ORGANOMETALLIC COMPLEXES WITH RSSR LIGANDS: A NEW SYNTHETIC METHOD

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Summary

Reactions of $[Me_2SSMe]BF_4$ with metal thiolate complexes have been used to prepare new complexes with coordinated organic disulfide ligands. Complexes prepared include $[CpFe(CO)(L)(PhSSMe)]BF_4$ ($L = CO$, PPh_3, PPh_2Me, PPh_2OMe, $P(OPh)_3$), $[CpFe(CO)_2(MeSSMe)]BF_4$ and $[CpW(CO)_3(MeSSMe)]BF_4$. A molybdenum analogue of the last compound and $[Mn(CO)_5(MeSSMe)]BF_4$ were identified in solution as products of this type of reaction, but these species were unstable and could not be isolated. Isomerization of $[CpFe(CO)\{P(OPh)_3\}(PhSSMe)]BF_4$ upon heating was noted. This synthetic method is easy and versatile, and is a useful alternative to other known routes to this type of complex.

Organometallic complexes with organic disulfide ligands were described by our research group several years ago [1]. The synthesis of these compounds was accomplished by two procedures (see Scheme 1). Oxidation of species having the formula CpFe(L)(L′)SPh (L,L′ = CO, phosphines, phosphites, CNR) led to complexes in which a disulfide bridged two metal atoms. Formation of these complexes containing bridging disulfide ligands is assumed to occur via intermediate formation of a sulfur centered radical species, oxidation occurring at the ligand rather than at the metal; this radical then dimerizes by formation of the sulfur–sulfur bond. The second synthetic procedure utilizes the precursor $[CpFe(CO)_2(THF)]BF_4$ for which the tetrahydrofuran ligand is known to be easily replaced [2]. In reactions of this species with organic disulfides, one can obtain either the complexes with bridging disulfides, described above, or complexes in which the disulfide functions as a monodentate ligand. The specific product obtained depends on the ratio of reactants. The former can be converted to the latter on dissolution in acetonitrile.

The stability of complexes with bridging disulfides with respect to sulfur–sulfur bond homolysis has been shown to vary considerably [3].

A recent paper from another group has extended the second synthetic method, preparing additional complexes of iron with monodentate disulfide ligands [4]. The
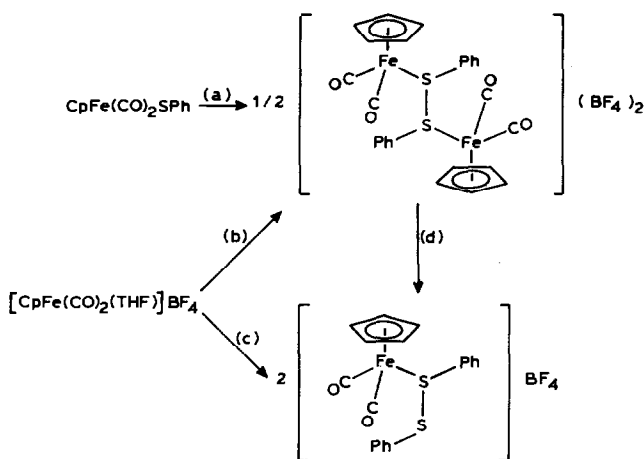
SCHEME 1. (a) AgBF$_4$ or NOPF$_6$ (yielding PF$_6^-$ salt); (b) 0.5 equiv. PhSSPh, (c) 1.0 equiv. PhSSPh; (d) CH$_3$CN; [CpFe(CO)$_2$(MeCN)]BF$_4$ is the second product.

general method of synthesis, displacement of a labile ligand by a disulfide, has been used in the synthesis of disulfide complexes of other metals [5–7].

We describe in this paper another synthetic route to complexes containing monodentate disulfide ligands. This route involves addition of the electrophilic RS$^+$ group to the thiolate ligand in a metal thiolate complex. Donors of RS$^+$ groups include [Me$_2$SSMe]BF$_4$, widely used in organic chemistry [8] and more recently used in organometallic synthesis [9], and N-benzenethiolatophthalimide (phthSPh). This latter species has found recent use in organometallic synthesis [10,11], and earlier use in the synthesis of coordination compounds [12]. The method described here is reasonably general and its use for the synthesis of many derivatives not available by the other routes is anticipated. It also has the value of permitting facile and specific synthesis of metal complexes of unsymmetrical disulfides, a difficult problem by the other known routes.

Experimental

The following compounds were prepared by literature methods: [Me$_2$SSMe]BF$_4$ [13]; phthSPh [14]; CpFe(CO)(L)SPh (L = CO [15], P(OPh)$_3$, PPh$_3$, PPh$_2$Me [1], PPh$_2$OMe [16]); PPN[M(CO)$_3$Cp] (M = Mo, W); PPN[Mn(CO)$_5$] (PPN$^+$ = Ph$_3$PNPPh$_3^+$) [17]; and CpW(CO)$_3$SMe [9,18]. Infrared spectra were recorded on a Beckman Model 4320 spectrophotometer, and ^{1}H NMR spectra were obtained on either IBM WP-200 or WP-270 spectrometers. Elemental analyses were performed by the Galbraith Laboratories, Knoxville, TN. All procedures were carried out under nitrogen.

Synthesis of CpFe(CO)$_2$SMe

This known compound was synthesized from Na[Fe(CO)$_2$Cp] and Me$_2$S$_2$, a route analogous to other procedures described by our group [9]. A solution of Na[CpFe(CO)$_2$] was prepared initially from [CpFe(CO)$_2$]$_2$ (1.77 g, 5.0 mmol) and

1% sodium amalgam (0.46 g Na, 20 mmol) in 60 ml THF. After removal of the excess amalgam, MeSSMe (3.60 ml, 40 mmol) in 5 ml THF was added; the solution turned brown. Stirring was continued 1 h. The solution was filtered, and the solvent evaporated. The residue was extracted with hexane, and after partial evaporation this solution was placed on a silica gel chromatography column. Elution with benzene yielded an initial large band of [CpFe(CO)$_2$]$_2$; this was followed by a yellow band eluting with acetone, which contained the product. Evaporation of the solvent and crystallization of the residue from pentane yielded the product, 0.13 g, 5.8% yield, m.p. 69–71°C (lit. [19], 68–70°C).

Synthesis of [CpFe(CO)$_2$(PhSSMe)]BF$_4$

Solid [Me$_2$SSMe]BF$_4$ (0.35 g, 1.8 mmol) was added to a solution of CpFe(CO)$_2$SPh (0.51 g, 1.8 mmol) in 25 ml of CH$_2$Cl$_2$. The mixture was stirred at room temperature for 1.0 h. The solution was then filtered, evaporated to approximately one-half of its original volume and 50 ml Et$_2$O added. This solution was cooled to −20°C; after a lengthy time yellow-orange crystals of the product formed. They were collected by filtration and dried in vacuo; yield 0.49 g, (64%); m.p. 110–112°C.

Anal. Found: C, 40.13; H, 3.30; S, 15.32. C$_{13}$H$_{13}$BF$_4$O$_2$S$_2$Fe calcd.: C, 40.00; H, 3.10; S, 15.24%. IR (CH$_2$Cl$_2$): 2068, 2025 cm^{-1}. NMR (CD$_3$CN): δ 2.50s (−SCH$_3$), 5.40s (C$_5$H$_5$), 7.55-770 m (C$_6$H$_5$).

Other compounds prepared by this procedure are listed below.

[CpFe(CO)(PPh$_3$)(PhSSMe)]BF$_4$ · MeCN. Red crystals of the product were recrystallized from MeCN/Et$_2$O (giving the complex with one MeCN of recrystallization). Yield. 61%, m.p. 77–80°C.

Anal. Found: C, 57.30; H, 4.93; S, 9.21. C$_{33}$H$_{31}$BF$_4$NOPS$_2$Fe calcd.: C, 57.00; H, 4.46; S, 9.21%. IR (CH$_2$Cl$_2$): 1987 cm^{-1}. NMR (CD$_3$CN): 2.55s (SCH$_3$); 5.04 d (J 1 Hz) (C$_5$H$_5$); 7.15-7.7m (C$_6$H$_5$).

CpFe(CO){P(OPh)$_3$}(PhSSMe)]BF$_4$. The product, a red solid, was recrystallized from MeOH: yield, 89%. m.p. 93–95°C.

Anal. Found: C, 53.06; H, 4.13; S, 9.24. C$_{31}$H$_{28}$BF$_4$NO$_4$PS$_2$Fe calcd.: C, 52.99; H, 3.99; S, 9.12%. IR(CH$_2$Cl$_2$): 2005 cm^{-1}. NMR (CD$_2$Cl$_2$): 2.49s (SCH$_3$); 4.67d (J 1 Hz) (C$_5$H$_5$), 7.07-7.8 m (C$_6$H$_5$).

When a methanol solution of this compound is heated for 15 min partial rearrangement occurs to give the product with the metal coordinated to the sulfur bearing the methyl group. Approximately equal amounts of the two isomers were judged to be present based on an NMR spectrum of the isolated product. Some decomposition (insoluble solids) also accompanied this rearrangement. An NMR spectrum of the second isomer contained resonances at 2.67d (J 10Hz) and 4.84 (J 1 Hz).

[CpFe(CO)(PPh$_2$Me)(PhSSMe)]BF$_4$. Prepared in a similar manner, this red crystalline species was obtained in 60% yield; m.p. 125–127°C.

Anal. Found: C, 52.50; H, 4.62; S, 10.72. C$_{26}$H$_{26}$BF$_4$OPS$_2$Fe calcd.: C, 52.70; H, 4.39; S, 10.81%. IR (CH$_2$Cl$_2$): 1985 cm^{-1}. NMR (CD$_3$CN): 2.28d, J 10 Hz (PCH$_3$); 2.54s (SCH$_3$) 5.11d, J 1 Hz (C$_5$H$_5$); 7.45 m (C$_6$H$_5$).

[CpFe(CO)(PPh$_2$OMe)(PhSSMe)]BF$_4$. Red crystals, 23%. m.p. 122–124°C. Anal. Found: C, 50.93; H, 4.42; S, 10.74. C$_{26}$H$_{26}$BF$_4$O$_2$PS$_2$Fe calcd.: C, 51.32; H, 4.28; S, 10.53%. IR (CH$_2$Cl$_2$): 1992 cm^{-1}. NMR (CD$_3$CN): 2.50 s (SCH$_3$), 3.47d, J 12 Hz (POCH$_3$), 7.45-7.65m (C$_6$H$_5$).

[CpFe(CO)₂(MeSSMe)]BF₄. Dull gold crystals, 60% yield were obtained upon crystallization from CH_2Cl_2/ethyl acetate. This complex was identified through comparisons of infrared ($\nu(CO)$ at 2071, 2025 cm^{-1}) and ^1H NMR data (δ 2.79s, 2.95s, 5.76s), with literature data [2,4].

Reaction of CpW(CO)₃SMe and [Me₂SSMe]BF₄

A sample of $CpW(CO)_3SMe$ (0.10 g, 0.23 mmol) was dissolved in 50 ml CH_2Cl_2 and solid $[Me_2SSMe]BF_4$ (0.050 g, dissolved in 50 ml CH_2Cl_2) added rapidly. The reaction occurred rapidly; an infrared spectrum taken immediately after mixing (~ 2 min) showed only product and no starting material. The reaction mixture was filtered and the filtrate evaporated to dryness. Crystallization from CH_2Cl_2/Et_2O yielded a pure sample of the product; 0.11 g, 90% yield.

Anal. Found: C, 21.63; H. 2.23. $C_{10}H_{11}BF_4O_3S_2W$ calcd.: C, 23.37; H, 2.16%. IR (CH_2Cl_2): 2060s, 1980sh, 1968s cm^{-1}. NMR (CD_2Cl_2): 2.72s (W-S-SCH_3), 3.06s (W-SCH_3), 6.09s (C_5H_5).

This compound could also be prepared from $PPN[W(CO)_3Cp]$ and $[Me_2SSMe]BF_4$, if these reactants were in a 1/2 ratio. It is also formed in reactions of these reagents in a 1/1 reaction if the addition of $[Me_2SSMe]BF_4$ was rapid, or if $PPN[W(CO)_3Cp]$ was added to a slurry of $[Me_2SSMe]BF_4$ in CH_2Cl_2. Work-up of these reactions was carried out by the method described above, generally with about 50% yields of product being obtained. Note that when $[Me_2SSMe]BF_4$ is added slowly to $PPN[W(CO)_3Cp]$ (1/1 stoichiometry) in MeCN the product is $CpW(CO)_3SMe$ exclusively and in high yield [9].
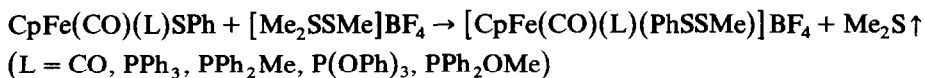
Reaction of PPN[Mo(CO)₃Cp] and [Me₂SSMe]BF₄

A reaction between these reagents in 1/1 molar ratio is known to procedure $CpMo(CO)_3SMe$ which will subsequently degrade to $Cp_2Mo_2(\mu\text{-}SMe)_2(CO)_4$. If, however, a second equivalent of $[Me_2SSMe]BF_4$ is added to the reaction product that is initially formed, the formation of $[CpMo(CO)_3(MeSSMe)]BF_4$ can be detected by IR ($\nu(CO)$ at 2070s, 1998sh, 1976s, br cm^{-1}) and by NMR (in CD_2Cl_2: δ2.74s (Mo-SSCH_3), 2.97s (MoSCH_3), 6.00s (C_5H_5)). This product is quite unstable and all attempts to isolate it led to noncarbonyl containing decomposition products.

Reaction of PPN[Mn(CO)₅] and [Me₂SSMe]BF₄

A 1/1 reaction of these reagents in CH_2Cl_2 at 0°C produces $Mn(SMe)(CO)_5$ initially (~ 4 min); this species will lose CO and form $Mn_2(\mu\text{-}SMe)_2(CO)_8$ within about 10 min total elapsed time. If a 1/2 ratio of these reagents is used (0°C), one can detect (by IR) initial formation of $Mn(SMe)(CO)_5$ followed by rapid conversion to a species assumed to be $[Mn(CO)_5(MeSSMe)]BF_4$ ($\nu(CO)$: 2145w, 2059vs, 2036m cm^{-1}). This species rapidly decomposes and could not be isolated.

Discussion

Use of the reagent $[Me_2SSMe]BF_4$ [14] as a donor of the MeS^+ group provided a new and simple route to the syntheses of complexes containing monodentate disulfide ligands. Five new iron complexes were synthesized through reactions summarized in the following equation:

$$CpFe(CO)(L)SPh + [Me_2SSMe]BF_4 \rightarrow [CpFe(CO)(L)(PhSSMe)]BF_4 + Me_2S\uparrow$$

$$(L = CO, PPh_3, PPh_2Me, P(OPh)_3, PPh_2OMe)$$

In addition the known complex [CpFe(CO)$_2$(MeSSMe)]BF$_4$ [2,4] was prepared by this route. Starting materials are easily accessible and the reactions, carried out in CH$_2$Cl$_2$ at ambient temperature, are complete in a short time (< 1 h). Apart from minor difficulties encountered in the crystallization of several of these compounds, the reaction work-up is quite straightforward. The products are gold to red crystalline species for which appropriate analytical data were obtained.

An obvious advantage to this method is that one can easily prepare complexes of asymmetric disulfides, such as PhSSMe. Disulfides of this type are not very stable toward disproportionation and their use as ligands would be quite limited if one had to prepare them preliminarily as precursors to such complexes. Furthermore, this route gives one specific isomer of these asymmetric disulfides which retains coordination to the metal by the sulfur in the thiolate group which initially was coordinated to the metal.

Infrared spectra for these compounds contain absorptions due to the carbonyl groups. Monocarbonyl complexes have a single absorption in the 1985–2005 cm^{-1} range. The precise value is dependent in a predictable way on the donor ability of L, the progression of values of ν(CO) occurring in the order L = P(OPh)$_3$ > PPh$_2$OMe > PPh$_3$ > PPh$_2$Me. The specific ν(CO) values found are somewhat higher than those seen for a variety of other [CpFe(CO)(L)$_2$]$^+$ cationic species, such as [CpFe(CO)(PPh$_3$)$_2$]PF$_6$ (1970 cm^{-1}), [CpFe(CO)(MeCN)(PPh$_3$)]PF$_6$ (1970 cm^{-1}) [20], [CpFe(CO)(dppe)]BF$_4$ (1980 cm^{-1}) [21]; but equal to or lower than ν(CO) values seen in several complexes of the same general stoichiometry and carbon based ligands like [CpFe(CO)(PPh$_3$)(C=CH$_2$)]BF$_4$ (2035 cm^{-1}) [22]; and [CpFe(CO)(PPh$_3$)(CMeOMe)]BF$_4$ (1990 cm^{-1}) [23]. The values of ν(CO) for the two [CpFe(CO)$_2$(RSSMe)]BF$_4$ species, 2065 and 2028 cm^{-1} for the PhSSMe complex and 2071 and 2025 cm^{-1} for the MeSSMe complex, are not much different than the absorptions in [CpFe(CO)$_2$(SMe$_2$)]BF$_4$ [24] at 2065 and 2024 cm^{-1}.

Proton NMR spectra contained resonances appropriate to the indicated species. Notably the values for the protons of the uncoordinated SCH_3 group are shifted downfield, from δ 2.33 in the free ligand [25] to values between δ 2.49 and 2.55. This shift is smaller than found when MeSSMe (δ 2.39) undergoes complexation in [CpFe(CO)$_2$(MeSSMe)]BF$_4$ (δ 2.80, 2.98) [4].

When heated in CH$_2$Cl$_2$ [CpFe(CO){P(OPh)$_3$}(PhSSMe)]BF$_4$ was found to undergo partial isomerization, forming the species in which the sulfur of the SCH$_3$ group is coordinated to the metal. In this new isomer, the resonance of the methyl protons in the coordinated SCH_3 group occurs at δ 2.67; in addition a small coupling to phosphorus was seen. The difference between resonance positions of the SCH$_3$ protons in the coordinated and uncoordinated isomers, 0.18 ppm, is precisely the difference in chemical shift of the SCH_3 resonances in [CpFe(CO)$_2$-(MeSSMe)]BF$_4$. This allows one to argue with some certainty that the δ 2.98 peak in this species is due to the coordinated SCH_3 protons, while the δ 2.80 peak can be assigned to the uncoordinated SCH_3 protons. The rearrangement process observed here has been seen previously by others [4,5]. Unfortunately some decomposition accompanies the isomerization in our system.

Attempts to extend this procedure to synthesis of disulfide complexes of several other metals met with limited success. A tungsten complex, [CpW(CO)$_3$-(MeSSMe)]BF$_4$ was isolated and characterized from the reaction shown below:

CpW(CO)$_3$SMe + [Me$_2$SSMe]BF$_4$ → [CpW(CO)$_3$(MeSSMe)]BF$_4$ + Me$_2$S
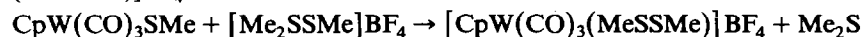
Note that CpW(CO)$_3$SMe is the product obtained when [Me$_2$SSMe]BF$_4$ is added to PPN[W(CO)$_3$Cp] [9]; this means that the disulfide compound can also be obtained if these reagents are employed in a 1/2 molar ratio. The rate of addition of [MeS]$^+$ to the coordinated thiolate complex appears to be faster than the rate of the initial reaction; consequently [CpW(CO)$_3$(MeSSMe)]BF$_4$ also becomes a product in reactions of [Me$_2$SSMe]BF$_4$ and PPN[W(CO)$_3$Cp] when reagents were added in the opposite order. The tungsten complex has ν(CO) values at 2060s, 1980sh, and 1968s cm^{-1}; in its ^{1}H NMR spectrum, resonances at δ 2.72 and 3.06 may presumably be assigned to coordinated and uncoordinated SCH_3 groups respectively.

Both IR and ^{1}H NMR data were obtained for the formation of an analogous molybdenum complex by the same type of reaction; however [CpMo(CO)$_3$(MeSSMe)]BF$_4$ decomposed too rapidly to permit its isolation. Likewise [Mn(CO)$_5$(MeSSMe)]BF$_4$ was postulated as the product of a reaction PPN[Mn(CO)$_5$] with two equivalents of [Me$_2$SSMe]BF$_4$ based on infrared evidence, but it was also not isolated because of its low stability. Decomposition products in these reactions did not contain carbonyl ligands.

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