Py (I, III, IV, respectively). They are similar to the $CpCrX_2 \cdot I$ complexes (L = X, THF or Py) generated in reactions of Cp_2Cr with CCl_4 or C_3H_5Br with subsequent treatment with THF and other L [1]. It should be pointed out that the reaction of Cp_2Cr with HX (X = F, Cl, Br, I) leads primarily to H^+CpCrX_3 acids which then form the ammonium salts [1]. Although the corresponding acid $H^+[CpCr(OOCCF_3)_3]^-$ was not identified, its formation may be explained by a ready elimination of the second cyclopentadienyl ligand on consecutive treatment of III with an equimolar quantity of CF_3COOH and excess pyridine:

$$\mathrm{CpCr(OOCCF_3)_2 \cdot THF} \xrightarrow{\mathrm{HOOCCF_3}} \{\mathrm{H^+[CpCr(OOCCF_3)_3]^-}\} \xrightarrow[-\mathrm{C_5H_6}]{3\ \mathrm{Py}} \mathrm{Py_3Cr(OOCCF_3)_3}$$

(V)

However, the action of pyridine alone on III leads to only a replacement of the coordinated THF molecule by pyridine, giving IV without ring elimination. It is probable that the presence of a proton, transforming the pyridine-replaced cyclopentadienyl anion into cyclopentadiene, is a stimulus for the entire C_5H_5 ring elimination. Complex V was obtained also by an authentic synthesis from the binuclear complex $(CpCrSCMe_3)_2S$ (VI) (its Cr—Cr bond length is 2.689 Å [3]) on successive treatment with three moles of trifluoroacetic acid and excess pyridine. The black crystals of the known tetramer $[CpCrS]_4$ [4] precipitated in the first step are identified from the presence of molecular ion peaks (*m/e* 596) in the mass spectra and of the products of sequential elimination of C_5H_5 groups down to Cr_4S_4. We have previously shown that the tert-butylthiolate bridges in VI could be readily substituted by the stronger donors EPh (E = S, Se), retaining the binuclear structure [2]. The formation of the complex $(CpCrOOCCF_3)_2S$ (A) was thus assumed. At the same time, the replacement of the monoatomic thiolate bridges in the sterically crowded binuclear complex VI by the triatomic OCO carboxylate groups should result in significant steric strain in complex A with weakening of the Cr—Cr bond.



(A)

Thus the probable intermediate A may disproportionate to $CpCr(OOCCF_3)_2$ and the mononuclear fragment {CpCrS} which tetramerizes to the known complex $[CpCrS]_4$ [1]. In turn, $CpCr(OOCCF_3)_2$ reacts with CF_3COOH and then with pyridine to afford V.

Experimental

All operations were carried out under a pure argon stream. Chromocene [8] and $(CpCrSCMe_3)_2S$ [3] were prepared by the procedures described in the literature. Commercial trifluoroacetic acid was distilled under a stream of pure argon. Pyridine, benzene and other hydrocarbons were purified by distillation under an argon atmosphere over sodium dispersion, while tetrahydrofuran was distilled over benzophenoneketylsodium.

The IR spectra were taken on an UR-20 instrument in KBr pellets. The static magnetic susceptibility was studied by Faraday's method.

$[(C_5H_5)_2Cr]^+[C_5H_5Cr(OOCCF_3)_3]^-$ (I)

A solution of 2.0 g (17.79 mmol) of CF_3COOH in 10 ml of benzene was added to a filtered red solution of 0.6 g (3.29 mmol) of Cp_2Cr in 10 ml of benzene while shaking. After 2—3 drops had been added, the solution became green-brown and then blue during the addition, and finally a blue-green crystalline solid precipitated. The crystals were separated from the solution, washed with benzene and dried under vacuum. The yield was 63%. (Found: C, 39.49; H, 2.47. $C_{21}H_{15}Cr_2F_9O_6$ calcd.: C, 39.40; H, 2.35%.) IR spectrum (cm^{-1}): 530w, 580w, 732s, 835s, 900w, 1022m, 1220vs, 1440m, 1500s, 1600w, 1720vs, 3120w.

$C_5H_5Cr(OOCCF_3)_2 \cdot THF$ (III)

A solution of 0.3 g (0.47 mmol) of I was heated in 25 ml of boiling THF for 30 min. The tetrahydrofuran solution was concentrated and the blue needles precipitated were washed with benzene/THF (1/1) mixture and dried at 20°C/ 0.1 Torr. The yield was 85%. (Found: C, 37.40; H, 3.00. $C_{13}H_{13}CrF_6O_5$ calcd.:

C, 37.49; H, 3.13%.) IR spectrum (cm^{-1}): 535m, 580w, 625m, 730s, 800s, 835m, 1025m, 1055m, 1165vs, 1215vs, 1360w, 1445m, 1500m, 1590m, 1655(sh)s, 1700vs, 2920w, 2980w, 3140w.

$C_5H_5Cr(OOCCF_3)_2 \cdot C_5H_5N$ (IV)

0.29 g (3.70 mmol) of pyridine was added to a blue solution of 1.5 g (3.63 mmol) of III in 50 ml of benzene/THF (3/1) mixture. Then 5 ml of heptane was added to the resultant black-violet solution and this was concentrated until precipitation of first crystals and then cooled to —5°C. The violet needles precipitated were separated from the solution, washed with benzene/heptane (1/1) mixture and dried at 20°C/0.1 Torr. The yield was 75%. (Found: C, 39.70; H, 2.40; N, 3.40. $C_{14}H_{10}CrF_6NO_4$ calcd.: C, 39.81; H, 2.37; N, 3.31%.) IR spectrum (cm^{-1}): 515w, 528m, 622m, 649w, 698m, 728s, 772m, 800m, 848s, 1022m, 1060w, 1078m, 1159vs, 1205vs, 1240(sh)s, 1370w, 1420s, 1460m, 1505w, 1595w, 1620w, 1712vs, 3122m, 3142w.

$(C_5H_5N)_3Cr(OOCCF_3)_3$ (V)

1) A solution of 0.058 ml (0.77 mmol) of CF_3COOH in 0.3 ml of THF was added to a solution of 0.3 g (0.73 mmol) of III in 30 ml of THF, and the mixture was refluxed for 30 min. After cooling, 1 ml of pyridine was added. The violet solution obtained was concentrated to 5 ml, diluted with 1 ml of heptane and cooled to —78°C. The violet prisms precipitated were washed with heptane and dried under vacuum. The yield was 85%.

2) A solution of 0.4 ml (4.86 mmol) of CF_3COOH in 20 ml of THF was added dropwise to a solution of 0.7 g (1.65 mmol) of $(CpCrSCMe_3)_2S$ in 50 ml of THF. The mixture was heated for 30 min until a black-violet colour appeared. The black crystalline $[CpCrS]_4$ precipitated was separated (the complex is identical to a known sample in its IR and mass spectra). 1 ml of pyridine was added to the brown mother liquid. The violet solution produced was concentrated until precipitation of the first crystals and cooled to —5°C. The violet prisms precipitated were separated from the solution, washed with THF/heptane (1/3) mixture and dried under vacuum. The yield was 62%. (Found: C, 39.98; H, 2.54; N, 6.97. $C_{21}H_{15}CrF_9N_3O_6$ calcd.: C, 40.32; H, 2.40; N, 6.72%.) IR spectrum (cm^{-1}): 530m, 630m, 650m, 705s, 727m, 770s, 792s, 845s, 885w, 1025m, 1055s, 1080s, 1140—1240vs, 1410s, 1440s, 1500w, 1580w, 1630w, 1770vs, 3075m, 3118m, 3150s.

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