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Characterization of the μ-(η^1-C: η^2-S,S′) dithiocarboxylate complexes $Cp(CO)_2Fe{-}CS_2{-}Zr(X)Cp_2$ (X = Cl, $OCMe_3$); CS_2 insertion into the FeZr bond of the heterobimetallic complex $Cp(CO)_2Fe{-}Zr(OCMe_3)Cp_2$

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Abstract

Treatment of the carbon disulfide adducts $FpCS_2K$ and $Fp'CS_2K$ [$Fp' = (\eta^5\text{-}C_5H_4CH_3)Fe(CO)_2$] with Cp_2ZrCl_2 affords the μ-(η^1-C: η^2-S,S′) dithiocarboxylate complexes $FpCS_2ZrClCp_2$ (**1**) and $Fp'CS_2ZrClCp_2$ (**2**). Both stable products were fully characterized. Metathesis between $FpCS_2K$ and $Cp_2ZrCl(OCMe_3)$ provided $FpCS_2Zr(OCMe_3)Cp_2$ (**3**), which was not obtained analytically pure. This product was characterized by comparison of its IR and ^1H-, $^{13}C\{^1H\}$-NMR spectral data with that for **1** and **2**. The iron–zirconium complex $FpZr(OCMe_3)Cp_2$ (**4**) was transformed by one equivalent of CS_2 to **3** (75% spectroscopic yield), a reaction that did not occur for $FpZrClCp_2$. An insertion pathway is discussed for incorporating the CS_2 into the Fe–Zr bond of $FpZr(OCMe_3)Cp_2$. © 1998 Elsevier Science S.A. All rights reserved.

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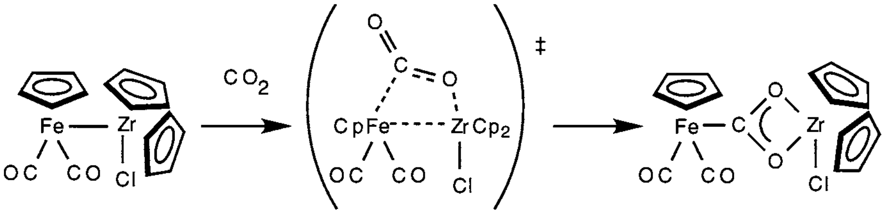
1. Introduction

Recently we reported that $Fp{-}ZrClCp_2$ [$Fp = Fe(CO)_2Cp$; $Cp = \eta^5\text{-}C_5H_5$] incorporates carbon dioxide and efficiently gives the known [1] FeZr μ-(η^1-C: η^2-O,O′) bimetallocarboxylate $FpCO_2ZrClCp_2$, Eq. 1 [2]. A CO_2 insertion pathway requiring bifunctional activation and insertion of the CO_2 was favored. An alternative pathway required prior ionization of the iron–zirconium bond on $Fp{-}ZrClCp_2$ to give Fp^- and $Cp_2ZrCl(THF)^+$; the resulting Fp^- could intercept the CO_2 as $FpCO_2^-$ [3], which then trapped the zirconocene electrophile and produced the observed $FpCO_2ZrClCp_2$. This ionization pathway, however, was inconsistent with the results of carbon disulfide trapping experiments. If $Fp{-}ZrClCp_2$ did ionize under the conditions of the CO_2 insertion experiments (THF, 0°C), then it should intercept CS_2 as the relatively stable dithiocarboxylate $FpCS_2^-$ [4] and perhaps form the (then unreported) $FpCS_2ZrClCp_2$ (**1**). We observed however that $Fp{-}ZrClCp_2$ was inert towards CS_2 under comparable reaction conditions.



(1)

Other examples of CO_2 incorporation into metal–metal bonds of heterobimetallic complexes have been reported [5]. Several examples of CS_2 insertion into

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metal–metal bonds also are known ([5]b,c), the most recent example having been reported for the Fe–Zr complex $HC(SiMe_2NC_6H_4F\text{-}2)_3ZrFe(CO)_2Cp$ ([5]c, [6]). We now report the synthesis and characterization of the μ-(η^1-C: η^2-S,S′) dithiocarboxylate complexes $FpCS_2ZrClCp_2$ (**1**) and $Fp'CS_2ZrClCp_2$ (**2**) [Fp′ = $Fe(CO)_2(\eta^5\text{-}C_5H_4CH_3)$], the partial characterization of $FpCS_2Zr(OCMe_3)Cp_2$ (**3**), and details on the reactions of CS_2 with $FpZr(X)Cp_2$ (X = Cl, $OCMe_3$).

2. Experimental section

2.1. Materials

Synthetic manipulations were performed in a nitrogen atmosphere using a combination of standard Schlenk line, glovebox, and vacuum line procedures [7]. Infrared spectra were recorded on a Perkin-Elmer Model 1600 spectrophotometer. ^{1}H- and $^{13}C\{^1H\}$-NMR spectra were recorded in C_6D_6 (which had been stored over 3A molecular sieves) using a Varian Unity 500 spectrometer, and the data were reported as δ values relative to residual C_6D_5H (^{1}H: 7.15 ppm) and C_6D_6 (^{13}C: 128.00 ppm). Tetrahydrofuran (THF), diethyl ether, pentane, and hexane were distilled from sodium/benzophenone ketyl, and methylene chloride was distilled from P_2O_5. The organometallic compounds $Cp(CO)_2FeK$ (FpK) [8], $[(\eta^5\text{-}C_5H_4CH_3)Fe(CO)_2]_2$ or (Fp'_2) [9], $Cp_2ZrCl(OCMe_3)$ [10], and $FpZr(X)Cp_2$ (X = Cl, $OCMe_3$) [11] were prepared by literature procedures and judged pure by IR and ^{1}H-NMR spectroscopy. Samples of $FpCS_2Fe(CO)Cp$ and FpC(S)SFp were available from a previous study [12]. All other reagents were used as received. Elemental microanalyses were performed by Quantitative Technologies, N.J.

2.2. Synthesis of $(\eta^5\text{-}C_5H_5)(CO)_2FeCS_2Zr(Cl)(\eta^5\text{-}C_5H_5)_2$ (1)

To a dark orange solution of FpK (218 mg, 1.0 mmol) in 10 ml of THF, precooled to −23°C, was added 60 µl of carbon disulfide (1.0 mmol). An IR spectrum of the orange-red solution after 20 min was consistent with quantitative transformation of FpK to $FpCS_2K$ ([4]a, [12]), υ(CO) 1999, 1945 cm^{-1}. To this solution was added Cp_2ZrCl_2 (293 mg, 1.0 mmol) in 10 ml of THF, and an IR spectrum of the crimson solution after 20 min showed only absorptions that were attributed to $FpCS_2Zr(Cl)Cp_2$ (**1**), υ(CO) 2029, 1982 cm^{-1}, along with residual CS_2, 1520 cm^{-1}. The THF was evaporated at room temperature and the resulting brown solid was suspended in 15 ml of benzene. Addition of 100 ml of hexane precipitated a greenish brown solid having a yellow hue and left a light orange supernatant solution, which was removed. The remaining solid was extracted with 75 ml of benzene, and the filtrate was evaporated to a green-brown solid. This solid was suspended in benzene (15 ml), treated with hexane (100 ml), and filtered. The 380 mg of greenish brown powder (with a yellowish hue) that remained after washing with hexane and vacuum drying was identified as $FpCS_2Zr(Cl)Cp_2$ (**1**), yield 70% and m.p. 187–191°C (decompositon). IR (CH_2Cl_2) 2034, 1987 cm^{-1}; IR (KBr) 2037, 1968 cm^{-1} υ(CO), 934, 851 cm^{-1} υ(SCS); ^{1}H-NMR (C_6D_6) δ 5.92 (s, Cp_2Zr), 4.13 (s, CpFe); $^{13}C\{^1H\}$-NMR ($CDCl_3$) 323.62 (s, CS_2), 212.05 (s, CO), 112.32 (Cp_2Zr), 87.84 (CpFe). Anal. Calc. for $C_{18}H_{15}O_2S_2FeZrCl$: %C, 42.40; %H, 2.96. Found: %C, 42.43; %H, 2.86. A somewhat lower yield (39%) was realized by working up the reaction by benzene extraction (5 × 5 ml) and precipitation from THF-pentane (5–25 ml, −20°C).

2.3. Synthesis of $(\eta^5\text{-}C_5H_4CH_3)(CO)_2FeCS_2Zr(Cl)(\eta^5\text{-}C_5H_5)_2$ (2)

A THF solution of Fp′K (1.0 mmol, 10 ml) was generated by sonication (1 h) of Fp'_2 (192 mg, 0.50 mmol) with potassium metal (150 mg) ([8]c), υ(CO) 1866, 1792 cm^{-1}. The dark red centrifugate was cooled to −23°C and treated with CS_2 (60 µl, 1.0 mmol); an IR spectrum of the resulting orange-red solution after 20 min indicated quantitative formation of $Fp'CS_2K$ ([4]a, [12]), υ(CO) 1966, 1942 cm^{-1}. Addition of a THF solution (10 ml) of Cp_2ZrCl_2 (293 mg, 1.0 mmol) to this precooled solution (−23°C) provided a dark red solution within 20 min, υ(CO) 2026, 1979 cm^{-1}. The reaction mixture was evaporated at room temperature and the green-brown residue was slurried with 5 ml of benzene before 100 ml of hexane was added. A light greenish brown solid and a light yellow-brown supernatant solution resulted, which was filtered. The remaining solid was extracted with 75 ml of benzene (light golden brown), filtered, and the filtrate was evaporated to a golden brown solid. This solid was suspended in 5 ml of benzene, diluted with excess hexane, and filtered. The remaining mustard-colored powder was washed with hexane (3 × 5 ml) and dried in vacuo, yielding 310 mg (59% yield) of $Fp'CS_2Zr(Cl)Cp_2$, m.p. 170–172°C (decomposition); IR (KBr) 2023, 1972 cm^{-1} υ(CO), 922, 848 cm^{-1} υ(SCS); ^{1}H-NMR (C_6D_6) δ 5.94 (s, Cp_2Zr), 4.13 (m), 4.00 (m) (Cp′Fe), 1.43 (s) (CH_3–Cp′); $^{13}C\{^1H\}$-NMR (C_6D_6) δ 325.59 (CS_2), 213.64 (CO), 112.58 (Cp_2Zr), 87.78, 86.72 (Cp′Fe), 12.38 (CH_3). Anal. Calc. for $C_{19}H_{17}O_2S_2FeZrCl$: %C, 43.55; %H, 3.27. Found: %C, 43.72;%H, 3.24.

2.4. Preparation of (η^5-C_5H_5)(CO)$_2$FeCS$_2$Zr[OCMe$_3$](η^5-C_5H_5)$_2$ (3)

A precooled (−23°C) solution of FpK (0.243 g, 1.12 mmol) in THF (10 ml) was treated with CS_2 (70 µl, 1.16 mmol) for 20 min before a 5 ml THF solution of $Cp_2ZrCl(OCMe_3)$ (0.371 g, 1.12 mmol) was added. An IR spectrum of the orange-red solution after 20 min was consistent with quantitative formation of $FpCS_2Zr(OCMe_3)Cp_2$ (**3**), υ(CO) 2024, 1976 cm^{-1}. The solution was warmed to room temperature and the solvent was evaporated. Benzene extraction (4 × 5 ml) and filtration followed by concentration of the solution to 5 ml left a red-brown suspension, which was diluted with 100 ml of pentane. The resulting brown precipitate was filtered, washed with pentane (3 × 10 ml), and dried in vacuo: yield 530 mg of material that contains 82% $FpCS_2Zr(OCMe_3)Cp_2$ (**3**) (as ascertained by ^{1}H-NMR spectral integration versus PhOMe internal standard) along with low concentrations of several unidentified Cp_2Zr-containing and other organic residues. IR (THF) 2024, 1976(vs), 1536(w), 1190(m), 1015(s), 834(m), 798(s) cm^{-1}; (KBr) 2031, 1960 cm^{-1} υ(CO); ^{1}H-NMR (C_6D_6) δ 6.03 (Cp_2Zr), 4.26 (CpFe), 1.18 (Me); $^{13}C\{^1H\}$-NMR (C_6D_6) δ 312.44 (s, CS_2), 214.27 (CO), 111.65 (Cp_2Zr), 87.84 (CpFe), 79.34 (O*C*Me$_3$), 32.46 (Me). Attempts to further purify **3** by precipitation from THF-pentane or toluene-pentane (−78°C to room temperature) inevitably reduced the purity of this material such that multiple impurity resonances also were detected in the Cp_2Zr, CpFe, and $OCMe_3$ regions.

^{1}H-NMR spectra of $FpCS_2Zr(OCMe_3)Cp_2$ (**3**) exhibited intense singlets (relative intensities, 10:5:9) in the appropriate Cp_2Zr, CpFe, and $OCMe_3$ regions, respectively. Although no other organometallic products were identified, the NMR spectra typically had several weak intensity singlets flanking the Fp and Cp_2Zr Cp singlets. The purity of 82% **3** was quantitated by integration of these spectra versus the anisole internal standard. All attempts to crystallize or precipitate **3** inevitably degraded it as evidenced by reduced yields and often an increased presence of impurities.

2.5. Preparation of (η^5-C_5H_5)(CO)$_2$Fe–Zr(OCMe$_3$)Cp$_2$ (4)

A 50 ml Schlenk flask was charged with FpK (72 mg, 0.333 mmol) and $Cp_2ZrCl(OCMe_3)$ (110 mg, 0.333 mmol) in the glove box. A magnetic stirbar was added, and the flask was attached to a vacuum line; THF (10 ml) was added to the flask and the yellow-brown slurry was stirred for 30 min. IR spectra of the resulting yellow-brown solution showed the presence of $FpZr(OCMe_3)Cp_2$ (**4**), υ(CO) 1942, 1887 cm^{-1} [11] along with at most traces of Fp_2 (1992, 1954, 1782 cm^{-1}) and FpH (2013, 1953 cm^{-1}). The solution was evaporated and benzene extracts of the residue (3 × 5 ml) were filtered through oven-dried Celite. After evaporation of the combined extracts, the residue was dissolved in 5 ml of toluene and the solution was cooled to −78°C. Bright yellow crystals deposited of **4** formed, which were separated from the supernatant solution, washed with ether (3 ml), and dried under vacuum. Yield **4** 30 mg (19%); IR (KBr) 1937, 1870 cm^{-1} υ(CO), 1358, 1182, 1002, 829, 797, 738 cm^{-1}; ^{1}H-NMR (C_6D_6) δ 5.91 (Cp_2Zr), 4.10 (CpFe), 1.14 (Me); $^{13}C\{^1H\}$-NMR (C_6D_6) δ 219.81 (CO), 110.58 (Cp_2Zr), 82.43 (CpFe), 80.67 (O*C*Me$_3$), 31.72 (Me).

2.6. Reaction of (η^5-C_5H_5)(CO)$_2$FeZr(OCMe$_3$)Cp$_2$ (4) with CS$_2$

A THF solution of $FpZr(OCMe_3)Cp_2$ (**4**) (1.0 mmol, 20 ml) was generated from FpK (218 mg) and $Cp_2ZrCl(OCMe_3)$ (330 mg); an IR spectrum of the yellow solution after 10 min was consistent with the presence of only **4**, υ(CO) 1942, 1887 cm^{-1} [11], along with at most trace amounts of Fp_2 (1992, 1950, 1782 cm^{-1}) and FpH (2012, 1990 cm^{-1}). CS_2 (60.0 µl, 1.0 mmol) was added by syringe, and the solution was stirred for 1 h at room temperature. IR spectral monitoring established that the υ(CO) bands at 1942, 1887 cm^{-1} had been replaced by two new bands at 2024, 1976 cm^{-1}, ca. 80% of the original intensity (absorbance), plus υ(CO) bands for Fp_2, the only other IR-detectable Fp compound (15% yield). The resulting reaction mixture was worked up by benzene extraction and precipitation from THF-pentane (−20°C) to give 530 mg of a gummy red-brown solid. It was assayed by ^{1}H-NMR spectroscopy using an anisole internal standard: **4** was the main product (75% yield), with the balance being Fp_2 (15%) plus the usual degradation residues.

2.7. Reaction of (η^5-C_5H_5)(CO)$_2$FeZr(OCMe$_3$)Cp$_2$ (4) with CS$_2$ in C$_6$D$_6$

An NMR tube was loaded with a C_6D_6 solution (0.75 ml) of $FpZr(OCMe_3)Cp_2$ (**4**) and anisole (3.0 µl, 27.6 µmol). ^{1}H-NMR spectroscopic integration of this sample was used to quantify the **4** (15.4 µmol), and degassed CS_2 (1.0 µl, 16.6 µmol) then was injected. The reaction was monitored by NMR spectroscopy as the initial yellow solution gradually turned orange and finally dark red over 48 h. At this time, 15% of **4** remained, and a 61% yield of $FpCS_2Zr(OCMe_3)Cp_2$ (**3**) was quantified.

2.8. Attempted reaction of (η^5-C_5H_5)(CO)$_2$FeZr(Cl)Cp_2 with CS_2

A THF solution (5 ml) of FpZrClCp_2 was generated from the reaction between FpK (54 mg, 0.25 mmol) and Cp_2ZrCl_2 (73 mg, 0.25 mmol). An IR spectrum of the resulting orange solution after 20 min registered intense υ(CO) absorptions of FpZrClCp_2 [11] at 1955, 1905 cm^{-1}, along with absorptions indicative of the presence of 4% Fp_2. Carbon disulfide (38.0 µl, 0.50 mmol) was added by syringe, and the solution was monitored by IR spectroscopy. The only reaction that was observed was the gradual conversion of FpZrClCp_2 into Fp_2 over 3 h. When the same reaction was conducted at 0°C, only a 10% conversion of FpZrClCp_2 to Fp_2 was noted; FpCS_2Zr(Cl)Cp_2 (**1**) was not detected during either reaction.

2.9. Attempted reactions of (η^5-C_5H_5)(CO)$_2$FeZr(Cl)Cp_2 with $Cp_2Zr(OCMe_3)Cl$ and of (η^5-C_5H_5)(CO)$_2$FeZr(OCMe$_3$)Cp_2 (4) with Cp_2ZrCl_2

FpZrClCp_2 was generated in a THF solution (20 ml) from FpK (75 mg, 0.35 mmol) and Cp_2ZrCl_2 (101 mg, 0.35 mmol). This solution was transferred via cannula to a second 100-ml Schlenk flask containing a magnetic stir bar and $Cp_2Zr(OCMe_3)Cl$ (121 mg, 0.35 mmol). The resulting orange solution showed no formation of **4**, as adduced via IR spectroscopy, over 1 h. (varying mixtures of both, Fp–zirconocene complexes easily could be distinguished, particularly by their lower frequency υ(CO) absorptions, 1905 and 1887 cm^{-1}, respectively; 5–10% quantities of either bimetallic compound was detected in the presence of the other.) The only discernible change for this reaction was a gradual darkening to orange-brown as increasing amounts of Fp_2 appeared. Essentially the same results were obtained after treating (η^5-C_5H_5)(CO)$_2$FeZr(OCMe$_3$)Cp_2 (**4**) (0.52 mmol in 20 ml of THF) with 1.0 equivalent of Cp_2ZrCl_2 under identical conditions.

2.10. Attempted reaction of (η^5-C_5H_5)(CO)$_2$FeZr(OCMe$_3$)Cp_2 (4) with ethyl bromide

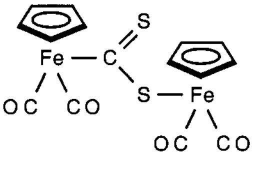
To a THF solution of **4** (0.054 mmol in 3.0 ml) was added excess ethyl bromide (10 µl, 0.13 mmol). The results of IR spectral examination over three quarters of an hour were consistent with the absence of FpCH_2CH_3, although a gradual increase of Fp_2 (20%) was noted. Control reaction: a THF solution of FpK (108 mg, 0.50 mmol in 20 ml) was treated with CH_3CH_2Br (40 µl, 0.52 mmol). Both the immediate change in color (dark orange to yellow) and in the IR spectrum (υ(CO) 1869, 1792, 1773 to 1991, 1941 cm^{-1}) were consistent with quantitative conversion of FpK to the well known [13] FpCH_2CH_3.

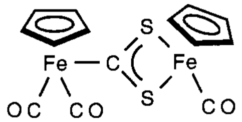
2.11. Thermal degradation of (η^5-C_5H_5)(CO)$_2$FeCS_2Zr(Cl)(η^5-C_5H_5)$_2$ (1)

A solution of FpCS_2Zr(Cl)Cp_2 (**1**) (50 mg, 0.098 mmol) in 2.5 ml of THF was maintained at room temperature for 12 h as its color changed from green to crimson. An infrared spectrum obtained after this time showed bands which correspond to an approximate 3:1 ratio of FpCS_2Fe(CO)Cp (**5**) [12] (2029, 2013, 1977 cm^{-1}) to FpC(S)SFp (**6**) (2029, 1982, 1937 cm^{-1}) [12], based upon the υ(CO) absorption intensities. The THF was evaporated and the ^{1}H-NMR spectrum that was recorded (C_6D_6) for the dark red residue had a 4:3:1 ratio of $(Cp_2ClZr)_2O$ [δ 6.02 (s, Cp_2Zr)], **5** [δ 4.27, 4.14 (s, CpFe)], and **6** [δ 4.17, 4.03 (s, CpFe)]. Only trace amounts of the (independently prepared) $(Cp_2ClZr)_2S$ [δ 5.87 (s, Cp_2Zr)] [14] were detected.

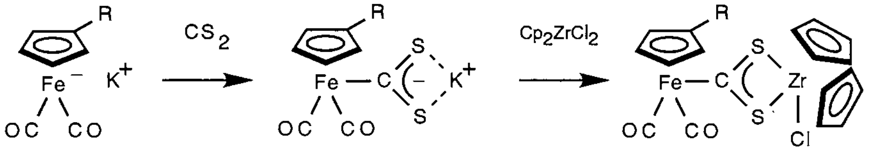
3. Results and discussion

The CS_2 adduct FpCS_2K is available in essentially quantitative yield by adding one equivalent (or more) of CS_2 to Fp^- in THF at ca. 0°C. Although this metallodithiocarboxylate, originally prepared by Ellis ([4]a), is stable up to at least at 0°C, it has not been isolated. Rather, it has been derivatized via its reactions with numerous organic and inorganic electrophiles that produce fully characterized dithiocarboxylate esters, e.g. FpCS_2Fp with FpI [4,15] and the μ-(η^1-C: η^2-S,S′) adduct FpCS_2Fe(CO)Cp with CpFe(CO)$(CH_3CN)_2^+$ BF_4^- [12].





Treatment of THF solutions of FpCS_2K or its methylcyclopentadienyl analog Fp′CS_2K at −23°C with one equivalent of zirconocene dichloride cleanly produced the μ-(η^1-C: η^2-S,S′) dithiocarboxylate complexes FpCS_2ZrClCp_2 (**1**) and Fp′CS_2ZrClCp_2 (**2**), Eq. 2. Monitoring the IR spectra of these reactions was especially useful: with the former reaction the intense terminal carbonyl υ(CO) bands of FpCS_2K, 1999, 1945 cm^{-1}, were replaced by those for **1**, 2029, 1982 cm^{-1}. Subsequent workup of the reaction by extraction and precipitation from benzene/hexane left analytically pure **1** as a greenish brown powder in 70% yield. A



(2)

1 (R = H)
2 (R = Me)

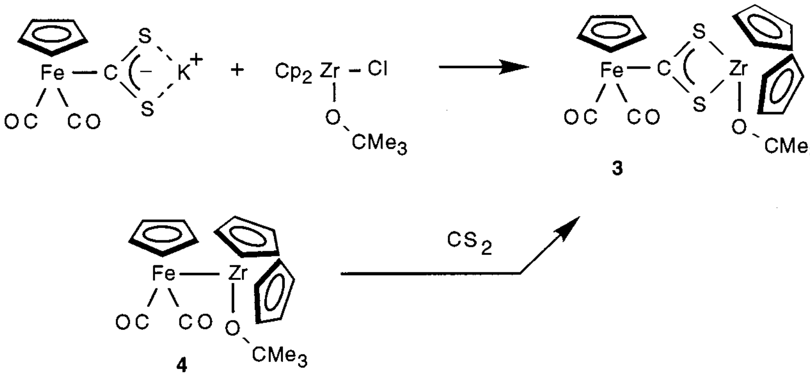
somewhat lower isolated yield of **2** (59%) was realized from an otherwise similar reaction.

Although both **1** and **2** appeared to be thermally stable as solids at room temperature, their THF solutions slowly degraded. Over 12 h, solutions of **1** at room temperature converted to 3:1 mixtures of $FpCS_2Fe(CO)Cp$ and FpC(S)SFp plus $(Cp_2ClZr)_2O$ as the major Cp_2Zr-containing species. The presence of both Fe_2 μ-CS_2 complexes was confirmed by IR and by ^{1}H- and $^{13}C\{^1H\}$-NMR spectroscopy, but curiously we detected only trace amounts of the (independently prepared) μ-sulfido zirconocene complex $(Cp_2ClZr)_2S$ [14]. This obviously complex degradation of **1** was not further investigated.

The IR and NMR spectroscopy of **1** and **2** is consistent with the presence of isolated Fp (or Fp′) and $Zr(Cl)Cp_2$ fragments that are bridged by μ-(η^1-C: η^2-S,S′) CS_2 ligands. Such structures resemble that proposed for the carbon dioxide analog $FpCO_2Zr(Cl)Cp_2$ [1,2] and substantiated for the isolobal heterobimetallic μ-(η^1-C: η^2-O,O′) CO_2 compounds $Cp^*(CO)_2RuCO_2ZrClCp_2$ and $Cp^*(CO)(NO)ReCO_2ZrClCp_2$ by X-ray crystallographic structure determinations [16]. ^{1}H-NMR spectra for **1** and **2** accordingly feature a 2:1 intensity relationship between Cp_2Zr resonance and the CpFe singlet (or Cp′Fe multiplets); for **1**, their chemical shifts (δ 5.92, 4.13, respectively) resemble those for $FpCO_2Zr(Cl)Cp_2$ (δ 6.09, 4.15) in C_6D_6. $^{13}C\{^1H\}$-NMR spectra of **1** and **2** feature a CS_2 absorption at δ 324–326, which is not far removed from that previously recorded for $FpCS_2K$ (δ 309) [12]. Other related CS_2 absorptions occur at δ 298 for $FpCS_2Fe(CO)Cp$ and at δ 306 FpC(S)SFp [12].

IR spectral data for **1** and **2** also can be compared with that for $FpCO_2Zr(Cl)Cp_2$. Thus, the two intense υ(CO) absorptions for **1** (2029, 1982 cm^{-1}) and for **2** (2026, 1979 cm^{-1}) attests to the presence of an electronic Fp environment resembling that observed for $FpCO_2Zr(Cl)Cp_2$ (2032, 1977 cm^{-1}) [2]. Instead of the appearance of the carboxylate υ(OCO) absorptions in the δ 1375–1250 cm^{-1} region for $FpCO_2Zr(Cl)Cp_2$, **1** and **2** exhibit two medium intensity υ(SCS) absorptions ([6]c) at 930, 850 cm^{-1} (KBr pellet); only the latter absorption could be assigned in THF solution (947–849 cm^{-1}) due to solvent interference. These dithiocarboxylate stretching frequencies were assigned only after also examining analogous spectral data for $FpZr(Cl)Cp_2$ and for $FpCS_2K$. Related υ(SCS) data (KBr) is available for $FpCS_2Fe(CO)Cp$ (914, 876 cm^{-1}, medium) and for FpC(S)SFp (1000 cm^{-1}, strong), which is consistent with the usual appearance of two υ(SCS) absorptions for μ-(η^1-C: η^2-S,S′) dithiocarboxylates and one for nonchelating μ-(η^1-C: η^1-S) dithiocarboxylates ([6]c, [12]).

The *t*-butoxy-substituted dithiocarboxylate $FpCS_2Zr(OCMe_3)Cp_2$ (**3**) also can be generated from metathesis of $FpCS_2K$ and the appropriate zirconocene chloride (Eq. 3), although isolating and working with **3** is limited by its relatively low thermal stability. IR spectral monitoring of the reaction mixture appeared similar to that observed for generating **1** and **2**: **3** was the only Fp-containing material present, other than for trace amounts of Fp_2. Workup of the reaction mixtures entailed benzene extraction and precipitation with pentane in order to produce a brown powder. ^{1}H-NMR spectra of this material were consistent with a single set of dominant Cp_2Zr, CpFe, and $OCMe_3$ resonances, although several very weak singlets appeared near each resonance for **3**. The 83% yield of **3** was quantitated by integration versus an internal standard. The purest samples resulted only after minimal handling and a brief workup: further attempts at purifying this material or indeed leaving it in THF or benzene solutions further degraded it to multiple unidentified products.



(3)

3

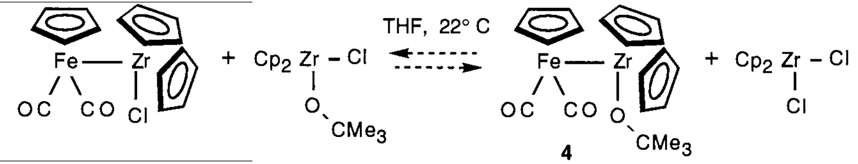
4

Identification of $FpCS_2Zr(OCMe_3)Cp_2$ (**3**) rests upon the resemblance of its IR and ^1H-, $^{13}C\{^1H\}$-NMR spectral data with that for **1** and **2**. The NMR chemical shifts for the Cp resonances of **3** are comparable to those for **1**, in addition to the 2:1 intensity relationship between Cp_2Zr and the CpFe singlets in the ^1H-NMR spectra. ^1H- and ^{13}C-NMR spectral absorptions for the zirconocene Cp and $OCMe_3$ groups on **3** (δ 6.03, 1.18 and 112, 79, 32) nevertheless can be differentiated from those observed for $Cp_2ZrCl(OCMe_3)$ (δ 5.99, 1.06 and 113, 80, 32). Although the presence of the bridging CS_2 ligand was established by its ^{13}C-NMR spectral absorption at δ 312, the assignment of the corresponding dithiocarboxylate IR υ(SCS) absorptions was precluded by the presence of interfering, broad $OCMe_3$ absorptions.

The dithiocarboxylate **3** also can be generated from the reaction between Casey's $FpZr(OCMe_3)Cp_2$ (**4**) [11] and CS_2, Eq. 3. One equivalent of CS_2 transformed **4** in THF solution at room temperature to **3** (75%) plus Fp_2 (15%). We used IR spectroscopy to monitor this clean transformation; ^1H-NMR spectra of the isolated material were consistent with a 75% yield of **3**. The same reaction in C_6D_6 solution took much longer, with a maximum 61% conversion recorded after 48 h. Preliminary observations likewise are available for converting **4** and carbon dioxide to a similar CO_2 adduct [17]. Surprisingly, $FpZrClCp_2$ [11] did not incorporate CS_2 under similar conditions. Reaction between $FpZrClCp_2$ and CS_2 at room temperature yielded Fp_2 promptly and quantitatively, whereas no detectable reaction occurred at 0°C over at least 3 h. Under either set of reaction conditions, $FpCS_2Zr(Cl)Cp_2$ (**1**) was not detected.

An unresolved issue concerns the facility with which CO_2 adds to both $FpZr(X)Cp_2$ (X = Cl, $OCMe_3$ (**4**)), whereas CS_2 incorporates into **4** but not $FpZrClCp_2$. One possible rational is that the CS_2 reaction requires ionization of the iron–zirconium bond and formation of $FpCS_2^-$, $Cp_2Zr(OCMe_3)(THF)^+$ (which converts to the observed **3**), whereas CO_2 insertion entails a direct, perhaps bimetallic, pathway [18]. Analogous autoionization of $FpZrClCp_2$ evidently would not be available under these conditions. The ionization pathway for **4**, however, can be ruled out on the basis of two observations.

First, treatment of **4** with ethyl bromide did not produce any $FpCH_2CH_3$ [13], which would have been expected if **4** had ionized in THF solution to Fp^-, $Cp_2Zr(OCMe_3)(THF)^+$. A 3–5% conversion of **4** to $FpCH_2CH_3$ [13] easily would have been detected by IR spectroscopy. In contrast, FpK immediately and quantitatively underwent alkylation by one equivalent of ethyl bromide under comparable reaction conditions to yield $FpCH_2CH_3$. The second observation pertains to the absence of any zirconocene exchange upon treating $FpZrClCp_2$ with one equivalent of $Cp_2ZrCl(OCMe_3)$, Eq. 4. Likewise, attempting the reaction in its reverse direction, mixing **4** with one equivalent of Cp_2ZrCl_2, likewise did not afford any detectable (5% limit by IR spectroscopy) $FpZrClCp_2$. If $FpZrClCp_2$ had ionized in THF solution in the presence of $Cp_2ZrCl(OCMe_3)$ (forward direction, Eq. 4), then some of the resulting Fp^- should have been intercepted and converted to **4**, which corresponds to its synthetic procedure. We conclude that **4** does not ionize in THF solution to give accessible Fp^-, consonant with our previous observations for $FpZrClCp_2$ [2].



(4)

4. Conclusions

We have synthesized the μ-(η^1-C: η^2-S,S′) dithiocarboxylate complexes $FpCS_2ZrClCp_2$ (**1**) and $Fp'CS_2ZrClCp_2$ (**2**) from the reactions between $FpCS_2K$ and zirconocene dichloride; both stable products were fully characterized. Although the iron-zirconium complex $FpZrClCp_2$ inserts carbon dioxide to give $FpCO_2ZrClCp_2$ [2], CS_2 incorporation into the same FeZr bimetallic complex was not observed. Metathesis between $FpCS_2K$ and $Cp_2ZrCl(OCMe_3)$ provided $FpCS_2Zr(OCMe_3)Cp_2$ (**3**), which was not obtained analytically pure. This product was characterized by comparison of its IR and ^1H-, $^{13}C\{^1H\}$-NMR spectral data with that for **1** and **2**. The iron–zirconium complex $FpZr(OCMe_3)Cp_2$ (**4**) adds carbon disulfide to give $FpCS_2Zr(OCMe_3)Cp_2$ (**3**) in at least 75% spectroscopic yield.

We are unable to resolve the dilemma concerning the ease with which CO_2 adds to both $FpZr(X)Cp_2$ (X = Cl, $OCMe_3$ (**4**)), forming the FeZr μ-CO_2 complexes, whereas only **4** interposes CS_2, giving **3**. The unique reactivity of **4** towards CS_2, however, can not be attributed to autoionization of **4** to Fp^- and $Cp_2Zr(OCMe_3)(THF)^+$ in order for the Fp^- to bind the CS_2 as $FpCS_2^-$ prior to reacting with the zirconium electrophile. All attempts to spectroscopically probe or otherwise encourage an ionization equilibrium involving $FpZr(X)Cp_2$ (via trapping of the Fp^-) have failed. Studies in progress address the reconfiguration of the coordination environments of heterobimetallic complexes in order to facilitate CO_2 and CS_2 'insertion' into the metal–metal bonds.

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[18] We thank a referee for this suggestion.