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The First Anionic Thia-Fries Rearrangement at the Cobaltocenium Cation

Geanne M. R. Boston[a] and Holger Butenschön*[a]

Dedicated to Professor K. Peter C. Vollhardt on the occasion of his 76th birthday.

While the chemistry of ferrocene is rich and widely explored, this is not the case for the isoelectronic cobaltocenium cation. Here we report the first syntheses of triflate substituted cobaltocenium cations based on respective (cyclopenta-dienone)(cylopentadienyl)cobalt(I) complexes, which have first been reported by Vollhardt et al. ca. forty years ago. Reaction with triflic anhydride affords the triflate substituted cobaltocenium cations, which upon treatment with lithium diisopropyla-mide undergo the first anionic thia-Fries rearrangements of cobaltocenium complexes. To our knowledge, this is, in addition, the first case of a deprotonation of a cobaltocenium complex by a lithium base. Alternatively, desilylation of silyl derivatives with cesium fluoride caused anion formation leading to the rearrangement products in higher yields. The 2-(trifluoromethylsulfonyl)(cyclopentadienone) complexes obtained were fully characterized including a crystal structure analysis. As with ferrocene, respective mesylates or tosylates do not undergo the rearrangement.
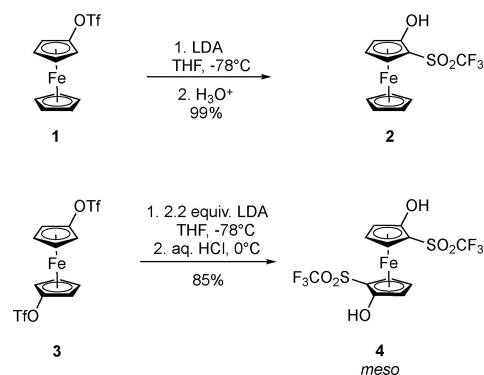
Introduction

The discovery of ferrocene in 1952[1,2] inspired the search for other metallocenes, many of which were published only a short time thereafter.[3] Cobaltocene [bis(cyclopentadienyl)cobalt(II)] was prepared by reaction of the cyclopentadienyl anion with cobalt(II) salts and was found to be highly air sensitive.[4] The oxidation of cobaltocene resulted in the formation of cobalto-cenium salts, the cobaltocenium cation being isoelectronic with ferrocene.[5] While a very rich chemistry of ferrocene followed its discovery over 70 years,[6,7] the chemistry of the cobaltocenium system has been explored to a much lesser extent, in spite of recent advances in the field.[8] Although similarities can be expected, the cationic nature of the cobaltocenium system might also lead to properties different from those of ferrocene. While the nucleophilic addition at the cobaltocenium cation represents one of its most prominent reactivities, electrophilic substitution at ferrocene is highly favored due to its electron rich nature. Whereas a deprotonation of ferrocene and its derivatives by lithium bases is quite common, a respective reactivity of the cobaltocenium cation has, to the best of our knowledge, not yet been reported.[9,10]

We have investigated the chemistry of ferrocene under a variety of aspects for a longer period of time.[11–25] Among these,

the first anionic thia-Fries rearrangements at ferrocene were reported, which start from ferrocenyl triflate (**1**) or from 1,1′-ferrocenediyl ditriflate (**3**) and gave rearranged products **2** or **4**, respectively in high yields under very mild reaction conditions (Scheme 1).[24] Remarkably, **4** was exclusively formed as the *meso* diastereomer, an unprecedented interannular stereo-induction, which was recently investigated by theoretical calculations.[22]

A number of electron rich derivatives of **1** were shown to undergo this reaction,[25] and most recently, ferrocenyl fluorosul-fonate was shown to react accordingly.[23] The first step of the reaction is a deprotonation by the strong non-nucleophilic lithium base at the *ortho* position next to the sulfonate group, which acts as an *ortho* directing group. Important reviews covering this chemistry have recently been published.[26,27]

In the course of the investigation, we reasoned that due to the positive charge the anionic thia-Fries rearrangement starting from the cationic cobaltocenium triflate salt might be facilitated making possible the use of a less strong base. Here

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Scheme 1. Anionic thia-Fries rearrangements of ferrocenyl triflate (**1**) and 1,1′-ferrocenediyl ditriflate (**3**). OTf = OSO$_2$CF$_3$.[24]

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we report the first anionic thia-Fries rearrangements at cobaltocenium salts.

Results and Discussion

According to the procedure by Vollhardt et al.,[28] dicarbonyl(cyclopentadienyl)cobalt(I) (**5**)[29] was treated with trimethylsilylethyne under photochemical reaction conditions affording cyclopentadienone complexes **6** and **7** in 83% and 13%, respectively (Scheme 2). The significantly increased yield and regioselectivity as compared to the original work is presumably due to longer reaction time and the use of a 150 W lamp instead of a 450 W lamp. Treatment of **6** with cesium
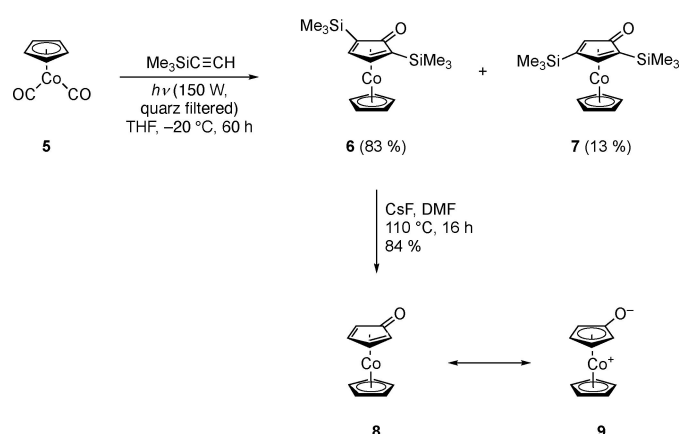
fluoride in dimethyl formamide at 110 °C afforded the unsubstituted cyclopentadienone complex **8** in 84% yield, the proton source being unclear. Possibly, dimethylamine formed from DMF served as the proton source. In contrast to the first report of **8** as a monohydrate by Vollhardt et al.[28] **8** was obtained here without any crystal water; however, **8** is highly hygroscopic as indicated by IR measurements 0 min, 10 min and 16 h after isolation (Figure 1). In addition to formulas **8** of the cyclopentadienone complex there is a resonance formula **9**, which indicates the propensity of the complex for an electrophilic attack at the oxygen atom.[30] This has been exploited by Gleiter et al. in the synthesis of alkoxycobaltocenium salts.[31]

Reaction of cyclopentadienone complex **8** with triflic anhydride at low temperature afforded (trifluoromethylsulfonyloxy)cobaltocenium triflate (**10**) in 81% yield as a yellow, air stable solid. Upon treatment of **10** with the non-nucleophilic base lithium diisopropylamide (LDA) starting material was consumed, and (cyclopentadienyl)[(trifluoromethylsulfonyl)cyclopentadienone]cobalt(I) (*rac*-**11**) was obtained in a moderate yield of 31% in spite of full consumption of starting material (Scheme 3). Nevertheless, this reaction is the first case of an anionic thia-Fries rearrangement at a cobalt complex. So far, (aryl triflate)tricarbonylchromium and ferrocenyl triflates were the only organometallic complexes, at which it had been observed.[22–25,32,33]

The first step of the anionic thia-Fries rearrangement is the deprotonation at the *ortho* position next to the triflate substituent. In view of the positive charge of the cobaltocenium ion anticipating an increased C−H acidity we saw the chance to realize the rearrangement with a weaker base than LDA. Accordingly, **10** was treated with 1,8-diazabicyclo[5.4.0]undec-
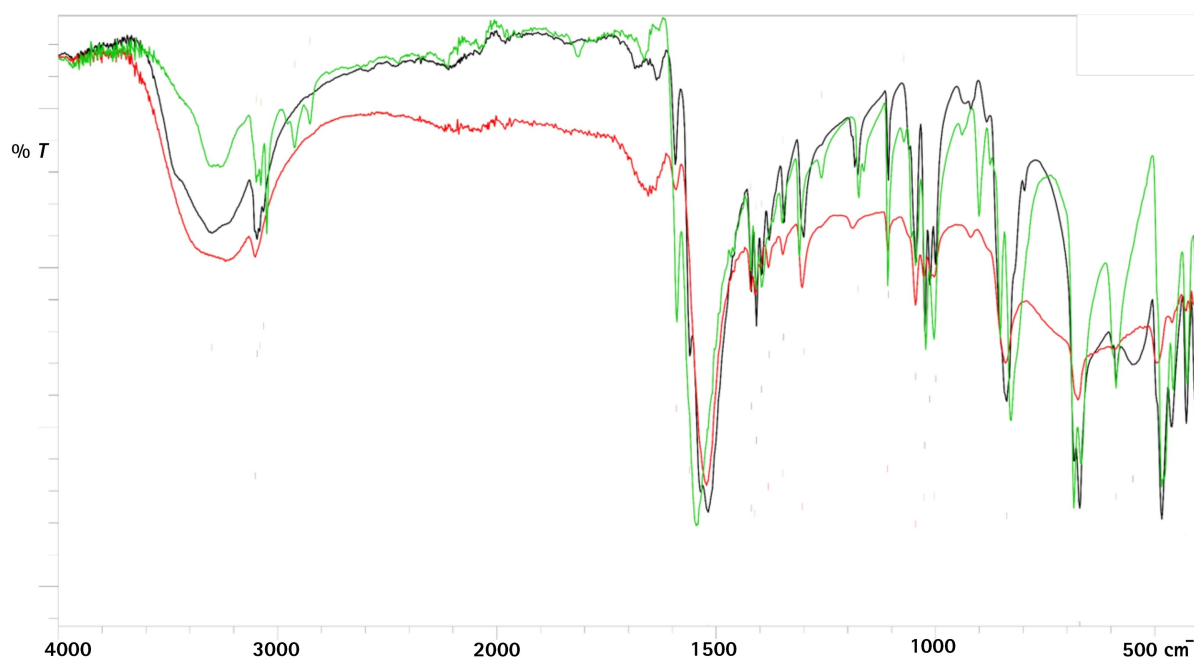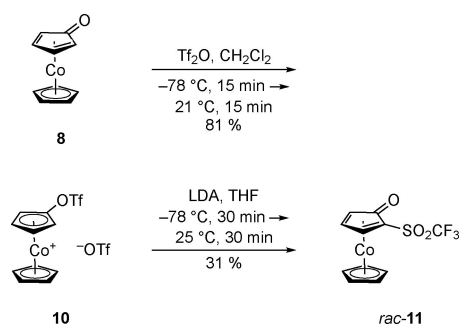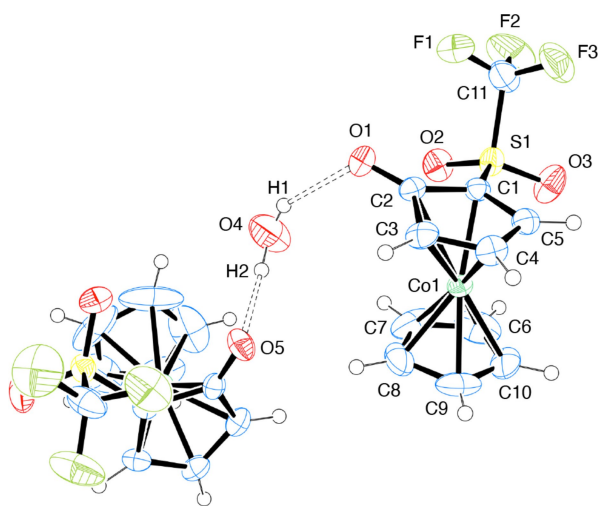
Scheme 2. Synthesis of cyclopentadienone complexes **6–8**.[28]

Figure 1. IR spectra of hygroscopic (cyclopentadienone)(cyclopentadienyl)cobalt(I) (**8**) 0 min (green, sample not exposed to the air), 10 min (black, sample exposed to the air), and 16 h (red, sample exposed to the air) after isolation. The increase in water content is reflected by an increase of the absorption band at >3000 cm⁻¹.

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Scheme 3. Synthesis of **10** followed by the first anionic thia-Fries rearrangement at a cobaltcenium complex. OTf = OSO_2CF_3.

7-ene (DBU) under various reaction conditions. Upon addition, the yellow solution immediately turned red. However, due to decomposition during the chromatographic separation, it was not possible to isolate the red product. As DBU can react as a nucleophile, we speculate that DBU might have attacked the electrophilic sulfur atom eventually causing decomposition with formation of **8**, which has been observed by thin layer chromatography.

It was possible to obtain a crystal structure analysis of the rearrangement product *rac*-**11** (Figure 2). The structure shows a monoclinic crystal system [space group *Cc* (9)] with two enantiomeric molecules of **11** connected by a water molecule forming hydrogen bridges to the two carbonyl oxygen atoms. The cyclopentadienone ligand is not completely planar with the
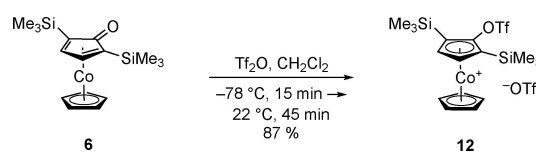
carbonyl group being bent away from the cobalt atom by about 13.3°. This is in accord with a change in hapticity from η^5 to η^4 in the course of the reaction, which is also reflected by the bond lengths between the cobalt atom and the cyclopentadienyl carbon atoms with Co–C2 showing the largest bond length [227.8(5) pm]. For obvious steric reasons the trifluoromethyl group points away from the cyclopentadienyl ligand, thereby maximizing the distance between the electronegative carbonyl oxygen atom and those at the sulfur atom.

In addition to the fact that the first anionic thia-Fries rearrangement at a cobalt complex has been found, it deserves mention, that the *ortho* deprotonation of **10** with LDA is, to the best of our knowledge, the first case of a deprotonation of a cobaltcenium complex with a lithium base. Usually, the reaction of cobaltcenium complexes with organometallic bases including lithium bases such as alkyllithium and even lithium piperidide results in a nucleophilic attack at one of the cyclopentadienyl ligands finally resulting in respective *exo* substituted (cyclopentadiene)(cyclopentadienyl)cobalt(I) complexes,[35,36] thereby significantly contrasting the reactivity of isoelectronic ferrocene analogues.[37,38]
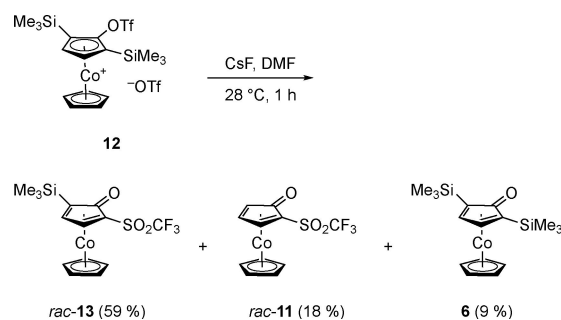
Next, the bis(trimethylsilyl) substituted cyclopentadienone complex **6** was treated with triflic anhydride affording cobaltcenium complex **12** in 87% yield as an air stable yellow solid (Scheme 4).

Compound **12** was then treated with cesium fluoride in dimethyl formamide at 28 °C. The yellow solution immediately turned red, and after chromatographic separation of the resulting mixture *rac*-**13** was obtained in 59% yield in addition to *rac*-**11** (18%) and **6** (9%) (Scheme 5). *rac*-**13** and *rac*-**11** are the result of an anionic thia-Fries rearrangement with an overall yield of 77%, the formation of *rac*-**11** resulting from a desilylation.

As a decomplexation of cyclopentadienones from their cyclopentadienylcobalt(I) complexes is possible by treatment

Figure 2. Structure of *rac*-**11** in the crystal at 50% ellipsoid probability level.[34] Two enantiomeric molecules are connected by a water molecule forming hydrogen bridges to the carbonyl oxygen atoms. Color code: C blue, O red, Co green, S yellow, F bright green, H white. Corresponding atoms are marked with an asterisk (*). Selected bond lengths (pm), bond angles (°), and dihedral angles (°): Co1–C1 202.1(5), Co1–C2 227.8(5), Co1–C3 204.8(6), Co1–C4 201.4(6), Co1–C5 199.5(6), C1–S1 172.2(6), C2–O1 123.0(7), S1–O2 142.2(4), S2–O3 143.0(6), S1–C11 183.1(7), C11–F1 132(1), C11–F2 132.4(9), C11–F3 130.5(9), O1–H1 210(10), O5–H2 190(10), O4–H1 80(10), O4–H2 90(20); C1–C2–O1 129.2(5), O2–S1–O3 121.0(3), C1–S1–C11 103.8(3), C3–C2–O1 129.3(5), C1–S1–O2 111.5(3), C1–S1–O3 109.8(3),; Co1–C1–S1-C11 −178.1(3), O1–C2–C1–S1 7.8(9).

Scheme 4. Synthesis of cobaltcenium complex **12**.

Scheme 5. Fluoride induced anionic thia-Fries rearrangement of **12**.

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with cerium ammonium nitrate,[28] the reaction provides a new access to substituted cyclopentadienone derivatives as building blocks for further syntheses of compounds such as interesting aromatic systems,[39,40] cycloheptatrienes,[41,42] anellated cyclopentanones,[43] norbornenones,[44] triptycenes,[45] and various heterocycles,[46,47] often by Diels-Alder cycloadditions.[48]

In the course of our investigations with ferrocene systems it was shown that the anionic thia-Fries rearrangement does not take place with ferrocenyl mesylate or tosylate.[23] This gave rise to check, if the corresponding cobaltocenium salts behave accordingly, or if the rearrangement took place with them. When cyclopentadienone complex **6** was treated with methanesulfonic anhydride, the required reaction temperature was higher than with triflic anhydride, presumably due to the decreased electrophilicity of the anhydride. Cobaltocenium mesylate **14** was obtained as an air stable, hygroscopic yellow solid in 74% yield; a small amount of **6** could not be removed. It is unclear if this is an impurity or a result of an equilibrium under the reaction conditions. The corresponding reaction of **6** with tolylsulfonyl anhydride gave **15** in 73% yield based on NMR measurements; as before, a small amount of **6** could not be removed (Scheme 6). Unfortunately, it was not possible to induce an anionic thia-Fries rearrangement with **15** or **16** upon addition of cesium fluoride under various reaction conditions.

Conclusions

In conclusion, we reported the first anionic this-Fries rearrangements with cobaltocenium complexes. The reaction takes place with cobaltocenium triflates either by an unprecedented deprotonation of the *ortho* position or by fluoride induced desilylation of the respective silyl-substituted cobaltocenium cations. Starting materials were obtained in high yields from the respective (cyclopentadienone)(cyclopentadienyl)cobalt(I) complexes by treatment with triflic anhydride. As with the respective ferrocene derivatives, the reaction does not take place when triflate is replaced by mesylate or tosylate.
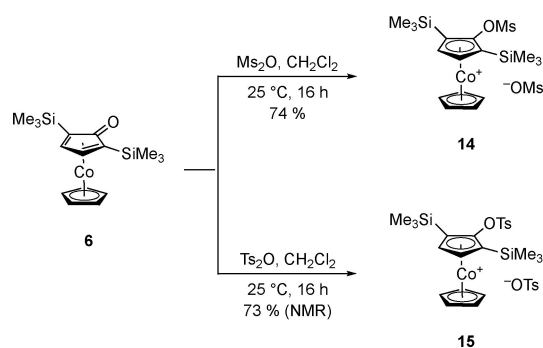
Scheme 6. Syntheses of cobaltocenium salts **14** and **15** as substrates for attempted anionic thia-Fries rearrangements.

Experimental Section

General: All reactions were carried out in an inert atmosphere (Argon) using the Schlenk technique. THF was dried at reflux over sodium/benzophenone, dichloromethane by stirring over calcium hydride, and diisopropylamine (DIPA) by stirring over potassium hydroxide. All solvents were freshly distilled before use. Dimethylformamide (DMF) was purchased from commercial suppliers and used without further purification. Deuterated chloroform was dried by heating at reflux over calcium hydride and distilled in an inert atmosphere. IR: Fourier transform infrared spectrophotometer Shimadzu IRAffinity 1S with quest ATR unit (32 scans). Signal intensities: strong (s), medium (m), weak (w), broad (br). High resolution electron ionization (HR-EI) mass spectra were measured using a Micromass GCT spectrometer with direct insertion probe, 70 eV electron ionization energy and 250 °C source temperature. High resolution electrospray ionization (HR-ESI) mass spectra were measured using a Waters LCT Premier instrument with Alliance 2695 HPLC (Waters), 2700 V capillary voltage, 650 l/h desolvation gas and 250 °C desolvation temperature. NMR: Bruker Ascend (^{1}H: 600.1 MHz, ^{13}C: 150.9 MHz, ^{19}F: 376.5 MHz) with Avance NEO Console at 298 K, Ascend (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz) with Avance III Console or Ascend with Avance III HD Console and Ultrashield (^{1}H: 500.1 MHz, ^{13}C: 125.8 MHz) with Avance-III HD console. The chemical shift of the residual solvent signal of the deuterated solvent (CDCl$_3$: ^{1}H $\delta = 7.26$ ppm, ^{13}C 77.16 ppm; CD$_3$OD: ^{1}H $\delta = 3.31$ ppm, ^{13}C 49.00 ppm; C$_6$D$_6$: ^{1}H $\delta = 7.16$ ppm, ^{13}C 128.06 ppm; CD$_2$Cl$_2$, ^{1}H: $\delta = 5.32$ ppm) was used as the internal standard. ^{19}F NMR: Spectrometer frequency for ^{1}H was multiplied by 0.94094008 and the resulting value entered as the spectrometer frequency for ^{19}F according to the IUPAC convention.[49] Cp' refers to the unsubstituted cyclopentadienyl ligand (C$_5$H$_5$). Melting points (m. p.) were measured using Electrothermal IA 9000 Series Melting Point Apparatus. Medium pressure liquid chromatography (MPLC): Büchi Chromatography Pump 688, Büchi gradient Former B687, Büchi Fraction collector B684 and a Knauer UV detector K-2501. Cyclopentadiene was used freshly after distillation. Cyclopentadienylcobalt(I) dicarbonyl used in this work was synthesized based on Bergman's[50] adapted procedure of Rausch et al.[29] LDA was always prepared from freshly distilled diisopropylamine. All other reagents were bought from commercial suppliers and used without further purification.

(Cyclopentadienone)(cyclopentadienyl)cobalt(I) (8):[28] A suspension of [2,5-bis(trimethylsilyl)cyclopentadienone](cyclopentadienyl)cobalt(I)[28] (**6**, 867 mg, 2.5 mmol) and cesium fluoride (1134 mg, 7.5 mmol) in DMF (40 mL) was vigorously stirred at 110 °C (oil bath) in a two-neck PTFE 100 mL flask for 16 h. The mixture was filtered through a P3 frit into a Schlenk flask. After solvent removal at reduced pressure at 70 °C (oil bath) ethyl acetate (3×20 mL) was added to the crude mixture, which was filtered into another Schlenk flask through a P3 frit. The solvent was removed at reduced pressure, and the remaining red solid was recrystallized by slow diffusion of hexane (50 mL) into the ethyl acetate solution of **8** (10 mL) at 21 °C. The remaining solution was transferred into another Schlenk flask, and after solvent removal at reduced pressure the recrystallization was repeated using half of the volume of solvents used previously. After removal of the supernatant the remaining solvent was removed at reduced pressure, and (cyclopentadienone)(cyclopentadienyl)cobalt(I) (**8**, 428 mg, 2.1 mmol, 84%) was obtained as a crystalline red/orange solid (m. p. 46 °C). The data diverges a little from the literature data, because **8** was obtained anhydrous as compared with the monohydrated product from the literature.[28]

^{1}H NMR (400.1 MHz, CDCl$_3$): $\partial = 4.45 + 5.07$ (AA'BB', $J = 2.1$ Hz, 2× 2H, C$_5$H$_4$O), 5.11 (s, 5H, Cp') ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$, HSQC, HMBC): $\partial = 64.4$ (OCCHCH), 75.1 (OCCH), 81.4 (Cp'), 161.6 (C=O)

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ppm. IR: $\tilde{\nu} = 3098$ (m), 3049 (m), 1589 (m), 1545 (s), 1422 (m), 1410 (m), 1396 (m), 1348 (m), 1310 (m), 1260 (m), 1175 (m), 1109 (m), 1072 (m), 1045 (m), 1022 (m), 1003 (m), 901 (m), 853 (m), 827 (s), 685 (s), 667 (s), 588 (m), 484 (s), 457 (m), 426 (m) cm^{-1}. HRMS (EI): Calcd. for $C_{10}H_9CoO$ [M$^+$] 203.9985, found 203.9989.

[(Trifluoromethylsulfonyl)oxy]cobaltocenium trifluoromethanesulfonate (10): At $-78\,°C$, triflic anhydride in dichloromethane (1.0 M, 0.88 mL, 0.9 mmol) was added dropwise to a solution of (cyclopentadienone)(cyclopentadienyl)cobalt(I)[28] (**8**, 60 mg, 0.3 mmol) in dichloromethane (10 mL). The red solution immediately turned yellow. The solution was stirred at $-78\,°C$ for 15 min, slowly warmed to $21\,°C$ and further stirred for another 15 min. The solvent was evaporated and collected in a cold trap (to be later carefully quenched and neutralized), and a yellow oil was obtained. The oil was washed with diethyl ether (110 mL), and [(trifluoromethylsulfonyl)oxy]cobaltocenium trifluoromethanesulfonate (**10**, 116 mg, 81%) was obtained as a yellow solid (m. p. $176\,°C$, dec.).

^{1}H NMR (400.1 MHz, CD$_3$OD): $\partial = 5.79 + 6.32$ (AA'BB', $J = 2.3$ Hz, 2 × 2H, OCCH, OCCHC*H*), 6.01 (s, 5H, Cp') ppm. ^{13}C NMR (100.6 MHz, CD$_3$OD, HSQC, HMBC): $\partial = 78.1$ (OCC*H*CH), 81.8 (OC*C*H), 88.1 (Cp'), 119.8 (q, $^1J_{C,F} = 320.5$ Hz, CF$_3$), 121.8 (q, $^1J_{C,F} = 321.5$ Hz, CF$_3$), 125.9 (CO) ppm. ^{19}F NMR (376.5 MHz, CD$_3$OD): $\partial = -74.1$ (OSO$_2$CF$_3$), -80.1 (OSO$_2$CF$_3$) ppm. IR: $\tilde{\nu} = 3120$ (m), 1441 (m), 1420 (m), 1375 (w), 1279 (m), 1213 (s), 1165 (m), 1132 (s), 1022 (s), 932 (m), 870 (m), 839 (m), 814 (m), 768 (m), 712 (m), 635 (m), 617 (s), 598 (s), 573 (m), 517 (s), 463 (s), 424 (m) cm^{-1}. HRMS (ESI, MeOH): Calcd. for $C_{11}H_9CoF_3O_3S$ [M$^+$] 336.9556, found 336.9557. Calcd. for CF$_3$O$_3$S [M$^-$] 148.9520, found 148.9516.

***rac*-(Cyclopentadieny)[2-(trifluoromethylsulfonyl)cyclopentadienone]cobalt(I) (*rac*-11):** At $-78\,°C$ lithium diisopropylamide [prepared from butyllithium in hexane (2.5 M, 0.78 mL, 1.9 mmol) and diisopropylamine (0.82 mL, 5.8 mmol) in THF (5 mL)] was added dropwise to [(trifluoromethylsulfonyl)oxy]cobaltocenium trifluoromethanesulfonate (**10**, 315 mg, 0.6 mmol) in THF (5 mL). The dark yellow solution immediately turned red and then brown. The solution was stirred at $-78\,°C$ for 30 min, slowly warmed to $25\,°C$ and further stirred for another 15 min. The solvent was removed at reduced pressure and the remaining solid redissolved in dichloromethane (20 mL). The solution was acidified by addition of oxygen free 37% aq. HCl under pH control until pH 6. After solvent and water removal at reduced pressure the crude product was purified by column chromatography {3 × 10 cm, alumina [deactivated with water (15% w/v)], ethyl acetate followed by acetone/ methanol 7:3} affording (cyclopentadienyl)[2-(trifluoromethylsulfonyl)cyclopentadienone]cobalt(I) (*rac*-11, 67 mg, 0.2 mmol, 31%) as a red/orange solid (m. p. $158\,°C$, dec.).

^{1}H NMR (400.1 MHz, CDCl$_3$): $\partial = 4.76$ (dd, $J = 3.3$ Hz, $J = 1.7$ Hz, 1H, OCCHCHC*H*), 5.41 (t, $J = 3.3$ Hz, 1H, OCCHC*H*), 5.42 (s, 5H, Cp'), 5.73 (dd, $J = 3.3$ Hz, $J = 1.7$ Hz, 1H, OCCH) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$, HSQC, HMBC): $\partial = 65.5$ (OCCHC*H*CH), 70.2 (OCCS), 76.0 (OCC*H*CH or OC*C*H), 77.7 (OC*C*H or OCHC*H*), 83.3 (Cp'), 119.2 (q, $^1J_{C,F} = 325.6$ Hz, CF$_3$), 158.6 (CO) ppm. ^{19}F NMR (376.5 MHz, CDCl$_3$): $\partial = -78.0$ (SO$_2$CF$_3$) ppm. IR: $\tilde{\nu} = 3078$ (w), 2922 (w), 2856 (w), 1734 (w), 1612 (s), 1584 (m), 1364 (s), 1198 (s), 1186 (s), 1175 (s), 1113 (s), 1080 (m), 997 (m), 837 (m), 793 (w), 764 (w), 708 (m), 692 (s), 631 (m), 610 (s), 569 (m), 517 (m), 503 (m), 469 (m), 432 (m), 413 (m) cm^{-1}. HRMS (ESI, MeCN): Calcd. for $C_{11}H_8CoF_3O_3SNa$ [M + Na] 358.9376, found 358.9391.

Crystal structure analysis:[34] Single crystals suitable for X-ray analysis were obtained by slow evaporation of an ethyl acetate solution of *rac*-11. $C_{22}H_{18}Co_2F_6O_7S_2$ (Two enantiomeric molecules of **11** and one water molecule), orange plate, $M_r = 690.34$, crystal

system monoclinic, space group C1c1, $a = 9.750(6)$, $b = 9.775(5)$, $c = 26.071(15)$ Å, $\alpha = 90°$, $b = 97.54(3)°$, $\gamma = 90°$, $V = 2463.0(3)$ Å^3, $Z = 4$, $d_{calc} = 1.861$ g·cm^{-3}, $\mu = 1.605$ mm^{-1}, crystal size 0.25 × 0.21 × 0.10 mm^3, $F(000) = 1384$, Bruker SMART X2S diffractometer, graphite crystal monochromator, $T = 300$ K, Mo-K$_a$ radiation ($l = 0.71073$ Å), $2.96° \leq \theta \leq 29.70°$, index ranges $-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-36 \leq l \leq 36$, reflections collected/unique 6795/5358, numerical absorption correction, structure solution and refinement with SHELXL-2018/3,[51] parameter/restraints 361/2, $R_1 = 0.0458$ [$I > 2\sigma(I)$], $wR_2 = 0.0980$ (all data), $S = 0.983$, finals maximum/minimum difference electron density 0.379/-0.478 eÅ^{-3}.

1-[(Trifluoromethylsulfonyl)oxy]-2,5-bis(trimethylsilyl)cobaltocenium trifluoromethanesulfonate (12): At $-78\,°C$ triflic anhydride (0.03 mL, 0.2 mmol) was added dropwise to [2,5-bis(trimethylsilyl)cyclopentadienone](cyclopentadienyl)cobalt(I)[28] (**6**, 40 mg, 0.1 mmol) in dichloromethane (8 mL). The red solution immediately turned yellow. The solution was stirred at $-78\,°C$ for 15 min, slowly warmed to $22\,°C$ and further stirred for another 15 min. The solvent was evaporated and collected in a cold trap (to be later carefully quenched and neutralized). The remaining yellow greenish solid was washed with diethyl ether (3 × 5 mL). The remaining solvent was removed at reduced pressure and the residue redissolved in dichloromethane (1 mL). Diethyl ether (1 mL) was added, and the mixture was left at $-30\,°C$ for 48 h. The solvent was removed with a syringe and 1-[(trifluoromethylsulfonyl)oxy]-2,5-bis(trimethylsilyl)cobaltocenium trifluoromethanesulfonate (**12**, 63 mg, 0.1 mmol, 87%) was obtained as a yellow crystalline solid (m. p. $178\,°C$, dec.).

^{1}H NMR (600.3 MHz, CD$_3$OD): $\partial = 0.51$ (s, 18 H, 2 × SiMe$_3$), 5.87 (s, 2H, SiCC*H*), 6.00 (s, 5H, Cp') ppm. ^{13}C NMR (150.9 MHz, CD$_3$OD, HSQC, HMBC): $\partial = -0.7$ (2 SiMe$_3$), 87.9 (Cp'), 90.2 (SiC*C*H), 92.0 (C$_{Cp}$Si), 119.4 (q, $^1J_{C,F} = 319.6$ Hz, CF$_3$), 121.8 (q, $^1J_{C,F} = 318.4$ Hz, CF$_3$), 130.5 (C$_{Cp}$O) ppm. ^{19}F NMR (376.5 MHz, CD$_2$Cl$_2$): $\partial = -72.6$ (SO$_2$CF$_3$), -78.9 (SO$_2$CF$_3$) ppm. IR: $\tilde{\nu} = 3107$ (w), 3071 (w), 1412 (m), 1304 (m), 1263 (s), 1217 (s), 1148 (s), 1126 (s), 1088 (m), 1032 (s), 1015 (m), 891 (m), 835 (s), 822 (s), 764 (m), 723 (m), 708 (m), 637 (s), 611 (s), 573 (m), 536 (m), 517 (m), 503 (m), 474 (m), 424 (s) cm^{-1}. HRMS (ESI, MeOH): Calcd. for $C_{17}H_{25}CoF_3O_3SSi_2$ [M$^+$] 481.0347, found 481.0347. Calcd. for CF$_3$O$_3$S [M$^-$] 148.9520, found 148.9524.

***rac*-(Cyclopentadienyl)[2-(trifluoromethylsulfonyl)-5-(trimethylsilyl)cyclopentadienone]cobalt(I) (*rac*-13):** At $25\,°C$ 1-[(trifluoromethylsulfonyl)oxy]-2,5-bis(trimethylsilyl)cobaltocenium trifluoromethanesulfonate (**12**, 148 mg, 0.2 mmol) in DMF (5 mL) was added to a suspension of cesium fluoride (36 mg, 0.2 mmol) in DMF (1 mL). The yellow solution immediately turned red. The mixture was stirred for 1 h at $28\,°C$, and the solvent was removed at $70\,°C$ (oil bath temperature) at reduced pressure. Dichloromethane (25 mL) was added, and the solution was filtered. The solvent was removed at reduced pressure. Column chromatography [3 × 25 cm, SiO$_2$, (deactivated with Et$_3$N), petroleum ether/ethyl acetate 6:4 gradient to 8:2 (v/v)] afforded three products.

I: **6**, 8 mg, 0.02 mmol, 9%

II: (Cyclopentadienyl)[2-(trifluoromethylsulfonyl)-5-(trimethylsilyl)-cyclopentadienone]cobalt(I) (*rac*-13, 57 mg, 0.1 mmol, 59%), orange solid (m. p. $130\,°C$, dec.). ^{1}H NMR (600.3 MHz, C$_6$D$_6$): $\partial = 0.14$ (s, 9H, CH$_3$), 4.40 (d, $^3J = 3.1$ Hz, 1H, SiCC*H*), 4.57 (s, 5H, Cp'), 5.28 (d, $^3J = 3.1$ Hz, 1H, SCC*H*) ppm. ^{13}C NMR (150.9 MHz, C$_6$D$_6$, HSQC, HMBC): $\partial = -1.3$ (SiMe$_3$), 69.8 (OCCS or OCCSi), 72.0 (OCCS or OC*C*Si), 77.4 (SiC*C*H), 82.2 (Cp'), 82.4 (SCC*H*), 120.0 (q, $^1J_{C,F} = 326.2$ Hz, CF$_3$), 162.9 (CO) ppm. ^{19}F NMR (376.5 MHz, C$_6$D$_6$): $\partial = -78.2$ (SO$_2$CF$_3$) ppm. IR: $\tilde{\nu} = 3115$ (w), 2959 (w), 1614 (s), 1358 (s), 1252 (m), 1209 (s), 1186 (s), 1146 (m), 1125 (m), 1111 (m), 1094 (m), 1011 (m), 866 (m), 824 (s), 762 (m), 727 (m), 706 (m), 692 (m), 669 (m), 619 (s), 569 (s), 523

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(m), 509 (m), 474 (m), 455 (m), 412 (m) cm^{-1}. HRMS (ESI, MeCN): Calcd. for $C_{14}H_{16}CoF_3O_3SSiNa$ [M$^+$ + Na] 430.9771, found 430.9758.

III: *rac*-**11** (14 mg, 0.04 mmol, 18%).

1-(Methanesulfonyloxy)-2,5-bis(trimethylsilyl)cobaltocenium methanesulfonate (14): At 25 °C [2,5-bis(trimethyl-silyl)cyclopentadienone](cyclopentadienyl)cobalt(I)[28] (**6**, 26 mg, 0.07 mmol) in dichloromethane (6 mL) was added to methanesulfonic anhydride (13 mg, 0.07 mmol) in dichloromethane (1 mL). The red solution turned orange/yellow after approximately 2 h. The solution was stirred at 25 °C for 16 h. The solvent was evaporated and collected in a cold trap (to be later carefully quenched and neutralized). The remaining yellow solid was washed with diethyl ether (0 °C, 3×5 mL). The remaining solvent was removed at reduced pressure and the residue redissolved in dichloromethane (1 mL). Diethyl ether (1 mL) was added, and the mixture was left at −30 °C for 48 h. The solvent was removed with a syringe and 1-[(methanesulfonyl)oxy]-2,5-bis(trimethylsilyl)cobaltocenium methanesulfonate [**14**, 29 mg, 0.05 mmol (89% based on NMR integration), isolated yield 66%] was obtained as a yellow crystalline solid containing residual **6** and methanesulfonic anhydride (^{1}H NMR)

^{1}H NMR (400.1 MHz, CDCl$_3$): ∂ = 0.45 (s, 18 H, SiCH$_3$), 2.95 (s, 3H, $^-$OSO$_2$CH$_3$), 3.32 (s, 3H, SiCCOSO$_2$CH$_3$), 5.81 (s, 5H, Cp′), 5.92 (s, 2H, SiCCH) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$, HSQC, HMBC): ∂ = −0.3 (SiMe$_3$), 39.6 (SiCCOSO$_2$CH$_3$), 39.6 ($^-$OSO$_2$CH$_3$), 86.3 (Cp′), 89.4 (C$_{Cp}$H), 90.8 (SiCCO), 129.2 (SiCCO) ppm. IR: $\tilde{\nu}$ = 3422 (w), 3096 (w), 3015 (w), 1418 (m), 1356 (m), 1341 (m), 1323 (m), 1252 (m), 1180 (s), 1136 (m), 1096 (m), 1022 (m), 972 (m), 893 (m), 833 (s), 814 (s), 770 (s), 752 (s), 700 (m), 640 (m), 540 (s), 517 (s), 473 (m), 420 (s) cm^{-1}. HRMS (ESI, MeCN): Calcd. for $C_{17}H_{28}CoO_3SSi_2$ [M$^+$] 427.0624, found 427.0629. Calcd. for CH$_3$O$_3$S [M$^-$] 97.9803, found 94.9803.

1-(*p*-Toluenesulfonyloxy)-2,5-bis(trimethylsilyl)cobaltocenium *p*-toluenesulfonate (15): At 25 °C [2,5-bis(trimethylsilyl)cyclo-pentadienone](cyclopentadienyl)cobalt(I)[28] (**6**, 98 mg, 0.3 mmol) in dichloromethane (5 mL) was added to toluenesulfonic anhydride (92 mg, 0.3 mmol) in dichloromethane (2 mL) at 25 °C. The red solution turned orange/yellow after approx. 2 h. After stirring at 25 °C for 16 h the solvent was evaporated and collected in a cold trap (to be later carefully quenched and neutralized). The remaining yellow solid was washed with diethyl ether (0 °C, 3×5 mL). As crystallization attempts failed, the remaining solvent was removed at reduced pressure. 1-(*p*-Toluenesulfonyloxy)-2,5-bis(trimethylsilyl)cobaltocenium *p*-toluenesulfonate (**15**, 138 mg, 73%, based on NMR integration) was obtained as a mixture with starting material and *p*-toluenesulfonic anhydride as a yellow solid. Most of the ^{13}C NMR peaks were assigned, but due to the mixture and an unclear HMBC, signals of two quarternary carbon atoms (COS and COSO$_2$C) could not be assigned.

^{1}H NMR (400.1 MHz, CDCl$_3$): ∂ = 0.40 (s, 18 H, SiMe$_3$), 2.34 (s, 3H, $^-$OSO$_2$CCHCHCC**H**$_3$), 2.50 (s, 3H, COSO$_2$CCHCHCC**H**$_3$), 5.79 (s, 5H, Cp′), 6.10 (s, 2H, SiCCH), 7.14 + 7.78 (2d, *J* = 7.8 Hz, 2×2H, $^-$OSO$_2$CC**H**CHCH$_3$), 7.43 + 7.83 (2d, *J* = 8.2 Hz, 2×2H, CpOSO$_2$CC**H**CHCH$_3$) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$, HSQC, HMBC): ∂ = −0.17 (SiMe$_3$), 21.5 ($^-$OSO$_2$CCHCHCC**H**$_3$), 22.0 (CpOSO$_2$CCHCHCC**H**$_3$), 86.3 (Cp′), 90.2 (SiCCH), 90.3 (SiCCH), 126.5 ($^-$OSO$_2$C**C**H or $^-$OSO$_2$CCH**C**H), 128.6 (C$_{Ph}$), 129.0 ($^-$OSO$_2$C**C**H or $^-$OSO$_2$CCH**C**H), 130.6 (OSO$_2$C**C**H or OSO$_2$CCH**C**H), 140.8 ($^-$OSO$_2$CCHCH**C**), 141.0 ($^-$OSO$_2$**C**), 147.3 (OSO$_2$CCHCH**C**) ppm. IR: $\tilde{\nu}$ = 2955 (m), 2920 (s), 2853 (m), 1715 (w), 1458 (m), 1418 (m), 1377 (m), 1364 (m), 1319 (m), 1258 (m), 1192 (m), 1177 (m), 1059 (m), 1024 (m), 1009 (m), 893 (m), 833 (m), 812 (s), 800 (s), 758 (m), 704 (m), 679 (m), 664 (m), 640 (m), 615 (m), 565 (m), 546 (m), 496 (m), 463 (m), 407 (m) cm^{-1}. HRMS (ESI, MeCN): Calcd. for $C_{23}H_{32}CoO_3SSi_2$ [M$^+$] 503.0937, found 503.0939.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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