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Rapid $[\text{SR}]^+$ exchange between metal-thiolate and metal-organic disulphide complexes

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Abstract

Exchange of the uncoordinated thiolate group, $[\text{SMe}]^+$, in $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]^+$ with $\text{CpFe}(\text{CO})_2\text{SMe}$ is rapid on the NMR timescale, leading to average cyclopentadienyl and methyl proton environments even at -78°C . Similar behavior is observed with fast $[\text{SMe}]^+$ exchange between metal centres in other complexes ($\text{CpFe}(\text{CO})_2\text{SPh}$; $\text{CpFe}(\text{CO})(\text{L})\text{SMe}$, $\text{L} = \text{PPh}_3$, $\text{P}(\text{OPh})_3$; $\text{CpW}(\text{CO})_3\text{SMe}$) and for the $[\text{SPh}]^+$ exchange between $\text{CpFe}(\text{CO})_2\text{SPh}$ centres. Experiments involving exchange between dissimilar metal groups indicate site preferences for the $[\text{SR}]^+$ group which parallel the anticipated basicity of the thiolate group.

Introduction

Our group has made use of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ in syntheses of various organometallic thiolate complexes [1]. Often in this work, we chose to monitor the progress of a reaction by recording NMR spectra on samples taken from the reaction mixture. This allowed us to detect intermediates and ultimately to ascertain when the reaction had reached completion.

The most common mode of reaction of $[\text{Me}_2\text{SSMe}]\text{BF}_4$ involves displacement of Me_2S from $[\text{MeS}]^+$ by a nucleophile. However, in such reactions, NMR fails to detect the expected singlet resonance of Me_2S at δ 2.08 in the intermediate stages of the reaction. This is the consequence of a very fast exchange process between Me_2S and $[\text{Me}_2\text{SSMe}]\text{BF}_4$. The NMR spectrum contained a singlet for the Me_2S units with the chemical shift reflecting the averaged environment, weighted to reflect the relative concentration of each reagent [2].

Recently we investigated the reaction of $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{Me}_2\text{SSMe}]\text{BF}_4$. This system is unusually complicated, giving four organometallic products $\text{CpFe}(\text{CO})_2\text{SMe}$, $[\text{CpFe}(\text{CO})_2(\text{Me}_2\text{S})]\text{BF}_4$, $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$, and $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-SMe})\text{Fe}(\text{CO})_2\text{Cp}]\text{BF}_4$ in varying amounts depending on procedures and reaction conditions [3]. In an attempt to sort out the various pathways available in that system, we carried out the reaction of $\text{CpFe}(\text{CO})_2\text{SMe}$ and $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ monitoring the reaction using NMR. Immediately it

became evident that this system was similar to the $[\text{Me}_2\text{SSMe}]\text{BF}_4/\text{Me}_2\text{S}$ system; the spectrum contained only a single cyclopentadienyl resonance and two rather than three methyl resonances.

Further study of $[\text{SMe}]^+$ exchange between organometallic thiolate centers was then undertaken. The results are presented in this paper.

Experimental

The following compounds were prepared by literature methods: $\text{CpW}(\text{CO})_3\text{SMe}$ [1a], $[\text{CpW}(\text{CO})_3(\text{MeSSMe})]\text{BF}_4$ [1b], $\text{CpFe}(\text{CO})_2\text{SR}$ ($\text{R} = \text{Me}, \text{Ph}$) [4], $[\text{CpFe}(\text{CO})(\mu\text{-SMe})_2]$ [5], $[\text{CpFe}(\text{CO})_2(\text{RSSR})]\text{BF}_4$ ($\text{R} = \text{Me}, \text{Ph}$) [6] and $[\text{CpFe}(\text{CO})_2(\text{PhSSMe})]\text{BF}_4$ [1b]. Preparations of $\text{CpFe}(\text{CO})(\text{L})\text{SMe}$ and $[\text{CpFe}(\text{CO})(\text{L})(\text{MeSSMe})]\text{BF}_4$ ($\text{L} = \text{PPh}_3, \text{P}(\text{O}Ph)_3$) are described below. All ^1H NMR spectra were obtained using a Bruker WP-200 except for the low temperature spectra for which a Bruker WP-270 was used. Infrared spectra were recorded on a Beckman Model 4230 spectrophotometer or on 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. Elemental analyses were performed by the Galbraith Laboratories, Knoxville, TN.

Preparation of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SMe}$. A solution of $[\text{CpFe}(\text{CO})(\mu\text{-SMe})_2]$ (2.01 g, 5.13 mmol) and PPh_3 (2.65 g, 10.1 mmol) in 50 mL toluene was heated at 90°C for 2 h. The solution was cooled to room temperature, the volume reduced on a rotary evaporator, layered with pentane, and stored overnight at -20°C . A dull red solid (0.942 g, 20% yield) precipitated from the dark orange-brown solution; this was identified as $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SMe}$, m.p. $138\text{--}141^\circ\text{C}$, dec. More solid was collected by layering with more pentane. Anal. Found: C, 65.51; H, 5.02. $\text{C}_{25}\text{H}_{23}\text{FeOPS}$ calcd.: C, 65.51; H, 5.06%. IR: $\nu(\text{CO})$ 1945 cm^{-1} . ^1H NMR (CD_2Cl_2): δ 7.35–7.65 m (C_6H_5), 4.51 (d, C_5H_5 , $J(\text{Cp-P}) = 1.12\text{ Hz}$), 1.51 (d, SCH_3 , $J(\text{SMe-P}) = 1.40\text{ Hz}$).

This compound could also be made by refluxing a 1:1 mixture of the mononuclear $\text{CpFe}(\text{CO})_2\text{SMe}$ and PPh_3 in benzene; the same workup was employed to give a good yield of the product.

Preparation of $\text{CpFe}(\text{CO})[\text{P}(\text{O}Ph)_3]\text{SMe}$. A similar procedure was employed. The product obtained was recrystallized from toluene/hexane to give this orange-red solid, m.p. $132\text{--}135^\circ\text{C}$ dec., 33% yield. Anal. Found: C, 49.41; H, 4.18. $\text{C}_{25}\text{H}_{23}\text{FeO}_4\text{PS}$ calcd.: C, 50.30; H, 4.58%. IR: $\nu(\text{CO})$ 1968 cm^{-1} . ^1H NMR: δ 7.50–7.20 (m, C_6H_5), 4.19 (s, C_5H_5), 1.60 (d, SCH_3).

Preparation of $[\text{CpFe}(\text{CO})(\text{L})(\text{MeSSMe})]\text{BF}_4$ ($\text{L} = \text{PPh}_3$). A solution of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SMe}$ (0.702 g, 1.53 mmol) in 30 mL of CH_2Cl_2 was treated with $[\text{Me}_2\text{SSMe}]\text{BF}_4$ (0.300 g, 1.53 mmol). A subtle colour change from dark orange brown to dark red developed. The solution was stirred for 45 min, filtered, ethyl acetate added and the volume reduced using a rotary evaporator until solid began to precipitate. After storing at -20°C overnight, a dark red crystalline solid was collected by filtration. 0.799 g, m.p. $146\text{--}149^\circ\text{C}$ dec., 87% yield. Anal. Found: C, 52.80; H, 4.45. $\text{C}_{26}\text{H}_{26}\text{BF}_4\text{FeOPS}_2$ calcd.: C, 52.73; H, 4.42%. IR $\nu(\text{CO})$: 1991 cm^{-1} . ^1H NMR: δ 7.4–7.7 (m, C_6H_5), 5.23 (br, C_5H_5), 2.74 (s, $\text{FeSCH}_3\text{SCH}_3$), 2.37 ($\text{FeSCH}_3\text{SCH}_3$).

Preparation of [CpFe(CO)(L)(MeSSMe)]BF₄ (L = P(OPh)₃). A similar procedure was used. During the reaction, the solution changed from brownish-red to light yellow-orange. The solution was filtered, the solvent evaporated to leave an oily residue, washed with ether and recrystallized from CH₂Cl₂/Et₂O to give 0.196 g of light orange solid, m.p. 113–116°C dec., 61% yield. Anal. Found: C, 48.89; H, 4.16. C₂₆H₂₆BF₄FeO₄PS₂ calcd.: C, 48.78; H, 4.09%. IR ν (CO): 2015 cm⁻¹. ¹H NMR: δ 7.36–7.56 (m, C₆H₅), 5.16 (d, C₅H₅, J(H–P) = 1.16 Hz), 2.84 (s, FeSCH₃SCH₃), 2.73 (FeSCH₃SCH₃).

[SMe]⁺ exchange between identical metal centers

Reaction of CpFe(CO)₂SMe (1a) and [CpFe(CO)₂(MeSSMe)]BF₄ (2a). Accurately weighed samples of these two compounds were added to a dry solvent (CD₃CN, acetone-*d*₆, CH₂Cl₂ or CD₂Cl₂) under nitrogen. Aliquots were withdrawn by syringe, transferred (with filtration) to an NMR tube or IR cell, and the various data recorded.

Using acetone-*d*₆ as solvent, ambient temperature NMR spectra were recorded for mixtures of **1a** and **2a** in 1:1, 1:2, and 1:3 mole ratios. Each spectrum contained three resonances: a sharp cyclopentadienyl singlet, a sharp singlet for the exchanging SCH₃ group protons, and a broad singlet for the metal bound SCH₃ protons. Relative intensities were those predicted based on amounts of the two species. The positions of the resonances shifted predictably as a function of relative concentration, as shown in Table 1.

Additional NMR data on 1:1 mixtures of **1a** and **2a** in two other solvents, CD₂Cl₂ and CD₃CN, gave the same result except for small variations in chemical shift values. In addition, in these solvents, a small amount of Me₂S₂ was noted; this arises from a known reaction [3] of these two species giving Me₂S₂ and [CpFe(CO)₂(μ -SMe)Fe(CO)₂Cp]BF₄ (δ 5.245 (s), 2.406 (s) in CD₂Cl₂). Concentrations of these latter species increased over time, with the reaction being about 25% complete after 1 h.

Solutions of **1a** and **2a** in CH₂Cl₂ with relative concentrations of 2:1, 1:1, and 1:2 were prepared. Infrared spectra of these mixtures were superpositions of the spectrum of **1a** (2032, 1985 cm⁻¹) and **2a** (2070, 2030 cm⁻¹) with intensities determined by the relative amounts.

Related reactions. Similar reactions were carried out with five other systems. A summary of spectroscopic data is also given in Table 1.

Decomposition in the **1f/2f** system, (the cyclopentadienyl tungsten carbonyl thiolate system) was somewhat more rapid. Spectra were recorded for a 1:1 mixture at intervals over 90 min, during which time a resonance for Me₂S₂ grew and the cyclopentadienyl and metal bound SCH₃ resonances shifted back to the positions for **1e**. There was an additional small resonance in the spectrum at δ 6.25 ([CpW(CO)₃(acet)]⁺?). Decomposition was seen in the system; apparently degradation of **2e** to Me₂S₂ and non-carbonyl containing products is the facile process.

Variable temperature NMR studies on the CpFe(CO)(L)SMe–[CpFe(CO)(L)(MeSSMe)]BF₄ system (L = P(OPh)₃). Equimolar quantities of these two compounds (**1d** and **2d**) were dissolved in acetone-*d*₆. The solution was filtered into an NMR tube using syringe techniques. The tube was flushed with nitrogen and sealed. Spectra were recorded at ambient temperature, –11, –32, –51, –73 and

Table 1

Exchange of $[\text{SMe}]^+$ between several metal thiolate complexes

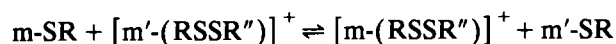
Compounds	NMR chemical shifts ^a				IR $\nu(\text{CO}), \text{cm}^{-1} (\text{CH}_2\text{Cl}_2)$
	Cp	m-SMe	m-SSMe	Other	
A. $\text{CpFe}(\text{CO})_2\text{SMe} (\mathbf{1a})$	5.14	1.65			2615, 1960
1:1 $\mathbf{1a} + \mathbf{2a}$	5.485	2.392	2.788		2071, 2020, 1960
1:2 $\mathbf{1a} + \mathbf{2a}$	5.529	2.501	2.783		
1:3 $\mathbf{1a} + \mathbf{2a}$	5.590	2.633	2.778		
$[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4 (\mathbf{2a})$	5.573	2.94	2.76		2071, 2025
B. $\text{CpFe}(\text{CO})_2\text{SPh} (\mathbf{1b})$	5.18				2035, 1988
1:1 $\mathbf{1b} + \mathbf{2b}$	5.438		2.643	7.2–7.7	2075, 2035, 1989
$[\text{CpFe}(\text{CO})_2(\text{PhSSMe})]\text{BF}_4 (\mathbf{2b})$	5.72		2.622	7.2–7.7	2072, 2032
C. $\text{CpFe}(\text{CO})_2\text{SPh} (\mathbf{1b})$	5.19			6.5–7.0	2034, 1987
2:1 $\mathbf{1b} + \mathbf{2c}$	5.37				2070, 2034, 1987
1:1 $\mathbf{1b} + \mathbf{2c}$	5.49				
1:2 $\mathbf{1b} + \mathbf{2c}$	5.58				
$[\text{CpFe}(\text{CO})_2(\text{PhSSPh})]\text{BF}_4 (\mathbf{2c})$	5.811				2070, 2031
D. $\text{CpFe}(\text{CO})(\text{L})\text{SMe} (\mathbf{1d})$	4.17 d	1.59 d			1971
2:1 $\mathbf{1d} + \mathbf{2d}$	4.49 d	2.00 br,s	2.70	7.2–7.5	2014, 1971
1:1 $\mathbf{1d} + \mathbf{2d}$	4.67 d	2.222 br,s	2.716		
1:2 $\mathbf{1d} + \mathbf{2d}$	4.81	2.385 br,s	2.701		
$[\text{CpFe}(\text{CO})(\text{L})(\text{MeSSMe})]\text{BF}_4 (\mathbf{1d})$ (L = P(OPh) ₃)	5.172 d	2.840 s	2.722	7.2–7.7	2014
E. $\text{CpFe}(\text{CO})(\text{L}')\text{SMe} (\mathbf{1e})$	4.51 d	1.51 d		7.35–7.65	1942
1:1 $\mathbf{1e} + \mathbf{2e}$	4.839	2.05 br	2.364 s	7.4–7.6	1989, 1938
$[\text{CpFe}(\text{CO})(\text{L}')(\text{MeSSMe})]\text{BF}_4 (\mathbf{2e})$ (L' = PPh ₃)	5.10	2.53 s	2.36 s		1991
F. $\text{CpW}(\text{CO})_3\text{SMe} (\mathbf{1f})$	5.881 s	1.954s			2030, 1949
1:1 $\mathbf{1f} + \mathbf{2f}^b$	6.116	2.53 b	2.808		2060, 2030, 1992 sh, 1972, 1949
$[\text{CpW}(\text{CO})_3(\text{MeSSMe})]\text{BF}_4$	6.426	3.266 s	2.811 s		2062, 1995 sh, 1975

^a Acetone-*d*₆, ambient temperature, NMR resonances singlets except as noted. ^b Complete decomposition to give free Me₂S₂ and CpW(CO)₃SMe occurred over 90 min.

–83°C. In this sequence of spectra (going from higher to lower temperature) the cyclopentadienyl proton resonance gradually broadened and the broadened methyl proton resonance (associated with the metal bound SCH₃ group) gradually sharpened. The extent of these changes in line width was not large. In addition, the chemical shifts for each resonance shifted minimally (less than 0.1 ppm). At –83°C, some of the sample had precipitated from solution and the resolution of the spectrum had degraded. Warming caused these changes to be reversed.

Exchange of $[\text{SR}]^+$ between dissimilar metal centers, testing migratory preferences

The goal of this series of experiments was qualitatively to assess the position of the equilibrium:



These data would provide information on the basicity of metal thiolate complexes relative to the electrophile $[\text{SR}]^+$ group.

Measured quantities of two compounds, either *m*-SR and $[m'-(RSSR'')]^+$ or $[m-RSSR'']^+$ and *m'*-SR, were dissolved in acetone- d_6 . The solution was filtered and transferred into an NMR tube by syringe: the tube was capped and the NMR spectrum recorded. In all instances, the system had reached equilibrium by the time the spectrum was recorded. Generally, spectra taken after longer periods of time indicated in the presence of small amounts of Me_2S_2 ($\delta = 2.40$), showing that some decomposition had occurred.

In carrying out these studies, deviations from 1:1 stoichiometry are a significant factor in determining the spectrum. Such deviations could arise from inaccurate weighing, from use of impure samples, and from decomposition of one species. The result of deviations from 1:1 stoichiometry is that the symmetric exchange process occurs concurrently and affects chemical shift values. For instance, in the example to follow ($1a + 2d \rightleftharpoons 1d + 2a$) a ratio of $2a : 1d$ of $> 1:1$ leads to a system containing both $2a$ and $1a$ along with $2d$; a ratio of $< 1:1$ results in a mixture of $1d$ and $2d$ along with $1a$. In both instances, positions of the resonances then depend on relative amounts of these substances.

The integrated intensities of each peak and the overall intensities of groups of peaks (phenyl, cyclopentadienyl, and methyl protons) were usually very helpful in the interpretation of these spectra.

Reactions between 1a and 2d ($CpFe(CO)_2SMe + [CpFe(CO)(L)(MeSSMe)]BF_4$) and *between 1d and 2a* ($CpFe(CO)(L)SMe + [CpFe(CO)_2(MeSSMe)]BF_4$). Infrared data on a 1:1 mixture of $1d$ and $2a$ in CH_2Cl_2 were collected. Strong peaks at 2030 and 1980 cm^{-1} (for $1a$) and at 2014 cm^{-1} (for $2d$) were seen. The unique absorptions at 2071 cm^{-1} (for $1d$) and 1968 cm^{-1} (for $2a$) were not seen (although it is likely that the presence of small quantities of these species would avoid detection). These data indicate that the position of the equilibrium $1a + 2d \rightleftharpoons 1d + 2a$ significantly favors species on the left side of this equation.

Assuming a complete, or nearly complete, reaction between $1d$ and $2a$ in a 2:1 ratio, we expect a mixture of $1a$, $2a$, and $2d$ in equal quantities; the NMR spectrum supports this. There are singlet cyclopentadienyl resonances at δ 5.47 (a 1:1 mixture of $1a$ and $2a$) and at δ 5.11 (all or mostly $2d$) with a 2:1 ratio of intensities. Sharp methyl resonances were seen δ 2.73 and 2.78, the former with greater intensity; and there is a broad resonance at δ 2.5. The third peak represents the metal bonded SCH_3 groups in the 1:1 mixture of $1a$ and $1b$, (cf. Table 1) the two resonances at higher field are from the remaining SCH_3 groups in $2d$ and the two exchanging methyls.

A further reaction between $1d$ and $2a$ was carried out; although intended to be a 1:1 reaction, in fact $2a$ was in slight excess. The NMR spectrum contained resonances at δ 5.25 ($1a + \text{excess } 2a$) and at δ 5.05. The latter was a doublet; its position was 0.1 ppm lower than that of pure $2d$ suggesting that possibly some $1d$ might also be present. There was one sharp resonance at about δ 2.72 and estimates based on relative amounts placed a second broad resonance at the position of the resonance of residual protons in acetone- d_6 , δ 1.95. The intensity of the sharp resonance at δ 2.72 indicated this resonance to be the superposition of resonances for exchanging SCH_3 groups of $2d$ and the metal bonded SCH_3 of $1d + 2d$.

An NMR spectrum of a mixture of $1a$ and $2d$ duplicated these data.

Other reactions. Data from several other systems are given in Table 2.

Table 2

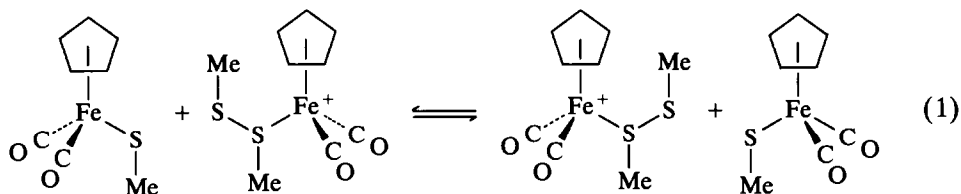
Exchange of SR^+ between dissimilar metal thiolate complexes

Reactants (1:1)	Products (NMR) ^a
$\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SMe} + [\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$	$[\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{MeSSMe})]\text{BF}_4$ (δ 8.00–7.44 (m), 5.10 (s), 2.53 (s), 2.36 (s)) and $\text{CpFe}(\text{CO})_2\text{SMe}$ (δ 5.13 (s), 1.65 (s,br))
$\text{CpFe}(\text{CO})_2\text{SMe} + [\text{CpFe}(\text{CO})_2(\text{PhSSPh})]\text{BF}_4$	$[\text{CpFe}(\text{CO})_2(\text{MeSSPh})]\text{BF}_4$ (δ 7.8–7.1 (m), 5.79 (s), 2.94 (s)) and $\text{CpFe}(\text{CO})_2\text{SPh}$ (δ 7.8–7.1 (m), 5.19 (s))
$\text{CpFe}(\text{CO})_2\text{SMe} + [\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$	No reaction (resonances for starting materials only)
$\text{CpFe}(\text{CO})_2\text{SMe} + [\text{CpW}(\text{CO})_3(\text{MeSSMe})]\text{BF}_4$	$[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ (δ 5.73 (s), 2.94 (s), 2.76 (s) and $\text{CpW}(\text{CO})_3\text{SMe}$ (δ 5.93 (s) and 2.02 (s))
$\text{CpW}(\text{CO})_3\text{SMe} + [\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$	No reaction (resonances for starting materials only)

^a Acetone- d_6 , ambient temperatures; spectra recorded immediately after mixing.

Discussion

The ^1H NMR spectrum of a solution of $\text{CpFe}(\text{CO})_2\text{SMe}$ and $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]\text{BF}_4$ in several solvents (acetone- d_6 , CD_3CN , CD_2Cl_2) contains three resonances. These are: a sharp cyclopentadienyl singlet, a sharp methyl singlet, and a broad methyl singlet. Intensities identify the latter two resonances as the uncoordinated SMe group of the ligated dimethyl disulfide and both metal coordinated SMe groups, respectively. The positions of the resonances for the cyclopentadienyl and metal coordinated SMe groups are the weighted averages for resonances in the respective starting materials. These data indicate that the uncoordinated $[\text{SMe}]^+$ group is rapidly exchanging between the two metal groups as shown below (eq. 1):



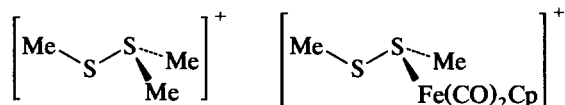
Since an infrared spectrum of this solution contained only $\nu(\text{CO})$ absorptions for the two starting materials, 1:1 adduct formation via the sulfur ligand is ruled out. Such a species seemed unlikely since this would require hypervalent disulfide(IV) atoms in the bridging $[\text{MeSSMeSMe}]^+$ unit.

Further study indicated that exchange of $[\text{SR}]^+$ in such systems is a general phenomenon. Similar results were obtained with four additional metal groups ($\text{CpFe}(\text{CO})(\text{L})\text{SMe}$, $\text{L} = \text{PPh}_3$, $\text{P}(\text{OPh})_3$; $\text{CpFe}(\text{CO})_2\text{SPh}$; and $\text{CpW}(\text{CO})_3\text{SMe}$), and also shown in the rapid exchange of $[\text{SPh}]^+$ between $\text{CpFe}(\text{CO})_2\text{SPh}$ units.

With one system, $\text{CpFe}(\text{CO})(\text{L})\text{SMe}$ ($\text{L} = \text{P}(\text{OPh})_3$) + $[\text{SMe}]^+$, ^1H NMR spectra were recorded at lower temperatures in an attempt to slow the exchange process.

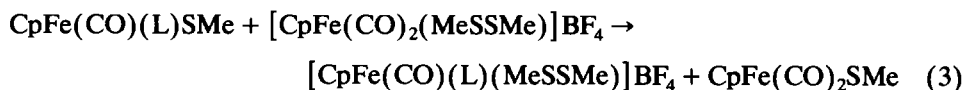
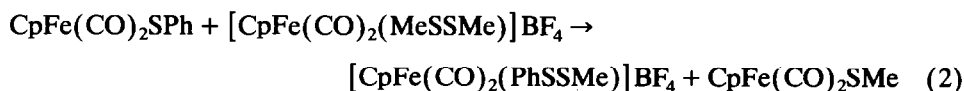
The basic pattern of resonances did not change at temperatures down to -80°C , although some changes in line widths were noted. Decreasing solubility precluded study at lower temperatures and the original spectrum was restored when the temperature was raised. The minimal changes in the NMR spectra over this range of temperatures precluded a detailed assessment of rate.

In retrospect, facile exchange is not surprising. A similar very rapid exchange process occurs between Me_2S and $[\text{MeSSMe}_2]\text{BF}_4$ [2]. Indeed, for this system, the rate is also too fast to be measured by NMR procedures. The metal complexes studied here are similar to those organosulfur species, differing only in that a metal group has replaced a methyl group in the general structure:



The exchange processes for the organic and organometallic moieties are presumed to be mechanistically similar, involving nucleophilic attack at the MeS group with displacement of Me_2S (from $[\text{Me}_2\text{SSMe}]^+$) or $\text{MeSFe}(\text{CO})_2\text{Cp}$ (from $[\text{CpFe}(\text{CO})_2(\text{MeSSMe})]^+$).

In the course of this work we investigated situations in which an $[\text{SR}]^+$ group might partition between dissimilar centres. These experiments provided data on the relative basicities of sulfur in metal-bonded thiolate groups. Two experiments are described by the chemical equations below:



($\text{L} = \text{PPh}_3, \text{P}(\text{O}Ph)_3$)

The equilibrium given in eq. 2 lies on the left hand side (reactants) as expected based on the relative donor abilities of the methyl and phenyl group. The equilibrium in eq. 3 lies at the right hand side (products), the higher donor ability of phosphorus ligands (relative to CO) contributing to a higher basicity at sulfur.

These latter systems proved difficult to analyze for two reasons. Deviation from a precise 1:1 stoichiometry gave a system in which exchange between equivalent centres was occurring. In addition there was evidence of fairly rapid decomposition (to Me_2S_2). Thus, the composition, and hence the NMR spectrum of the mixture, changed over time. These factors made it impossible precisely to establish an equilibrium position.

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