

Syntheses and reactions of dinuclear μ -methylthiolate organometallic complexes¹

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Received 30 June 1995; in final form 18 September 1995

Abstract

Products from reactions between $[\text{CpM}(\text{CO})_2]_2$ ($\text{M} = \text{Fe}, \text{Ru}$) and $[\text{Me}_2\text{SSMe}]\text{BF}_4$ depend on the ratio of reactants, reaction time, and solvent. Two organometallic products, $[\text{Cp}_2\text{M}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ and $[\text{CpM}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ are generally formed. A proposed mechanism for this reaction involves initial addition of an SMe^+ group to the bimetallic complex, followed by displacement of a $\text{CpM}(\text{CO})_2$ moiety by L ($\text{L} = \text{Me}_2\text{S}, \text{CpM}(\text{CO})_2\text{SMe}$, or solvent). The reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ with a mixture of $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{MeCpFe}(\text{CO})_2]_2$, which gives a statistical mixture of the possible thiolate-bridged species, is accommodated by this mechanism. Alternative syntheses of $[\text{cp}_2\text{M}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ ($\text{cpM} = \text{CpFe}, \text{MeCpFe}, \text{CpRu}$) and $[\text{CpFe}(\text{CO})_2(\mu\text{-SMe})\text{M}(\text{CO})_2\text{cp}]\text{BF}_4$ from $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$ and $\text{cpM}(\text{CO})_2\text{SMe}$ ($\text{cpM} = \text{MeCpFe}, \text{CpRu}$) provided pure samples of the thiolate-bridged complexes. Photolyses of these complexes result in formation of $[\text{CpFe}(\text{CO})(\mu\text{-SR})(\mu\text{-CO})\text{M}(\text{CO})\text{Cp}]\text{BF}_4$ ($\text{M} = \text{Fe}, \text{Ru}$).

Keywords: Iron; Ruthenium; Thiolate complexes; Cyclopentadienyls

1. Introduction

Our research group has shown that $[\text{Me}_2\text{SSMe}]\text{BF}_4$ is a useful reagent for preparation of organometallic thiolate complexes. In this context, two modes of reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ have been encountered. The most common is nucleophilic attack by an organometallic reagent at the thiomethyl sulfur in this species, with displacement of Me_2S and incorporation of an MeS^+ group into the product. Both anionic [1] and neutral [2] organometallic complexes react in this way, and the nucleophilic site of the organometallic reagent can be either the metal center or an atom in a ligand. An example of a ligand-centered reaction is the formation of a complex having an organic disulfide ligand from this reagent and a metal thiolate complex [3].

It is convenient when studying these reactions to draw an analogy between reactions involving addition of SMe^+ and protonation reactions. Each of the complexes that have been shown to react with $[\text{Me}_2\text{SSMe}]\text{BF}_4$ can also be protonated. In general, complexes

known to protonate would appear to be logical candidates to react with $[\text{Me}_2\text{SSMe}]\text{BF}_4$.

The reaction of this species with compounds having a metal–metal bond was a logical step in this project. We have shown, for example, that the complexes $[\text{Fe}(\text{CO})_2\text{L}(\mu\text{-SMe})]_2$ ($\text{L} = \text{CO}$, phosphines) react with $[\text{Me}_2\text{SSMe}]\text{BF}_4$ to incorporate a third bridging methylthiolate group in place of the metal–metal bond [4].

However, a second type of reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ was encountered in studies involving metal–metal bonded dinuclear complexes like $\text{Mn}_2(\text{CO})_{10}$. Here, cleavage of the metal–metal bond and addition of SMe and Me_2S units to each monometallic unit occurs, with formation of $[\text{Mn}(\text{CO})_5(\text{SMe}_2)]\text{BF}_4$ and $\text{Mn}(\text{CO})_5\text{SMe}$. The second product from this reaction cannot be isolated since it rapidly undergoes further reaction (CO loss with dimerization, or further addition of an SMe^+ group) but a high yield of the cationic SMe_2 complex [5] is obtained in these reactions. The apparent mode of reaction is addition of the organosulfur reagent to the metal–metal bond, a reaction similar to that encountered with halogens. It is noted in passing that $\text{Mn}_2(\text{CO})_{10}$ does not protonate and the halogen reaction with this species in polar solvents is believed to occur via initial addition of an electrophile (X^+) [6].

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¹ Dedicated to Professor Marvin D. Rausch on the occasion of his 65th birthday.

Initial studies on the reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2]_2$ were begun prior to some of the work cited above, following the protonation–thiomethylation analogy. Protonation of $[\text{CpFe}(\text{CO})_2]_2$ is known and salts of the cation, $[\text{CpFe}(\text{CO})_2(\mu\text{-H})\text{Fe}(\text{CO})_2\text{Cp}]^+$, have been characterized [7], so an attempt to react this species with $[\text{Me}_2\text{SSMe}]\text{BF}_4$ in the course of our studies was logical. The reaction between $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2]_2$ turned out to be quite complicated with a mixture of products being formed and reaction conditions being important in determining the final outcome. We report on our studies of this reaction and also on a series of related reactions that followed from this work in this paper, along with speculation about the mechanisms of the different modes of reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ with metal–metal bonded complexes.

2. Experimental

The following compounds were prepared by literature methods: $[\text{CpFe}(\text{CO})_2]_2$ [8], $[\text{MeCpFe}(\text{CO})_2]_2$ [9], $[\text{CpRu}(\text{CO})_2]_2$ [10], $[\text{CpW}(\text{CO})_3]_2$ [11], $\text{Cp}(\text{CO})_2\text{FeRu}(\text{CO})_2\text{Cp}$ [12], $\text{Cp}(\text{CO})_2\text{FeW}(\text{CO})_3\text{Cp}$ [13], $[\text{CpFe}(\text{CO})_2(\text{THF})\text{BF}_4]$ and $[\text{MeCpFe}(\text{CO})_2(\text{THF})\text{BF}_4]$ [14], $[\text{CpFe}(\text{CO})_2(\text{RSSR})\text{BF}_4]$ (R = Me, Ph) [15,16], $\text{CpW}(\text{CO})_3\text{-SMe}$ [17], and $[\text{Me}_2\text{SSMe}]\text{BF}_4$ [18]. Samples of $\text{Cp}(\text{CO})_2\text{FeRu}(\text{CO})_2\text{Cp}$ were also prepared by UV photolysis of a 2:1 mixture of $[\text{CpRu}(\text{CO})_2]_2$ and $[\text{CpFe}(\text{CO})_2]_2$. All ^1H NMR spectra (in acetone- d_6 except as noted) were obtained using a Bruker WP-200. IR spectra (CH_2Cl_2 solution) were recorded with a Beckman Model 4230 or with a Mattson Polaris FT-IR spectrometer. Solvents were distilled under nitrogen from standard drying agents; reactions and manipulations were carried out under nitrogen as a precautionary measure. The ionic sulfur-containing organometallic compounds in this study were recrystallized by dissolving them in a minimum amount of CH_2Cl_2 , filtering, adding ethyl acetate, and chilling the solution. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

2.1. Reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2]_2$

A slurry of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ (0.573 g, 2.92 mmol) in 50 ml of CH_2Cl_2 was slowly added to a solution of the organometallic complex (1.239 g, 3.50 mmol) in 75 ml of CH_2Cl_2 . The mixture was stirred for 1 h at room temperature, then the solvent was evaporated. The residue was extracted using a minimum of CH_2Cl_2 and the solution then transferred to a silica gel– CH_2Cl_2 column. Unreacted $[\text{CpFe}(\text{CO})_2]_2$ eluted quickly using this solvent. A dark red band eluted next using 10% acetone in CH_2Cl_2 . Finally, elution with 100% acetone

brought down a bright yellow band. Solvent was evaporated from the second and third bands leaving solid residues.

The first product (the second band on the chromatographic column) was recrystallized as described above to give 0.537 g of dark red $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, 38% yield) m.p. 153–156°C (dec). Anal. Found: C, 36.86; H, 2.63. $\text{C}_{15}\text{H}_{13}\text{BF}_4\text{Fe}_2\text{O}_4\text{S}$. Calc.: C, 36.93; H, 2.69%. IR $\nu(\text{CO})$ 2060s, 2040s, 2005s cm^{-1} . ^1H NMR: δ 2.14s, (SCH₃), 5.53s, (C₅H₅).

The yellow solid (the second product, 0.385 g) was purified by crystallization. It was identified as the known compound $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$, 40% yield. IR: $\nu(\text{CO})$ 2065s, 2025s cm^{-1} . ^1H NMR: δ 2.56s (S(CH₃)₂), 5.70s (C₅H₅).

Variations of this reaction were attempted. In one instance, a 2:1 ratio of reactants was used (same reaction time and conditions). After the solvent was evaporated, the residue dissolved in acetone- d_6 and an ^1H NMR spectrum obtained; this showed approximately equimolar amounts of the known compounds $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$; δ 5.75s (C₅H₅), 2.96s (FeCH₃SSCH₃), 2.78s (FeCH₃-SSCH₃). In another instance, a 1:1 reaction was carried out by treating a CD₃CN solution of $[\text{CpFe}(\text{CO})_2]_2$ (0.051 g, 0.144 mmol) with $[\text{Me}_2\text{SSMe}]\text{BF}_4$ (0.020 g, 0.102 mmol). An ^1H NMR spectrum showed no sulfur reagent remained, although much of the organometallic starting material was still present. In the spectrum, peaks corresponding to $[\text{CpFe}(\text{CO})_2(\text{NCCD}_3)]\text{BF}_4$ (δ 5.36s, C₅H₅), $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ (δ 5.24s, C₅H₅ and 1.99s (SCH₃)) and a mixture of $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ and $\text{CpFe}(\text{CO})_2\text{SMe}$ were evident. (Rapid exchange causes averaging of signal from the SMe protons [19].) In addition, a small amount of $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ (δ 5.38s, C₅H₅ and 2.35s, S(CH₃)₂) was present. These identifications were made by comparison with spectra of the pure compounds recorded in CD₃CN.

2.2. Alternate synthesis of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$

A solution of $\text{CpFe}(\text{CO})_2\text{SMe}$ (1.405 g, 6.27 mmol) and $[\text{CpFe}(\text{CO})_2(\text{THF})\text{BF}_4]$ (2.076 g, 6.18 mmol) in 40 ml of CH_2Cl_2 was stirred for 0.5 h and then filtered. Solvent was evaporated and the residue recrystallized to give 1.855 g of red crystalline $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, 61% yield.

2.3. Synthesis of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ using $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ as the SMe^+ donor

A solution of $[\text{CpFe}(\text{CO})_2]_2$ (0.274 g, 0.774 mmol) and $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ (0.277 g, 0.774 mmol) in 20 ml CH_2Cl_2 was stirred for 15 h. The solution was

filtered, solvent evaporated, and the residue was recrystallized to give 0.188 g of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, 50% yield, identified by IR and NMR data.

2.4. Reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and $[\text{MeCpFe}(\text{CO})_2]_2$

This reaction using a 1:1 ratio of reactants gave results similar to those described above. A yellow compound $[\text{MeCpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ was obtained in 37% yield; m.p. 179–183°C (dec). Anal. Found: C, 35.34; H, 3.81. $\text{C}_{10}\text{H}_{13}\text{BF}_4\text{FeO}_2\text{S}$. Calc.: C, 35.33; H, 3.85%. IR: $\nu(\text{CO})$ 2061s, 2020s cm^{-1} . ^1H NMR: δ 5.59–5.52m ($\text{C}_5\text{H}_4\text{CH}_3$), 2.57s ($\text{S}(\text{CH}_3)_2$), 2.08 ($\text{C}_5\text{H}_4\text{CH}_3$). Difficulty was encountered in crystallizing the second product, $[(\text{MeCp})_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$; all attempts gave oils. However, the identity was confirmed by comparison of IR and NMR spectra with a known sample of the compound prepared by a different route, vide infra. (IR: $\nu(\text{CO})$ 2055s, 2045s, 2000 s, br cm^{-1} . ^1H NMR (CDCl_3): δ 5.15–5.02m, $\text{C}_5\text{H}_4\text{CH}_3$, 2.01s, SCH_3 , 1.96s, $\text{C}_5\text{H}_4\text{CH}_3$).

2.5. Alternate synthesis of $[(\text{MeCp})_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$

A solution of $[\text{MeCpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$ (1.20 g, 3.43 mmol) in 10 ml CH_2Cl_2 was added to a slurry of NaSMe in 20 ml of CH_2Cl_2 (approximately 20 mmol of NaSMe, prepared previously from Na and an excess of MeSSMe). The mixture was stirred for 45 min and then filtered. An IR spectrum of the solution showed two bands, $\nu(\text{CO})$ 2025s, 1979s cm^{-1} , corresponding to $\text{MeCpFe}(\text{CO})_2\text{SMe}$. This mixture was treated with a second equivalent of $[\text{MeCpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$ (0.700 g, 2.00 mmol) and stirred for 30 min. Evaporation gave a residue that was recrystallized using CH_2Cl_2 –diethyl ether at -78°C , giving 0.869 g of the dull red crystalline solid $[(\text{MeCp})_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, 84% yield; m.p. 61–63°C. Anal. Found: C, 39.52, H, 3.55. $\text{C}_{17}\text{H}_{17}\text{BF}_4\text{Fe}_2\text{SO}_4$. Calc.: C, 39.58; H, 3.32%. IR: $\nu(\text{CO})$ 2055s, 2045s, 2000s, br cm^{-1} . ^1H NMR (CDCl_3): δ 5.15–5.02m ($\text{C}_5\text{H}_4\text{CH}_3$), 2.01s (SCH_3), 1.96s ($\text{C}_5\text{H}_4\text{CH}_3$).

2.6. Synthesis of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SPh})]\text{BF}_4$

Reaction between $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$ and $\text{CpFe}(\text{CO})_2\text{SPh}$, carried out as described above, gave dark red crystalline $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SPh})]\text{BF}_4$ in 69% yield; m.p. 156–159°C (dec.). Anal. Found: C, 43.69; H, 2.75. $\text{C}_{20}\text{H}_{15}\text{BF}_4\text{Fe}_2\text{O}_4\text{S}$. Calc.: C, 43.68; H, 2.75%. IR: $\nu(\text{CO})$ 2055vs, 2041s, 2004s, br cm^{-1} . ^1H NMR: δ 7.33–7.61m (C_6H_5), 5.418s (C_5H_5).

Synthesis of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SPh})]\text{BF}_4$ by a reaction between $[\text{CpFe}(\text{CO})_2(\text{PhSSPh})]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2]_2$ using the procedure described above gave $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SPh})]\text{BF}_4$ in 56% yield.

2.7. Reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and a mixture of $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{MeCpFe}(\text{CO})_2]_2$

A 2:1:1 mixture of these reagents was chosen to give a 1:1 ratio of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ to iron complexes, a situation comparable with the first reaction described. The reaction was carried out in CH_2Cl_2 . After stirring for 1 h, the solution was filtered, and the solvent was evaporated leaving a red oily residue. This was extracted with acetone- d_6 , and filtered. An ^1H NMR spectrum of this solution showed the presence of three thiolate-bridged dimers, $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, $[\text{CpFe}(\text{CO})_2(\mu\text{-SMe})\text{Fe}(\text{CO})_2\text{MeCp}]\text{BF}_4$, and $[(\text{MeCp})_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ along with the two thioether complexes, $[\text{MeCpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$. Intensities of the ^1H NMR resonances established that these five complexes were present in a 1:2:1:2:2 ratio. (There were three resonances for the methyl protons in the $\mu\text{-SCH}_3$ region in a 1:2:1 ratio at δ 2.145s, 2.135s, and 2.121s corresponding to $(\text{MeCp})_2$, $(\text{Cp})(\text{MeCp})-$, and $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, and two very closely spaced singlets in the Cp region at δ 5.515s and 5.510 s (C_5H_5) of approximately equal intensities, corresponding to $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ to $[\text{CpFe}(\text{CO})_2(\mu\text{-SMe})\text{Fe}(\text{CO})_2\text{MeCp}]\text{BF}_4$. The signals assigned to the $\text{S}(\text{CH}_3)_2$ groups in $[\text{MeCpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ were at δ 2.564s and 2.554s respectively.)

2.8. Alternate synthesis of $[\text{CpFe}(\text{CO})_2(\mu\text{-SMe})\text{Fe}(\text{CO})_2\text{MeCp}]\text{BF}_4$

The reaction of $[\text{MeCpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$ with an excess of $\text{CpFe}(\text{CO})_2\text{SMe}$, carried out in the manner described above, gave $[\text{CpFe}(\text{CO})_2(\mu\text{-SMe})\text{Fe}(\text{CO})_2\text{MeCp}]\text{BF}_4$, m.p. 97–101°C. Anal. Found: C, 38.52; H, 3.02. $\text{C}_{16}\text{H}_{15}\text{BF}_4\text{Fe}_2\text{O}_4\text{S}$. Calc. C, 38.29; H, 3.01%. IR: $\nu(\text{CO})$ 2055s, 2038s, 2000s, br cm^{-1} . ^1H NMR: δ 5.518s (C_5H_5), 5.40–5.32 ($\text{C}_5\text{H}_4\text{CH}_3$), 2.14s ($\mu\text{-SCH}_3$), 2.030s ($\text{C}_5\text{H}_4\text{CH}_3$).

2.9. Reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and $[\text{CpRu}(\text{CO})_2]_2$

A 1:1 reaction was carried out as described above. After solvent had been evaporated an NMR spectrum of the solid residue showed that the products consisted of equimolar quantities of $[\text{CpRu}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ and $[\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$. In addition, some unreacted dimer remained as well. Purification was done by fractional crystallization. Four fractions were collected. The first, a bright lemon-yellow solid, was identified as $[\text{CpRu}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$, m.p. 200–210°C (dec.). Anal. Found: C, 28.95; H, 3.11. $\text{C}_9\text{H}_{11}\text{BF}_4\text{O}_2\text{RuS}$. Calc.: C, 29.13; H, 2.99%. IR: $\nu(\text{CO})$ 2072s, 2025s cm^{-1} . ^1H NMR: δ 6.01s (C_5H_5), 2.81s ($\text{S}(\text{CH}_3)_2$). The second and third fractions were mixtures. The fourth fraction,

containing mainly the second product, was further purified by chromatography. It was dissolved in CH_2Cl_2 , added to a silica gel– CH_2Cl_2 column and eluted with 10% acetone in CH_2Cl_2 . The first band was collected and recrystallized to give a light yellow solid, identified as $[\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, m.p. 113–115°C. Anal. Found: C, 31.01; H, 2.44. $\text{C}_{15}\text{H}_{13}\text{BF}_4\text{O}_4\text{Ru}_2\text{S}$. Calc.: C, 31.16; H, 2.27%. IR: $\nu(\text{CO})$ 2067s, 2054s,sh, 2010vs cm^{-1} . $^1\text{H NMR}$: δ 5.88s (C_5H_5), 2.54s (SCH_3).

2.10. Reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and $\text{Cp}(\text{CO})_2\text{FeRu}(\text{CO})_2\text{Cp}$

A 1:1 reaction was carried out in CH_2Cl_2 . Evaporation of solvent and recrystallization of the residue yielded red-orange $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{Ru}(\text{CO})_2\text{Cp}]\text{BF}_4$, 77% yield; m.p. 129–133°C (dec.). Anal. Found: C, 33.76; H, 2.5. $\text{C}_{15}\text{H}_{13}\text{BF}_4\text{FeO}_4\text{RuS}$. Calc.: C, 33.80; H, 2.46%. IR: $\nu(\text{CO})$ 2060s, 2046s, 2013sh, 2005s cm^{-1} . $^1\text{H NMR}$: δ 5.87s (RuC_5H_5), 5.50s (FeC_5H_5), 2.32s (SCH_3).

2.11. Alternate synthesis of $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{Ru}(\text{CO})_2\text{Cp}]\text{BF}_4$

A reaction using equimolar quantities of $\text{CpRu}(\text{CO})_2\text{SMe}$ and $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$ in CH_2Cl_2 gave orange crystals of $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{Ru}(\text{CO})_2\text{Cp}]\text{BF}_4$ in 78% yield.

2.12. Reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and a mixture of $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{CpRu}(\text{CO})_2]_2$

A 2:1:1 reaction of these complexes (1:1 ratio of metal dimers to $[\text{Me}_2\text{SSMe}]\text{BF}_4$) was carried out as described above. An NMR spectrum of the reaction mixture revealed that the three dinuclear cations $[\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{Ru}(\text{CO})_2\text{Cp}]\text{BF}_4$ and $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ were present in a ratio of approximately 2:1:1. In addition, $[\text{CpRu}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ were present with the ratio of Ru to Fe complex being slightly larger than 1:1. No $[\text{CpRu}(\text{CO})_2]_2$ remained, but a substantial fraction of the $[\text{CpFe}(\text{CO})_2]_2$ was still present.

2.13. Reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and $\text{Cp}(\text{CO})_2\text{FeW}(\text{CO})_3\text{Cp}$

A CH_2Cl_2 solution containing a 1:1 ratio of these reagents was stirred for 2 h. The solvent was evaporated, leaving a solid residue that was extracted with acetone- d_6 and filtered into an NMR tube. An $^1\text{H NMR}$ spectrum indicated that $[\text{CpW}(\text{CO})_3(\text{SMe}_2)]\text{BF}_4$, $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{W}(\text{CO})_3\text{Cp}]\text{BF}_4$, and $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ were present. There was also a trace of

$[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ and a considerable amount of the unreacted starting material, $\text{Cp}(\text{CO})_2\text{FeW}(\text{CO})_3\text{Cp}$.

The experiment was repeated, allowing 11 h reaction time. Present among the products at this time, according to NMR data, were $[\text{CpW}(\text{CO})_3(\text{SMe}_2)]\text{BF}_4$, $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{W}(\text{CO})_3\text{Cp}]\text{BF}_4$, $\text{CpW}(\text{CO})_3\text{SMe}$, $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$, and $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ in a ratio of 4:2:2:2:1.

2.14. Alternate synthesis of $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{W}(\text{CO})_3\text{Cp}]\text{BF}_4$

A reaction between $\text{CpW}(\text{CO})_3\text{SMe}$ and $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$ in CH_2Cl_2 gave $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{W}(\text{CO})_3\text{Cp}]\text{BF}_4$, a reddish-brown solid, m.p. 156–161°C (dec.), 40% yield. Anal. Found: C, 29.53; H, 2.17. $\text{C}_{16}\text{H}_{13}\text{BF}_4\text{FeO}_5\text{SW}$. Calc.: C, 29.85; H, 2.04%. IR: $\nu(\text{CO})$ 2058vs, 2045s, 2010s, 1978m, 1957sh, 1952vs,br cm^{-1} . $^1\text{H NMR}$ δ 6.18s (WC_5H_5), 5.52s (FeC_5H_5), 2.35s (SCH_3).

2.15. Related reactions

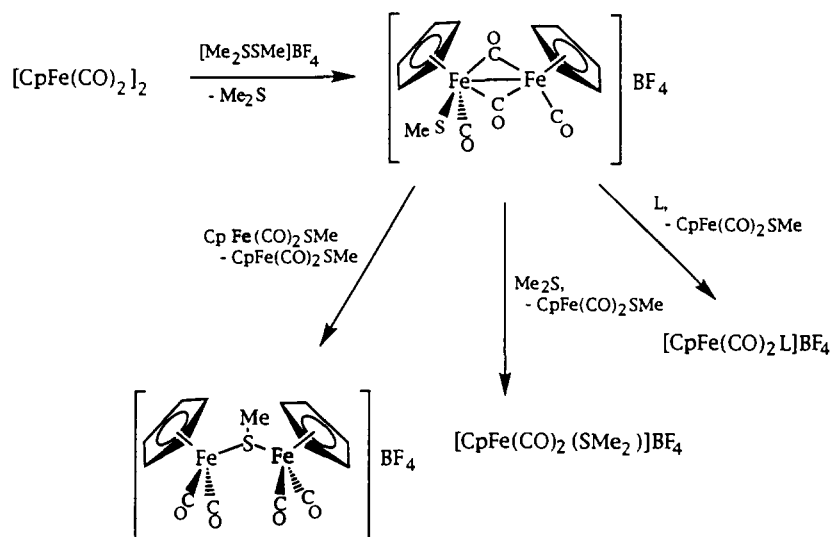
The reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and $[\text{CpW}(\text{CO})_3]_2$ (either 1:1 or 2:1 ratio) produces $[\text{CpW}(\text{CO})_3(\text{SMe}_2)]\text{BF}_4$ and $[\text{CpW}(\text{CO})_3(\text{MeSSMe})]\text{BF}_4$ in equimolar amounts; $[\text{Cp}_2\text{W}_2(\text{CO})_6(\mu\text{-SMe})]\text{BF}_4$ is not found as a product in this reaction. No reaction occurs between $[\text{CpFe}(\text{CO})_2(\text{RSSR})]\text{BF}_4$ ($\text{R} = \text{Me}, \text{Ph}$) and $[\text{CpW}(\text{CO})_3]_2$. However, there is a slow reaction between $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ and $\text{Cp}(\text{CO})_2\text{FeW}(\text{CO})_3\text{Cp}$. A 1:1 mixture of these species was stirred for 2 h in CH_2Cl_2 , solvent evaporated, the residue extracted with acetone- d_6 and filtered. An $^1\text{H NMR}$ spectrum showed that about 85% of the $\text{Cp}_2\text{FeW}(\text{CO})_5$ remained; along with this, small amounts of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ and $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{W}(\text{CO})_3\text{Cp}]\text{BF}_4$ were also present in a 2:1 ratio.

2.16. Decarbonylation of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$

A solution of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ in THF was photolyzed with a sunlamp positioned about 5 cm from the flask for 1.5 h. During this time, a green-brown precipitate formed. This solid was separated by filtration and recrystallized. The product was $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SMe})]\text{BF}_4$, m.p. 157–167°C (dec.). Anal. Found: C, 35.93; H, 3.03. $\text{C}_{14}\text{H}_{13}\text{BF}_4\text{Fe}_2\text{O}_3\text{S}$. Calc. C, 36.57; H, 2.85%. IR: $\nu(\text{CO})$ 2040vs, 1980m, 1853m, br cm^{-1} . $^1\text{H NMR}$: δ 5.687s (C_5H_5), 2.627 (SCH_3).

2.17. Decarbonylation of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SPh})]\text{BF}_4$

A similar procedure using $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SPh})]\text{BF}_4$ gave $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SPh})]\text{BF}_4$ in 59% yield; m.p., dec. Anal. Found: C, 43.45; H, 2.96. $\text{C}_{19}\text{H}_{15}\text{BF}_4$

Scheme 1. Proposed mechanism for the reaction of $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{Me}_2\text{SSMe}]\text{BF}_4$.

$\text{Fe}_2\text{O}_3\text{S}$. Calc.: C, 43.73; H, 2.90%. IR: $\nu(\text{CO})$ 2043s, 2003m, 1850w, br cm^{-1} . $^1\text{H NMR}$: δ 7.25–7.35 m (C_6H_5), 5.897s (C_5H_5).

2.18. Decarbonylation of $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{Ru}(\text{CO})_2\text{Cp}]\text{BF}_4$

A similar procedure using $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{Ru}(\text{CO})_2\text{Cp}]\text{BF}_4$ gave deep red solid $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-CO})(\mu\text{-SMe})\text{Ru}(\text{CO})\text{Cp}]\text{BF}_4$ in 80% yield; m.p., dec. Anal. Found: C, 33.49; H, 2.64. $\text{C}_{14}\text{H}_{13}\text{BF}_4\text{FeO}_3\text{RuS}$. Calc.: C, 33.30; H, 2.59%. IR (acetone): $\nu(\text{CO})$ 2029vs, 2002m, 1849s cm^{-1} . $^1\text{H NMR}$: δ 6.049s (RuC_5H_5), 5.612s (FeC_5H_5), and 2.749s (SCH_3).

3. Discussion

The reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2]_2$ was found to be unexpectedly complicated. The products usually (but not always) included $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$. The thiolate complex, $\text{CpFe}(\text{CO})_2\text{SMe}$, was not among the isolated products; however, monitoring the reaction by either IR or $^1\text{H NMR}$, did detect small quantities of this species at intermediate stages of the reaction. Other organometallic compounds were sometimes present, and the relative amounts of products varied depending on the ratio of reactants, time of reaction, and solvent. Reactions using $[\text{MeCpFe}(\text{CO})_2]_2$ and $[\text{CpRu}(\text{CO})_2]_2$ gave similar results. Owing to the complexity of the reaction, we decided to study the system further, in an attempt to decipher the various processes that were occurring.

The two likely reaction pathways, insertion of an SMe^+ group into the metal–metal bond and cleavage to form methylthiolate and dimethyl sulfide complexes,

both require a 1:1 ratio of the reactants. However, when equimolar amounts of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2]_2$ were used, varying amounts of unreacted $[\text{CpFe}(\text{CO})_2]_2$ were always found among the products. Using a 2:1 ratio of reactants, no starting material remained and there was only a trace of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ among the products. The products here are primarily $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ in approximately equimolar amounts. The observation of the latter species is the clue to explaining both the non-conformity with the expected stoichiometry and the absence of $\text{CpFe}(\text{CO})_2\text{SMe}$. Thiomethylation of $\text{CpFe}(\text{CO})_2\text{SMe}$ by $[\text{Me}_2\text{SSMe}]\text{BF}_4$ to form $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$, a known reaction [3], is apparently competitive with other reactions that are occurring. To the extent that this reaction occurs, unreacted $[\text{CpFe}(\text{CO})_2]_2$ remains.

Spectroscopic data (NMR) identified $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ as present in the reaction mixture of a 1:1 reaction, but in the isolation–purification processes this species decomposed. In previous experiments [3], chromatography had been found to cause decomposition of these compounds.

Amounts of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, and $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ were drastically reduced when the reaction of $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{Me}_2\text{SSMe}]\text{BF}_4$ was carried out in CD_3CN (monitoring by $^1\text{H NMR}$). In this experiment, $[\text{CpFe}(\text{CO})_2(\text{NCCD}_3)]\text{BF}_4$ is the major product. There is spectroscopic evidence for the presence of both $\text{CpFe}(\text{CO})_2\text{SMe}$ and $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ among the products. As discussed further below, the solvent (CD_3CN) apparently intercepts a key reaction intermediate. Separate experiments with purified samples, showed that neither $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$, nor $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ react with CD_3CN , eliminating possible

alternate routes to $[\text{CpFe}(\text{CO})_2(\text{NCCD}_3)]\text{BF}_4$ in this system.

The absence of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ among the products in the 2:1 reaction seemed curious, but ultimately this is another clue to a mechanistic scheme for this system. A reasonable conclusion is that formation of this species requires a reagent that is unavailable in this solvent. Again, suspicion points toward $\text{CpFe}(\text{CO})_2\text{SMe}$, absent in this system by virtue of its further reaction with $[\text{Me}_2\text{SSMe}]\text{BF}_4$.

A mechanism that accommodates the above information is given by Scheme 1. Addition of the electrophile, SMe^+ , to $[\text{CpFe}(\text{CO})_2]_2$ is postulated as the first step in the reaction. The known protonation of this iron species [7] is an appropriate analogue to this process. What next occurs is cleavage of the dimer by a ligand L to form $\text{CpFe}(\text{CO})_2\text{SMe}$ and $[\text{CpFe}(\text{CO})_2(\text{L})]\text{BF}_4$. The various reaction systems define the options for L. In CD_3CN , the solvent serves this function to produce $[\text{CpFe}(\text{CO})_2(\text{NCCD}_3)]\text{BF}_4$. Since CH_2Cl_2 is a poor donor, Me_2S , formed when SMe^+ is transferred from $[\text{Me}_2\text{SSMe}]\text{BF}_4$, is preferable; in addition, the $\text{CpFe}(\text{CO})_2\text{SMe}$ formed in the second step of the reaction is also a base and able to fulfill this function. The concentration of this species will slowly build up in the reaction mixture, and when this complex reacts at a competitive rate formation of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ is the result.

This mechanism would apply to the reactions of various metal–metal bonded systems studied previously. With $\text{Mn}_2(\text{CO})_{10}$, for example, initial addition of SMe^+ is followed by displacement of $\text{Mn}(\text{CO})_5$ by Me_2S . This sequence resembles the mechanism proposed for halogen cleavage in polar solvents [6].

We also explored the possibility that the formation of $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ in reactions of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2]_2$ could occur by other routes. One possibility was that there was initial addition of SMe^+ and SMe_2 across the iron–iron bond, followed by a recombination reaction. Reactions of either $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ or $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ with $\text{CpFe}(\text{CO})_2\text{SMe}$ lead to $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ but both reactions are much too slow to explain the formation of this product.

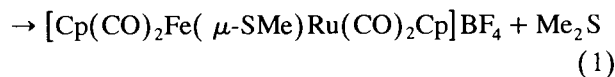
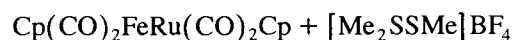
We also observed that the reaction of $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ leads to $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$. However, this reaction is also too slow to be the sole or primary process for formation for $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$.

The proposed mechanism suggested further experiments. Reactions of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ with mixtures of two bimetallic species provided an interesting test of the proposed mechanism. We first carried out a reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ with an equimolar mixture of $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{MeCpFe}(\text{CO})_2]_2$ monitoring the progress of the reaction by ^1H NMR. It was (correctly) assumed that reactions of these two organometallic species

$[\text{Me}_2\text{SSMe}]\text{BF}_4$ would have similar energetic and kinetic parameters and thus there should be significant amounts of a mixed metal complex formed. Indeed, the reaction using a 1:1:2 ratio of $[\text{CpFe}(\text{CO})_2]_2$, $[\text{MeCpFe}(\text{CO})_2]_2$, and $[\text{Me}_2\text{SSMe}]\text{BF}_4$ (equimolar amounts of iron and sulfur reagents) yielded a 1:2:1 ratio of the three possible products, $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, $[\text{MeCpFe}(\text{CO})_2(\mu\text{-SMe})(\text{CO})_2\text{FeCp}]\text{BF}_4$ and $[(\text{MeCp})_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, effectively a statistical distribution of the possible products. These cations can be readily distinguished from differences in the chemical shifts of the $\mu\text{-SCH}_3$ signals. The expected cationic Me_2S complexes, $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ and $[\text{MeCpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$, were present in the reaction mixture as well, in approximately equimolar quantities; they were identified by chemical shift of the protons in the coordinated $\text{S}(\text{CH}_3)_2$ ligand. (All of the products in this mixture were synthesized by alternate routes, purified, and well characterized as described below, providing the reference data for this experiment.)

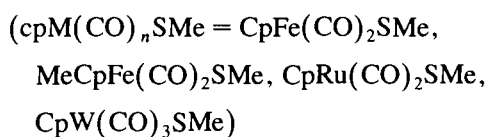
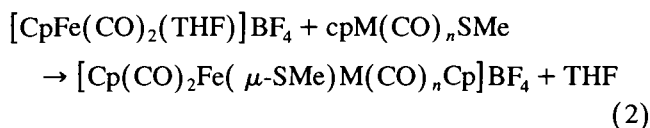
In a similar manner, a reaction was performed using a 1:1:2 ratio of $[\text{CpFe}(\text{CO})_2]_2$, $[\text{CpRu}(\text{CO})_2]_2$, and $[\text{Me}_2\text{SSMe}]\text{BF}_4$. With significantly different reactants, a statistical ratio of the product is less likely. The three possible products, $[\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{Ru}(\text{CO})_2\text{Cp}]\text{BF}_4$, and $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$, were found in a ratio of 2:1:1. The amount of $[\text{CpRu}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$ was somewhat higher than the amount of $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$. These results are consistent with $[\text{CpRu}(\text{CO})_2]_2$ reacting more rapidly than $[\text{CpFe}(\text{CO})_2]_2$. The initially higher concentration of reactive ruthenium species in solution then results in a higher percentage of $[\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$. In a separate experiment, a mixture of $[\text{Cp}_2\text{Ru}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ and $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ was shown not to be converted to $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{Ru}(\text{CO})_2\text{Cp}]\text{BF}_4$ over a 20 h period under similar conditions.

Interestingly, the reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ with the heterobimetallic species, $\text{Cp}(\text{CO})_2\text{FeRu}(\text{CO})_2\text{Cp}$, gave the highest yield of $\mu\text{-SMe}$ product of any $[\text{Me}_2\text{SSMe}]\text{BF}_4$ reaction carried out in this study. Formation of $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{Ru}(\text{CO})_2\text{Cp}]\text{BF}_4$ was observed by ^1H NMR (CD_2Cl_2) to be rapid and no crossover products were present. This suggests that the initial addition of SMe^+ occurs at only one of the two metal sites. It seems likely that the site of attack is the ruthenium atom, based on the apparent higher reactivity seen above for $[\text{CpRu}(\text{CO})_2]_2$ relative to $[\text{CpFe}(\text{CO})_2]_2$, Eq. (1).



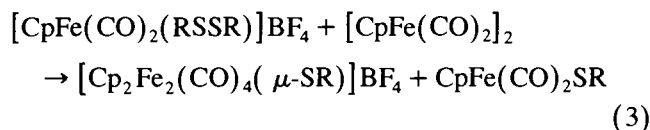
One further reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ with a heterobimetallic complex was studied. The reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ with $\text{Cp}(\text{CO})_2\text{FeW}(\text{CO})_3\text{Cp}$ gave a mixture of products that, although inseparable, was nevertheless readily analyzed from an ^1H NMR spectrum of the reaction mixture. After 11 h, the products included $[\text{CpW}(\text{CO})_3(\text{SMe}_2)]\text{BF}_4$, $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{W}(\text{CO})_3\text{Cp}]\text{BF}_4$, $[\text{CpFe}(\text{CO})_2(\text{SMe}_2)]\text{BF}_4$, $\text{CpW}(\text{CO})_3\text{SMe}$, and $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ in a ratio of 4:2:2:2:1. The last two species were not present at an earlier stage of the reaction (2 h); however, both starting material and $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ were detected along with the other products mentioned at this stage of reaction.

These studies on reactions of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ with metal–metal bonded species were assisted by the availability of pure samples of the thiolate-bridged products. These complexes could be prepared simply and in good yield by an alternate route, the reaction of $[\text{Cp}]\text{Fe}(\text{CO})_2(\text{THF})\text{BF}_4$ with a metal thiolate complex, as shown in the equation below. The sulfide complex readily displaces THF from $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$, Eq. (2):



Similar reactions were used here to prepare pure $[(\text{MeCp})_2\text{Fe}(\text{CO})_4(\mu\text{-SMe})]\text{BF}_4$ (from $[\text{MeCpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$ and $\text{MeCpFe}(\text{CO})_2\text{SMe}$) and $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SPh})]\text{BF}_4$ (from $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$ and $\text{CpFe}(\text{CO})_2\text{SPh}$).

One further route to thiolate-bridged dimetal complexes is also noted. Earlier, we had found that metal complexes with disulfide ligands are capable of acting as SMe^+ donors [19]. This behavior was borne out in reactions of $[\text{CpFe}(\text{CO})_2(\text{RSSR})]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2]_2$ to form $[\text{Cp}_2\text{Fe}_2(\text{CO})_4(\mu\text{-SR})]\text{BF}_4$, with isolated yield of the product of about 50%, Eq. (3):



(R = Me, Ph)

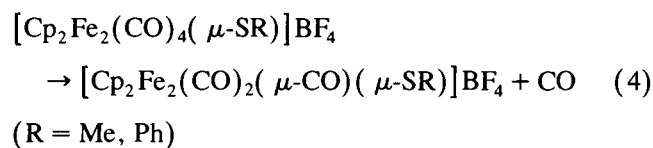
The second product $\text{CpFe}(\text{CO})_2\text{SR}$ (R = Me, Ph), was detected when reactions were monitored by ^1H NMR. In these experiments, the position of the various resonances vary because of rapid transfer of SR^+ with unreacted $[\text{CpFe}(\text{CO})_2(\text{RSSR})]^+$. As the reaction pro-

gresses, the concentration of $[\text{CpFe}(\text{CO})_2(\text{RSSR})]^+$ relative to $\text{CpFe}(\text{CO})_2\text{SR}$ decreases and the averaged Cp signal moves upfield toward the position of the Cp proton resonance in $\text{CpFe}(\text{CO})_2\text{SR}$.

We had observed that $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ was one product of the reaction of $[\text{CpFe}(\text{CO})_2]_2$, and $[\text{Me}_2\text{SSMe}]\text{BF}_4$. The ability of $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ to act as a SMe^+ donor (toward $[\text{CpFe}(\text{CO})_2]_2$, and possibly toward other species) means that this species probably has a more complicated role in reactions with longer reaction times that affects the product ratio. However, the formation of $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ and its reaction with $[\text{CpFe}(\text{CO})_2]_2$ are relatively slow, so this role is secondary in importance.

From the synthetic point of view, there may be an advantage to the use of metal complexes containing coordinated disulfide as a source of SR^+ in that the organometallic species is compatible with a wider variety of solvents. Use of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ is limited to a few solvents (CH_3CN , CH_2Cl_2 , MeNO_2) in which it is slightly soluble and does not react. Organometallic species containing coordinated RSSR ligands are compatible with carbonyl-containing solvents such as acetone or ethyl acetate.

The iron compounds in this study were found to undergo CO loss upon photolysis. The products, $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SR})]\text{BF}_4$ (R = Me, Ph), precipitated from solution, Eq. (4):



Irradiation of THF solutions of $[\text{CpFe}(\text{CO})_2(\mu\text{-SMe})\text{Ru}(\text{CO})_2\text{Cp}]\text{BF}_4$ gives $[\text{CpFe}(\text{CO})(\mu\text{-CO})(\mu\text{-SR})\text{Ru}(\text{CO})\text{Cp}]\text{BF}_4$. These three new complexes presumably have a bridging CO and thiolate group and a metal–metal bond (i.e. a coplanar $\text{Fe}_2(\text{CO})\text{S}$ or $\text{FeRu}(\text{CO})\text{S}$ core). Similar di-iron complexes with a *t*-butylthiolate and ethylthiolate ligand have been reported previously [20]. The new di-iron complexes exhibit single Cp ^1H NMR resonances, similar to the ethylthiolate complex whose structures is known [21]. Thus, it is reasonable to assume similar structures for these new complexes, with Cp ligands mutually cis, and the thiolate R group trans (relative to the planar core).

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