Reactions of [Me₂SSMe]BF₄ with organometallic complexes having metal–metal bonds

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(Received May 23rd, 1988)

Abstract

Reactions between [Me₂SSMe]BF₄ and dinuclear organometallic complexes having metal–metal bonds have been studied. Insertion of an SMe^+ group into the metal–metal bond to give a thiolate-bridged bimetallic compound had previously been demonstrated; here, we have described two other types of reactions. Certain organometallic precursors are found to be oxidized by the sulfur reagent; for example, $Fe_2(CO)_2(\mu\text{-dppm})(\eta\text{-}C_5H_5)_2$ is oxidized to a paramagnetic cation by [Me₂SSMe]BF₄. In addition, we have observed M–M bond cleavage and formation of a Me₂S complex (isolated) and MeS^- complex. Subsequently, the latter complex reacts with additional [Me₂SSMe]BF₄ to form complexes with a MeSSMe ligand, and when stable, these latter species can also be isolated. This second mode of reactivity is found for $Mn_2(CO)_{10}$, $M_2(CO)_8(PPh_3)_2$ (M = Mn, Re), $Mn_2(CO)_8(\mu\text{-dppm})$, $[M(CO)_3(\eta\text{-}C_5H_5)]_2$ (M = Mo, W) and $(CO)_5MnFe(CO)_2(\eta\text{-}C_5H_5)$; stable MeSSMe complexes of tungsten and iron were isolated from the appropriate reactions.

We have demonstrated that [Me₂SSMe]BF₄ is a useful reagent in organometallic synthesis [1,2]. A significant characteristic of this reagent is the fact that it functions as a donor of the electrophilic SMe^+ group; for example, it reacts with anionic carbonylmetallates to yield thiomethyl metal carbonyls [1].

$$PPN[W(CO)_3(\eta\text{-}C_5H_5)] + [Me_2SSMe]BF_4 \rightarrow W(SMe)(CO)_3(\eta\text{-}C_5H_5)$$
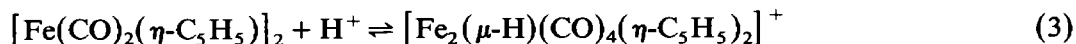$$+ Me_2S + [PPN]BF_4 \quad (1)$$
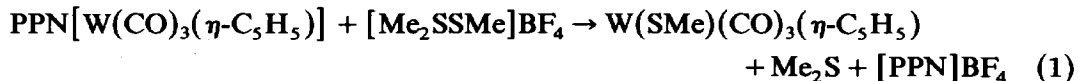
The mechanism of this reaction involves displacement of Me₂S by the nucleophilic metal carbonyl; there are numerous non-organometallic analogies to this reaction [3]. Another example is seen in the reaction of [Me₂SSMe]BF₄ with a metal thiolate species to give a complex having a monodentate organic disulfide ligand; for example:

$$W(SMe)(CO)_3(\eta\text{-}C_5H_5) + [Me_2SSMe]BF_4 \rightarrow [W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4$$
$$+ Me_2S \quad (2)$$
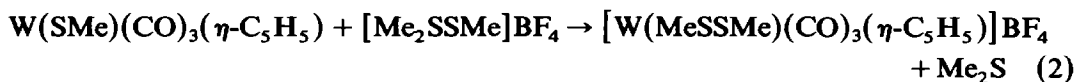
The mechanism of formation of the product is presumably analogous, i.e., Me_2S is displaced from [Me_2SSMe]BF_4 by the nucleophilic sulfur in the organometallic precursor [2].

The indicated procedures can provide convenient, high yield routes to organometallic product species. However, there is an inherent limitation in the general synthetic strategy in that the second reaction competes with the first. Use of this procedure is also limited by the small number of sufficiently nucleophilic metal carbonyls.

To pursue the further use of [Me_2SSMe]BF_4 in organometallic syntheses meant, logically, looking for other types of nucleophilic species that react with this reagent. Bimetallic compounds with metal–metal bonds were a logical choice. Studies originating many years ago indicated that it is possible to reversibly add another electrophile, H^+, to the metal–metal bond in many of these species. The first example of this [4] is in a report on protonation of species such as [Fe(CO)$_2$(η-C$_5$H$_5$)]$_2$:

$$\left[Fe(CO)_2(\eta\text{-}C_5H_5)\right]_2 + H^+ \rightleftharpoons \left[Fe_2(\mu\text{-}H)(CO)_4(\eta\text{-}C_5H_5)_2\right]^+ \tag{3}$$

Our first efforts in this project were to treat [Me_2SSMe]BF_4 with bimetallic species $Fe_2(\mu\text{-}SMe)_2(CO)_4(L)_2$ (L = CO, PMe_3, $PPhMe_2$, $PPhEt_2$, PPh_3). These reactions occurred in the expected fashion with formation of the complexes [$Fe_2(\mu\text{-}SMe)_3(CO)_4(L)_2$]$BF_4$ [5]. This was a designed reaction, since the precursors are often described (without formal evidence however!) as having a bent and therefore accessible metal–metal bond, and since the phosphine complexes are known to protonate [6]. Continuing this work, we next investigated reactions of other metal–metal bonded species, some of which are known to protonate, others which do not. The results are reported in this paper.

Experimental

The following materials were prepared according to the procedures given in the literature: $Fe_2(CO)_2(\mu\text{-}dppm)(\eta\text{-}C_5H_5)_2$ [7], $Fe_2(CO)_3\{P(OPh)_3\}(\eta\text{-}C_5H_5)_2$ [8], $Mn_2(CO)_8(PPh_3)_2$ and $Mn_2(CO)_9(PPh_3)$ [9], $Mn_2(CO)_8(\mu\text{-}dppm)$ [10], $Re_2(CO)_8(PPh_3)_2$ [11], $(CO)_5MnFe(CO)_2(\eta\text{-}C_5H_5)$ [12], [Me_2SSMe]BF_4 [13], and $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$ [1]. Other starting materials were commercial samples. Solvents were dried by standard methods. All reactions were carried out under dry N_2. Infrared spectra (CH_2Cl_2 solutions except as noted) were recorded on a Beckman Model 4230 spectrophotometer and ^1H NMR spectra (acetone-d_6 except as noted) on an IBM WP-200 spectrometer. Melting points were performed on a Thomas–Hoover apparatus. Elemental analyses were performed by the Galbraith Laboratory, Knoxville, TN.

Reaction of [Me_2SSMe]BF_4 and $Fe_2(CO)_3\{P(OPh)_3\}(\eta\text{-}C_5H_5)_2$

A slurry of [Me_2SSMe]BF_4 (0.098 g, 0.50 mmol) in 75 ml of CH_2Cl_2 was slowly added to a solution of $Fe_2(CO)_3\{P(OPh)_3\}(\eta\text{-}C_5H_5)_2$ (0.318 g, 0.50 mmol) in 100 ml CH_2Cl_2. The infrared spectrum was monitored and after about 1 h the reaction appeared to have ended. It was evident that starting material was present (ν(CO) at 1964 and 1749 cm^{-1}) along with product(s) (ν(CO) at 2080, 2040, 1990 cm^{-1}). Because of this, a second equivalent of [Me_2SSMe]BF_4 was added. An IR spectrum

of the green solution after this addition indicated that starting material was no longer present. The solvent volume was reduced to 20 ml and ethyl acetate layered carefully on top; the slow mixing of these solvents resulted in the deposition of a solid product. This was subjected to fractional crystallization using a CH_2Cl_2/ethyl acetate mixture. The first (least soluble) fraction was isolated and identified as $[Fe(CO)_2\{P(OPh)_3\}(\eta-C_5H_5)]BF_4$, 0.196 g, 34% yield based on iron. This known compound [14] was identified by its m.p., 139°, ^1H NMR, and infrared spectrum $(\nu(CO)(CHCl_3))$: 2078, 2035 cm^{-1}). The second compound in this product mixture, present in approximately the same amount, was not obtained pure. However, the infrared spectrum ($\nu(CO)$ at 1989 cm^{-1}) provided evidence that this green species is $[Fe_2(\mu-SMe)_2(CO)_2(\eta-C_5H_5)_2]BF_4$. The PF_6^- analogue of this cation is known [15].

A further experiment was performed to give additional information on this system. A solution of trans-$Fe_2(\mu-SMe)_2(CO)_2(\eta-C_5H_5)_2$ [16] in CH_2Cl_2 was prepared. Upon addition of one equivalent of $[Me_2SSMe]BF_4$ a rapid change in color from brown to green was observed and the $\nu(CO)$ absorption at 1947 cm^{-1} in the starting material was replaced by a new absorption at 1992 cm^{-1} corresponding to the value for the one-electron oxidation product. No attempt was made to isolate this product.

Reaction of [Me₂SSMe]BF₄ and Fe₂(CO)₂(μ-dppm)(η-C₅H₅)₂

A solution of the organometallic complex (0.332 g, 0.49 mmol) in 40 ml of CH_2Cl_2 was treated with a slurry of $[Me_2SSMe]BF_4$ (0.095 g, 0.49 mmol) in 20 ml CH_2Cl_2. The $\nu(CO)$ absorption at 1680 cm^{-1} disappeared and new absorptions at 1838 and 1777 cm^{-1} grew in, coincident with a color change of the solution from dark green to dark red. Workup, as described in the procedure above, yielded the red solid product, $[Fe_2(CO)_2(\mu-dppm)(\eta-C_5H_5)_2]BF_4$, 0.25 g (66%); m.p. 173°C dec.

IR: $\nu(CO)$ 1840w, 1775s,br cm^{-1}; ^1H NMR (CD_2Cl_2): δ 7.60–7.93m (C_6H_5), 6.83s,br (C_5H_5). These values agree with data reported on this paramagnetic cation known to be formed by oxidation of the precursor using various silver salts such as $AgPF_6$ [8].

Reaction of [Me₂SSMe]BF₄ and [Mo(CO)₃(η-C₅H₅)₂]

The reaction of 1.00 mmol of each reactant in CH_2Cl_2, and workup as described above produced a 16% yield of yellow needles of $[Mo(CO)_3(SMe_2)(\eta-C_5H_5)]BF_4$ m.p. 145°C dec.; there was also recovery of 43% of the organometallic starting material. A 2/1 reaction of these reagents gave the cationic product in 50% yield (based on Mo) with no starting material being recovered.

Anal. Found: C, 30.31; H, 2.76. $C_{10}H_{11}BF_4MoO_3S$ calcd.: C, 30.48; H, 2.81%. IR: $\nu(CO)$ at 2070s, 2000s,sh, 1977s cm^{-1}; ^1H NMR: δ 2.77s, (S(CH_3)$_2$), 6.26s, (C_5H_5).

Reaction of [Me₂SSMe]BF₄ and [W(CO)₃(η-C₅H₅)]₂

The reaction between these two reagents (1/1) was carried out in a similar fashion. After 1 h an infrared spectrum indicated the presence of considerable starting material so a second equivalent of $[Me_2SSMe]BF_4$ was added and the mixture stirred for 1 h. Workup as described produced an orange-brown solid. Its ^1H NMR showed that this was a mixture of two products in similar amounts which proved not easily separable. By ^1H NMR (CD_2Cl_2) the first was identified as

[W(CO)$_3$(MeSSMe)(η-C$_5$H$_5$)]BF$_4$, a known species [2]: δ 3.09s (WSCH_3SCH_3), 3.09s (WSCH$_3$SCH_3), 6.10s (C$_5$$H_5$). The second is the compound [W(CO)$_2$(SMe$_2$) (η-C$_5$H$_5$)]BF$_4$. A pure sample of this yellow-brown crystalline compound was prepared, for the purpose of comparison, by the reaction of W(SMe)(CO)$_3$(η-C$_5$H$_5$) and [Me$_3$O]BF$_4$ in CH$_2$Cl$_2$ (1 h): m.p. 140–145°C dec. IR: ν(CO) 2065s, 2000sh, 1978s cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$): δ 2.75 (S(CH_3)$_2$). 6.26s (C$_5$$H_5$).

Reaction of [Me$_2$SSMe]BF$_4$ and Mn$_2$(CO)$_{10}$

The reaction of these species (1/1 ratio) and subsequent workup as described above produced a 25% isolated yield of a light yellow crystalline product, [Mn(CO)$_5$(Me$_2$S)]BF$_4$, m.p. 163°C dec.; there was 49% recovery of Mn$_2$(CO)$_{10}$. A 2/1 reaction yielded [Mn(CO)$_5$(Me$_2$S)]BF$_4$ (48%) as the only isolable product. (Both yields quoted are on the basis of total manganese in the starting material.)

Anal. Found: C, 24.34; H, 1.75. C$_7$H$_6$BF$_4$MnO$_5$S calcd.: C, 24.44; H, 1.76%. IR: ν(CO) 2160m, 2065vs, 2020w cm^{-1}; ^{1}H NMR: δ 2.81s (S(CH_3)$_2$).

Reaction of [Me$_2$SSMe]BF$_4$ and Re$_2$(CO)$_{10}$

No reaction occurred when these reagents were mixed in CH$_2$Cl$_2$ and stirred for 2 days at room temperature.

Reaction of [Me$_2$SSMe]BF$_4$ and Mn$_2$(CO)$_8$(PPh$_3$)$_2$

The reaction of these reagents in a 1/1 ratio, as described above, yielded [Mn(CO)$_4$(SMe$_3$)(PPh$_3$)]BF$_4$ (m.p. 148°C dec.), as the only isolable product. The yield (based on the total quantity of manganese in the starting material) was 43%. A 2/1 reaction was performed as follows. First a 1/1 ratio of reactants was stirred for 30 min. An IR spectrum showed that a large amount of Mn$_2$(CO)$_8$(PPh$_3$)$_2$ remained. When a second equivalent of [Me$_2$SSMe]BF$_4$ was added, there was an immediate color change from orange to yellow and no Mn$_2$(CO)$_8$(PPh$_3$)$_2$ was detected by infrared spectroscopy. Evaporation of solvent and recrystallization of the residue using CH$_2$Cl$_2$ and ethyl acetate gave the solid yellow product, (yield 76% based on total manganese available).

Anal. Found: C, 49.78; H, 3.74. C$_{24}$H$_{21}$BF$_4$MnO$_4$PS calcd.: C, 49.85; H, 3.66%. IR: ν(CO) 2100w, 2000s cm^{-1}; ^{1}H NMR: δ 2.47s (S(CH_3)$_2$); 7.70m (C$_6$$H_5$).

Reaction of [Me$_2$SSMe]BF$_4$ and PPN[Mn(CO)$_4$(PPh$_3$)]

A slurry of PPN[Mn(CO)$_4$(PPh$_3$)] (0.406 g, 0.420 mmol) in 20 ml CH$_2$Cl$_2$ at −78°C was mixed with a slurry of [Me$_2$SSMe]BF$_4$ (0.164 g, 0.839 mmol) in 20 ml CH$_2$Cl$_2$ and stirred while the solution warmed to room temperature. The initially red-orange solution rapidly turned yellow-orange. The solution was evaporated overnight under a brisk flow of N$_2$. The residue was crystallized from CH$_2$Cl$_2$/ethyl acetate to give a white crystalline solid ([PPN]BF$_4$). Further reduction in volume and layering with additional ethyl acetate gave a light yellow solid, 0.208 g, identified by IR, NMR, and melting point as [Mn(CO)$_4$(SMe$_2$)(PPh$_3$)]BF$_4$, 86% yield based on manganese.

Reaction of [Me$_2$SSMe]BF$_4$ and Mn$_2$(CO)$_9$(PPh$_3$)

Reaction of these starting materials in a 2/1 ratio produced only [Mn(CO)$_4$(Me$_2$S)(PPh$_3$)]BF$_4$. The yield of this species was 43% based on total manganese (86% based on the availability of Mn(CO)$_4$(PPh$_3$)).

Reaction of [Me₂SSMe]BF₄ and Mn₂(CO)₈(μ-dppm)

A similar procedure was used, yielding a bright yellow crystalline product [{Mn(CO)$_4$(SMe$_2$)}$_2$μ-dppm](BF$_4$)$_2$, m.p. 152–155°C, in 34% yield.

Anal. Found: C, 42.67; H, 3.43. C$_{37}$H$_{34}$B$_2$F$_8$Mn$_2$P$_2$O$_8$S$_2$ calcd.: C, 43.72; H, 3.37%. IR: ν(CO) 2100w, 2015s cm^{-1}. ^{1}H NMR: δ 2.52s (S(CH$_3$)$_2$), 7.45–7.73m (C$_6$H$_5$).

Reaction of [Me₂SSMe]BF₄ and Re₂(CO)₈(PPh₃)₂

The reaction of these reagents in a 1/1 ratio, as described, gave a 18% yield of the white crystalline solid [Re(CO)$_4$(Me$_2$S)(PPh$_3$)]BF$_4$, m.p. 179–183°C dec.

Anal. Found: C, 40.43; H, 3.13%. C$_{24}$H$_{21}$BF$_4$ReO$_4$PS calcd.: C, 40.63; H, 2.98%. IR: ν(CO) at 2120w, 2000s cm^{-1}. ^{1}H NMR: δ 2.77s (S(CH$_3$)$_2$, 7.69m (C$_6$H$_5$).

Reaction of [Me₂SSMe]BF₄ and (CO)₅MnFe(CO)₂(η-C₅H₅)

A 2/1 reaction of these species was carried out as described above. An aliquot of the reaction solution was separated and the solvent evaporated under a stream of N$_2$. By ^{1}H NMR, intensities for the products [Mn(CO)$_5$(Me$_2$S)]BF$_4$ (δ 2.81s (S(CH$_3$)$_2$), [Fe(CO)$_2$(MeSSMe)(η-C$_5$H$_5$)]BF$_4$ (δ 2.95s (FeSCH$_3$SCH$_3$), 2.79s (FeSCH$_3$SCH$_3$), 5.76s (C$_5$H$_5$) [2]), and [Fe(CO)$_2$(Me$_2$S)(η-C$_5$H$_5$)]BF$_4$ (δ 2.61s (S(CH$_3$)$_2$, 5.77s (C$_5$H$_5$) [14]) were found to be present in relative amounts of 38, 33, and 28%, respectively. This mixture proved not to be amenable to separation. Attempted recrystallizations yielded mixtures of these compounds with varying compositions.

Discussion

The presumed analogy between the electrophiles H$^+$ and MeS$^+$ led us into this project; we hoped that this analogy would predict the behavior of [Me$_2$SSMe]BF$_4$ in reactions with organometallic species. At the same time, species which are H$^+$ donors are also known to be oxidizing agents (H$_2$ being evolved) so MeS$^+$ donors might also react in this way with certain organometallic precursors, presumably, yielding MeSSMe. Our general goal in this work was to develop useful synthetic methodology for organosulfur complexes which includes defining limitations for prescribed reagents such as [Me$_2$SSMe]BF$_4$. We also hoped to gain information on mechanisms of reactions under investigation.

The first reports on protonation of metal–metal bonds in bimetallic complexes dates back about 25 years [4] and many additional examples have been reported since that date. It seemed logical to determine whether an SMe$^+$ unit could also be interposed into the metal–metal bond in various bimetallic complexes. The product of such a reaction would contain the thiolate group bridging two metals, probably its most common mode of bonding in organometallic complexes.
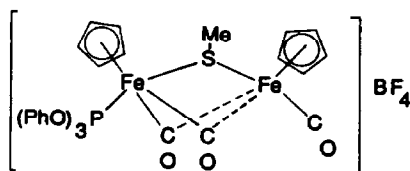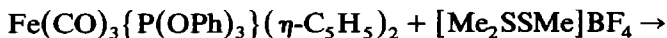
It had previously been established that this analogy between H$^+$ and MeS$^+$ holds for reactions of Fe(μ-SR)$_2$(CO)$_4$(L)$_2$ with [Me$_2$SSMe]BF$_4$ [5]. The products of these reactions have the formula [Fe$_2$(μ-SR)$_2$(μ-SMe)(CO)$_4$(L)$_2$]BF$_4$, analogous to the known species [Fe$_2$(μ-SR)$_2$(μ-H)(CO)$_4$(L)$_2$]X [6]. We have also determined that the reaction between [Fe(CO)$_2$(η-C$_5$H$_5$)]$_2$ and [Me$_2$SSMe]BF$_4$ yields [Fe$_2$(μ-SMe)(CO)$_4$(η-C$_5$H$_5$)$_2$]BF$_4$; this work will be reported elsewhere [17].

In contrast, the reactions reported here do not give products of insertion of MeS^+ into metal–metal bonds. One electron oxidation of the organometallic precursor by $[Me_2SSMe]BF_4$ is observed in certain predictable instances. In addition we have turned up a series of reactions which give metal Me_2S complexes. The likelihood that these reactions are mechanistically related to reactions involving MeS^+ insertion into the metal–metal bond is discussed below.
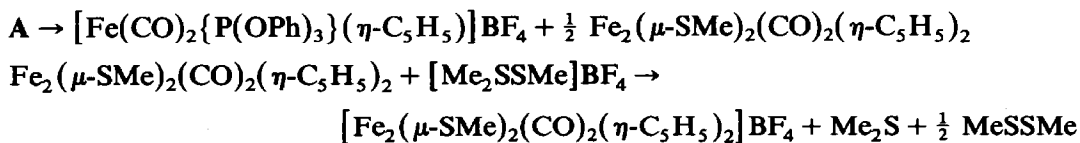
Reactions in which $[Me_2SSMe]BF_4$ serves as a one electron oxidant were encountered with derivatives of $[Fe(CO)_2(\eta-C_5H_5)]_2$ in which one or more carbonyl groups had been replaced by phosphines. Dimethylthiomethylsulfonium tetrafluoroborate cleanly oxidizes $Fe_2(CO)_2(\mu-dppm)(\eta-C_5H_5)_2$, a good yield of the paramagnetic red product $[Fe_2(CO)_2(\mu-dppm)(\eta-C_5H_5)_2]BF_4$ being obtained. The organic product from oxidation, MeSSMe, was detected in significant amounts by ^1H NMR on the reaction mixture. Oxidation of the organometallic precursor by silver ion is known [8] and this cation had been isolated previously as SbF_6^- and BPh_4^- salts. Our result is, as far as we can determine, the first reported instance in which $[Me_2SSMe]BF_4$ has been found to serve as a one-electron oxidant.

The reaction of red $Fe_2(CO)_3\{P(OPh)_3\}(\eta-C_5H_5)_2$ with $[Me_2SSMe]BF_4$ gave unexpected results. When these reagents were combined in a 1/1 ratio in CH_2Cl_2 an immediate reaction was evident, but an infrared spectrum indicated that the starting organometallic complex had not been completely consumed. Along with starting material peaks, there were new $\nu(CO)$ values at approximately 2080, 2040, and 1990 cm^{-1}. A second equivalent of $[Me_2SSMe]BF_4$ was required to completely consume the starting material, leaving a solution with only the three new $\nu(CO)$ absorptions. At this point, the solution was green in color. Two products, both previously known, were identified. One was the species $[Fe(CO)_2\{P(OPh)_3\}(\eta-C_5H_5)]BF_4$, a pale yellow compound ($\nu(CO)$ at 2078s, 2035s cm^{-1}). The second was identified as $[Fe_2(\mu-SMe)_2(CO)_2(\eta-C_5H_5)_2]BF_4$ ($\nu(CO)$ at 1992 cm^{-1}), a green paramagnetic compound [15] known to be formed by one-electron oxidation of $Fe_2(\mu-SMe)_2(CO)_2(\eta-C_5H_5)_2$ ($\nu(CO)$ at 1947 cm^{-1}) with a variety of oxidizing agents. Independently, we verified that $[Me_2SSMe]BF_4$ will cause this oxidation.

It is postulated that addition of MeS^+ to the metal–metal bond in $Fe_2(CO)_3\{P(OPh)_3\}(\eta-C_5H_5)_2$ yields an intermediate species which is unstable with respect to an unsymmetrical cleavage, giving $[Fe(CO)_2\{P(OPh)_3\}(\eta-C_5H_5)]BF_4$ and presumably $Fe(SMe)(CO)(\eta-C_5H_5)$ which dimerizes to form $Fe_2(\mu-SMe)_2(CO)_2(\eta-C_5H_5)_2$. The latter is oxidized immediately, giving the second product while consuming the additional $[Me_2SSMe]BF_4$. This second reaction must be fast relative to the preceding steps to allow starting material still to be present in a 1/1 reaction; also it is noted that $Fe_2(\mu-SMe)_2(CO)_2(\eta-C_5H_5)_2$ was not detected when this reactions was monitored by IR.

$$Fe(CO)_3\{P(OPh)_3\}(\eta-C_5H_5)_2 + [Me_2SSMe]BF_4 \rightarrow$$

A (postulated)

$$\mathbf{A} \rightarrow \left[Fe(CO)_2\{P(OPh)_3\}(\eta\text{-}C_5H_5)\right]BF_4 + \tfrac{1}{2}\,Fe_2(\mu\text{-}SMe)_2(CO)_2(\eta\text{-}C_5H_5)_2$$

$$Fe_2(\mu\text{-}SMe)_2(CO)_2(\eta\text{-}C_5H_5)_2 + [Me_2SSMe]BF_4 \rightarrow$$

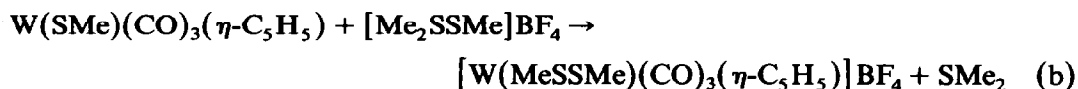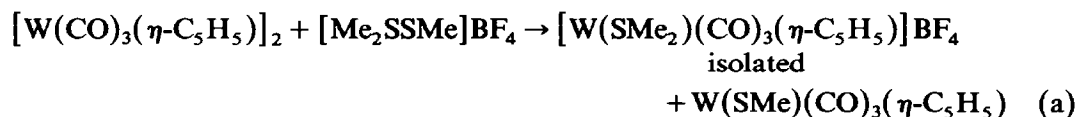$$\left[Fe_2(\mu\text{-}SMe)_2(CO)_2(\eta\text{-}C_5H_5)_2\right]BF_4 + Me_2S + \tfrac{1}{2}\,MeSSMe$$

The initial step in the reaction, the addition of an electrophile (MeS^+) to the electron pair available in the metal–metal bond, has precedent, as noted earlier. Since $P(OPh)_3$ is a better donor and somewhat poorer π-acceptor than CO, one can envision a somewhat polar intermediate with the positive charge mostly on the iron containing the phosphite ligand. To compensate for this, the two bridging carbonyl groups would be skewed towards this metal (becoming semibridging); this feature sets up the intermediate for the proposed asymmetric cleavage to follow. Unsymmetrical cleavage would appear to given the most thermodynamically stable products.

It is of interest that the products of halogen cleavage of $Fe_2(CO)_3\{P(OPh)_3\}(\eta\text{-}C_5H_5)_2$ include $[Fe(CO)_2\{P(OPh)_3\}(\eta\text{-}C_5H_5)]^+$ when the reaction is run in benzene [18].

In contrast to the examples above are a series of reactions with the metal carbonyl precursors $[M(CO)_3(\eta\text{-}C_5H_5)]_2$ (M = Mo, W), $Mn_2(CO)_{10}$ and $M_2(CO)_8$-$(PPh_3)_2$ (M = Mn, Re) and $Mn_2(CO)_9(PPh_3)$ and $Mn_2(CO)_8(\mu\text{-}dppm)$. All of these reactions give isolable products having Me_2S ligands. This type of reaction is illustrated by the reaction of $[W(CO)_3(\eta\text{-}C_5H_5)]_2$ with $[Me_2SSMe]BF_4$. Two equivalents of $[Me_2SSMe]BF_4$ are required to consume the $[W(CO)_3(\eta\text{-}C_5H_5)]_2$ and a near quantitative conversion to two organometallic species, $[W(CO)_2(SMe_2)(\eta\text{-}C_5H_5)]BF_4$ and $[W(CO)_3(MeSSMe)(\eta\text{-}C_5H_5)]BF_4$ occurs. These products are readily identified from their ^1H NMR spectra. Unfortunately, they have similar solubility characteristics so are not easily separable. Both products are known, the latter being characterized in earlier work in our group [2]. In addition, we prepared a pure sample of the former by methylation of $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$, to obtain precise values for the chemical shifts of the protons in this species for comparison.
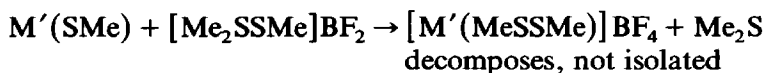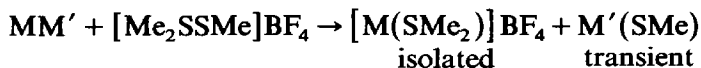
We believe that this reaction occurs with initial cleavage of the metal–metal bond to give $[W(SMe_2)(CO)_3(\eta\text{-}C_5H_5)]BF_4$ and $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$. The latter species then reacts rapidly with further $[Me_2SSMe]BF_4$ to give the complex having a dimethyl disulfide ligand, as given below.

$$\left[W(CO)_3(\eta\text{-}C_5H_5)\right]_2 + [Me_2SSMe]BF_4 \rightarrow \left[W(SMe_2)(CO)_3(\eta\text{-}C_5H_5)\right]BF_4$$
$$\text{isolated}$$
$$+ W(SMe)(CO)_3(\eta\text{-}C_5H_5) \quad (a)$$

$$W(SMe)(CO)_3(\eta\text{-}C_5H_5) + [Me_2SSMe]BF_4 \rightarrow$$
$$\left[W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)\right]BF_4 + SMe_2 \quad (b)$$

The first step of the reaction might be viewed as a simple cleavage of dimer by an unsymmetrical reagent $[XY]BF_4$ (X = SMe_2, Y = SMe). We do not presume to know exactly how this occurs, but reflect that the reaction is probably similar to the cleavage of the dimer by halogens. There is only limited mechanistic information for reactions of this type. Both radical and polar cleavage (via attack by X^+) mechanisms have been suggested, the choice depending on conditions.

Note that initial reaction between $[Me_2SSMe]BF_4$ and $Fe_2(CO)_3\{P(OPh)_3\}(\eta\text{-}C_5H_5)_2$ corresponds to the general idea of an initial X^+ attack on the complex.

Results on the reaction of [Me$_2$SSMe]BF$_4$ with [W(CO)$_3$(η-C$_5$H$_5$)]$_2$ guide interpretation of results with the other dinuclear species if one includes the fact that instability of MeSSMe complexes of Mo, Mn, and Re has been established in earlier work [1]. A single organometallic species with a Me$_2$S ligand, is isolated from these reactions in amounts appropriate if one assumes that half of the metal is available for product formation and half is lost through decomposition of the second product.

$$MM' + [Me_2SSMe]BF_4 \rightarrow \underset{\text{isolated}}{[M(SMe_2)]BF_4} + \underset{\text{transient}}{M'(SMe)}$$

$$M'(SMe) + [Me_2SSMe]BF_2 \rightarrow \underset{\text{decomposes, not isolated}}{[M'(MeSSMe)]BF_4} + Me_2S$$

(M = M' = Mo(CO)$_3$(η-C$_5$H$_5$), Mn(CO)$_5$, Mn(CO)$_4$(PPh$_3$), Re(CO)$_4$(PPh$_3$); M = Mn(CO)$_4$(PPh$_3$); M' = Mn(CO)$_5$)

Two equivalents of [Me$_2$SSMe]BF$_4$ are required to consume the starting material, and the Me$_2$S complex is usually obtained in amounts approaching one-half of the total metal available. The isolated organometallic complexes ([Mo(Me$_2$S)(CO)$_3$(η-C$_5$H$_5$)]BF$_4$, [Mn(CO)$_5$(Me$_2$S)]BF$_4$, trans-[M(CO)$_4$(PPh$_3$)(Me$_2$S)]BF$_4$ (M = Mn, Re)) have properties expected for their formulation.

The reaction of Mn$_2$(CO)$_9$(PPh$_3$) and [Me$_2$SSMe]BF$_4$ occurred in an analogous fashion with trans-[Mn(CO)$_4$(Me$_2$S)(PPh$_3$)]BF$_4$ being the only product. The asymmetric starting material undergoes preferential cleavage to give this product rather than [Mn(CO)$_5$(Me$_2$S)]BF$_4$. This is predictable based on polarity of the two reagents. Dirhenium decacarbonyl was found not to react with [Me$_2$SSMe]BF$_4$ at room temperature over a 2 day period.

In the reaction of Mn$_2$(CO)$_8$(PPh$_3$)$_2$ and [Me$_2$SSMe]BF$_4$ a higher proportion of the metal ended up in the product, trans-[Mn(CO)$_4$(Me$_2$S)(PPh$_3$)]BF$_4$ (43% yield for a 1/1 reaction, 76% yield for a 2/1 reaction). One way in which consumption of each mole of [Me$_2$SSMe]BF$_4$ would produce yields approaching one mole of trans-[Mn(CO)$_4$(Me$_2$S)(PPh$_3$)]BF$_4$ is that decomposition of [Mn(CO)$_4$(MeSSMe)(PPh$_3$)]BF$_4$ (from the second reaction) in the presence of SMe$_2$ also gives the observed product. We have demonstrated this fact; PPN[Mn(CO)$_4$(PPh$_3$)] was shown to react with two equivalents of [Me$_2$SSMe]BF$_4$ to give trans-[Mn(CO)$_4$(Me$_2$S)(PPh$_3$)]BF$_4$ in high yield. The reaction presumably occurs by initial formation of Mn(CO)$_4$(SMe)(PPh$_3$) which further reacts to give [Mn(CO)$_4$(MeSSMe)(PPh$_3$)]BF$_4$; the Me$_2$S remaining in solution then displaces MeSSMe to give the observed product.

The final reaction described in this paper is between [Me$_2$SSMe]BF$_4$ and (CO)$_5$MnFe(CO)$_2$(η-C$_5$H$_5$). A 2/1 reaction should theoretically have two possible outcomes; formation of [Mn(CO)$_5$(Me$_2$S)]BF$_4$ and Fe(SMe)(CO)$_2$(η-C$_5$H$_5$) the latter reacting further with [Me$_2$SSMe]BF$_4$ to form (stable) [Fe(CO)$_2$(MeSSMe)(η-C$_5$H$_5$)]BF$_4$ [2], and formation of [Fe(CO)$_2$(Me$_2$S)(η-C$_5$H$_5$)]BF$_4$ and Mn(CO)$_5$SMe, the second product reacting further with [Me$_2$SSMe]BF$_4$ to form [Mn(CO)$_5$(MeSSMe)]BF$_4$ which decomposes [1]. A ^{1}H NMR spectrum of the product mixture shows approximately equal percentages of [Mn(CO)$_5$(SMe$_2$)]BF$_4$, [Fe(CO)$_2$(MeSSMe)(η-C$_5$H$_5$)]BF$_4$, and [Fe(CO)$_2$(Me$_2$S)(η-C$_5$H$_5$)]BF$_4$, 38, 33, and 28%, respectively. (In a separate experiment, a sample of [Fe(CO)$_2$(MeSSMe)(η-C$_5$H$_5$)]BF$_4$ (monitored by ^{1}H NMR) did not react with an excess of Me$_2$S to give [Fe(CO)$_2$(Me$_2$S)(η-C$_5$H$_5$)]BF$_4$

and MeSSMe.) The conclusion reached is that there is no preferred direction of cleavage of the bimetallic precursor; both directions of cleavage appear to have occurred to a similar extent.

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