Journal of Organometallic Chemistry, 424 (1992) 71–77
Elsevier Sequoia S.A., Lausanne
JOM 22257

Use of $[Me_2SSMe]BF_4$ to prepare thiolate complexes of iron and ruthenium

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(Received April 10, 1991)

Abstract

The complexes $[Fe(CO)_3(L)_2SMe]BF_4$ (L = PPh_2Me, $PPhMe_2$ $P(OMe)_3$), $[Fe(CO)_2\{P(OMe)_3\}_3$-$SMe]BF_4$, and $[Ru(CO)_3(PPh_3)_2SMe]BF_4$ were prepared by reactions of $[Me_2SSMe]BF_4$ and the appropriate neutral $M(CO)_{5-n}(L)_n$ precursor. Several other analogous reactions were unsuccessful; in those cases, decomposition involving phosphine loss and ligand redistribution occurred.

Introduction

Our research group has shown that $[Me_2SSMe]BF_4$ reacts with nucleophilic metal carbonyl complexes. For example [1]:

$$Na[CpW(CO)_3] + [Me_2SSMe]BF_4 \rightarrow CpW(CO)_3SMe + Me_2S + NaBF_4 \qquad (1)$$

In most instances this is a useful synthetic procedure for the metal thiolate. We have been able to define the limitations of this type of reaction relative to possible alternative reactions such as oxidation [2], and subsequent reactions of the product, including a further reaction to give metal complexes of organic disulfides [3].

Mechanistically, reactions of the type given in eq. 1 occur by nucleophilic attack at the SMe^+ group of the sulfur-containing reactant with displacement of Me_2S. This is a general type of chemical behavior for $[Me_2SSMe]BF_4$ [4].

Many metal carbonyl complexes besides the well known anionic carbonylmetallates exhibit nucleophilic behavior. Thus, extending the use of $[Me_2SSMe]BF_4$ to other systems seemed an attractive possibility and worth pursuing. In the work reported in this paper, we describe reactions of $[Me_2SSMe]BF_4$ with several compounds of the form $M(CO)_{5-n}(L)_n$ (M = Fe, Ru; L = PR_3, $P(OMe)_3$; $n = 2, 3$).

Experimental

The following materials were prepared according to published methods: $[Me_2SSMe]BF_4$ [5], $Fe(CO)_3(AsPh_3)_2$ [6], $Ru(CO)_3(PPh_3)_2$ [7]. The $Fe(CO)_3L_2$ compounds (L = PPh_3, PPh_2Me, $PPhMe_2$, $P(OMe)_3$) were prepared by photolysis of $Fe(CO)_5$ with excess ligand in diethyl ether followed by chromatography or recrystallization. Samples of $Fe(CO)_2[P(OMe)_3]_3$ were prepared by the method of Hieber and Muschi [8]. All reactions were carried out under dry nitrogen. Infrared spectra (CH_2Cl_2 solutions except as noted] were recorded on a Beckman Model 4230 spectrophotometer. ^1H NMR spectra (acetone-d_6 except as noted) were recorded on a Bruker WP-200 spectrometer. Melting points were performed on a Thomas-Hoover apparatus. Elemental analyses were performed by the Galbraith Laboratory, Knoxville, TN.

Preparation of $Fe(CO)_2(PPh_3)[P(OMe)_3]_2$

A solution of $Fe(CO)_3(PPh_3)I_2$ (3.28 g, 5.00 mmol) and $P(OMe)_3$ (1.2 mL, 1.2 g, 10 mmol) in 70 mL of THF was stirred for 75 min. The solution was transferred to another flask containing sodium amalgam (0.30 g, 13 mmol of Na, in 2 mL of Hg) and stirred until the solution turned yellow-orange. The solution was filtered, the solvent evaporated, and the residue dissolved in a minimum of CH_2Cl_2; elution from an alumina column with benzene gave a yellow solution. The solvent was evaporated, the residue dissolved in a minimum of diethyl ether, and the solution chilled to −78 °C. The resulting precipitate was filtered to give 0.658 g of light yellow solid, 21% yield, m.p. 108–113°C dec, identified as $Fe(CO)_2(PPh_3)[P(OMe)_3]_2$. Anal. Found: 622.0716. $C_{26}H_{33}FeO_8P_3$ calc.: 622.0729 (parent peak match obtained using Kratos MS-80 high resolution mass spectrometer). IR: ν(CO) 1920, 1857vs cm^{-1}. ^1H NMR: δ 7.72–7.34 (m, $P(C_6H_5)_3$), 3.44 (t, $P(OCH_3)_3$) ppm.

Reaction of $Fe(CO)_3(PPh_2Me)_2$ and $[Me_2SSMe]BF_4$

A solution of $Fe(CO)_3(PPh_2Me)_2$ (0.270 g, 0.500 mmol) in 30 mL of CH_2Cl_2 was treated with a slurry of $[Me_2SSMe]BF_4$ (0.098 g, 0.500 mmol) in 20 mL of CH_2Cl_2. The solution turned from the initial yellow color to orange-red. An IR spectrum recorded after 5 min showed no starting material. The solution was filtered and solvent evaporated *in vacuo*. The residue was recrystallized from CH_2Cl_2/hexane to give 0.283 g of bright red solid, m.p. 115–119 °C, identified as $[Fe(CO)_3(PPh_2Me)_2(SMe)]BF_4$. Anal. Found: C, 51.35; H, 4.18. $C_{30}H_{29}BF_4FeO_3P_2S \cdot 0.5\ CH_2Cl_2$ calc.: C, 51.12; H, 4.22%. IR: ν(CO) 2103s, 2040vs,br cm^{-1}. ^1H NMR: δ 8.05–7.55 (m, $P(C_6H_5)_2CH_3$), 2.69 (t, $P(C_6H_5)_2CH_3$), 0.89 (s, SCH_3) ppm. (The presence of solvent was verified by NMR.)

Reaction of $Fe(CO)_3(PPhMe_2)_2$ and $[Me_2SSMe]BF_4$

A 1:1 reaction was carried out using $Fe(CO)_3(PPhMe_2)_2$ as described above. A red-orange solid, $[Fe(CO)_3(PPhMe_2)_2(SMe)]BF_4$, was collected; this represents an 88% yield based on the starting compound, m.p. 110 °C dec. Anal. Found: C, 43.38; H, 4.60. $C_{20}H_{25}BF_4FeO_3P_2S$ calc.: C, 43.67; H, 4.58%. IR: ν(CO) 2105s, 2040vs,br cm^{-1}. ^1H NMR: δ 8.00–7.50 (m, $PC_6H_5(CH_3)_2$, 2.31 (t, $PC_6H_5(CH_3)_2$, J(P–Me) 4.6 Hz), 1.18 (s, SCH_3).

Reaction of $Fe(CO)_3[P(OMe)_3]_2$ and $[Me_2SSMe]BF_4$

A 1:1 reaction was carried out as described above, with the initial pale yellow solution immediately turning orange. Work up gave a yellow-orange solid, 27% yield, identified as $[Fe(CO)_3\{P(OMe)_3\}_2(SMe)]BF_4$, m.p. 184–189°C. Anal. Found:

C, 22.20; H, 4.64. $C_{10}H_{21}BF_4FeO_9P_2S$ calc.: C, 23.01; H, 4.06%. IR: ν(CO) 2060s, 2040vs,br cm^{-1}. ^1H NMR (CD_2Cl_2): δ 3.90 (t, $P(OCH_3)_3$), 1.91 (5 lines) (SCH_3).

Reaction of $Fe(CO)_2[P(OMe)_3]_3$ and $[Me_2SSMe]BF_4$

A 1:1 reaction gave a bright yellow solution which showed two new infrared absorptions at 2055s, 2020s cm^{-1}. The bright yellow solid obtained from recrystallization was identified as $[Fe(CO)_2\{P(OMe)_3\}_3(SMe)]BF_4$, m.p. 165–167°C. Anal. Found: C, 21.08; H, 4.70. $C_{12}H_{30}BF_4FeO_{11}P_3S$ calc.: C, 23.32; H, 4.89%. IR: ν(CO) 2117vw, 2055vs, 2030vw cm^{-1}. ^1H NMR: δ 4.26 (t), 4.19 (d, $P(OCH_3)_3$), 2.84 (5 lines) (SCH_3), of the correct integration (27:3, phosphite/SMe), respectively.

Reaction of $Ru(CO)_3(PPh_3)_2$ and $[Me_2SSMe)BF_4$

A 1:1 reaction was carried out as described above. The solution turned from bright yellow to deep yellow. A bright lemon-yellow solid, identified as $[Ru(CO)_3(PPh_3)_2(SMe)]BF_4$, was isolated on work up, in 66% yield; m.p. 193–195°C dec. Anal. Found: C, 56.67; H, 4.25. $C_{40}H_{33}BF_4O_3P_2RuS$ calc.: C, 56.95; H, 3.94%. IR: ν(CO) 2130w, 2067s, 2058s,sh cm^{-1}. ^1H NMR: δ 7.90–7.55 (m, $P(C_6H_5)_3$), 1.06 (s, SCH_3).

Details on several similar reactions that failed to give the expected organometallic thiolate complex are provided below. Neither $Fe(CO)_5$ nor several monosubstituted derivatives $Fe(CO)_4(L)$ (L = PPh_3, PPh_2Me) were found to react with $[Me_2SSMe]BF_4$.

Reaction of $Fe(CO)_2(PPh_3)[P(OMe)_3]_2$ and $[Me_2SSMe]BF_4$

A solution of $Fe(CO)_2(PPh_3)[P(OMe)_3]_2$ (0.658 g, 1.06 mmol) in 30 mL of CH_2Cl_2 was treated with a slurry of $[Me_2SSMe]BF_4$ (0.207 g, 1.06 mmol) in 30 mL of CH_2Cl_2. The solution turned from deep yellow to orange-yellow to red-orange. An IR spectrum showed new peaks at 2060s, 2035sh, 2000vs, 1975s, and 1915sh cm^{-1} as well as very large peaks due to starting material (at 1920 and 1857 cm^{-1}). After 15 min, the IR pattern did not change, so another equivalent of $[Me_2SSMe]BF_4$ (0.207 g, 1.06 mmol) in 20 mL of CH_2Cl_2 was added. The IR spectrum now showed a different pattern, 2060vs, 2040s, 2020s cm^{-1}, which also continued to change with time. No starting material remained at this time. The solution was filtered and the solvent evaporated. An IR spectrum of the dark yellow residue showed two bands at 2061s, 2035vs,br cm^{-1}; these values correspond with those for $[Fe(CO)_3\{P(OMe)_3\}_2SMe]BF_4$. Also present was the compound $[MeSPPh_3]BF_4$. This was identified by comparison of its NMR data with data on a known sample of $[MeSPPh_3]BF_4$, prepared from equimolar amounts of PPh_3 and $[Me_2SSMe]BF_4$ in CH_2Cl_2. (^1H NMR: δ 8.07–7.83 (m, $P(C_6H_5)_3$), 2.61 (d, SCH_3, J(P–Me) 15 Hz) ppm).

Reaction of $Fe(CO)_3(PPh_3)_2$ and $[Me_2SSMe]BF_4$

A solution of $Fe(CO)_3(PPh_3)_2$ (0.664 g, 1.00 mmol) in 40 mL of CH_2Cl_2 was treated with a slurry of $[Me_2SSMe]BF_4$ (0.196 g, 1.00 mmol) in 30 mL of CH_2Cl_2. Upon addition, the solution turned from bright yellow to deep red. An IR spectrum taken after 2 min reaction time showed new peaks at 2100w, 2043s,br, 2000s, 1980sh, and 1940 cm^{-1} along with the 1881 cm^{-1} of the starting material.

Subsequent spectra recorded after 20 and 30 min reaction time were essentially identical. A second equivalent of $[Me_2SSMe]BF_4$ was added (20 mL of CH_2Cl_2). An IR spectrum showed no more starting material at that point; peaks present were 2010m, 2052s, 2000s,br, 1978s, 1940vs,br cm^{-1}. The solution was filtered, reduced in volume, and layered with ethyl acetate to precipitate a white solid, 0.402 g, identified as $[Ph_3PSMe]BF_4$ by its ^1H NMR spectrum.

In another experiment using a 2:1 ratio, the neutral products were separated and identified. The reaction solution was chromatographed on alumina/benzene to elute a dark red band. The solvent was evaporated, the residue dissolved in CH_2Cl_2, and chromatographed on alumina with 10% CH_2Cl_2 in Skelly B. A yellow band was collected, the solvent removal by evaporation, and the solid residue recrystallized, giving $Fe(CO)_4PPh_3$ (31% yield based on iron; ν(CO) at 2059, 1978, 1940 cm^{-1}). A small orange band eluted with CH_2Cl_2. The component of this band was identified as $Fe_2(\mu\text{-}SMe)_2(CO)_5PPh_3$ by comparison of its IR spectrum with that of the same compound made from $Fe_2(\mu\text{-}SMe)_2(CO)_6$ and PPh_3.

An additional experiment was performed at −78°C. A slurry of $Fe(CO)_3(PPh_3)_2$ (0.664 g, 1.00 mmol) in 30 mL of CH_2Cl_2 at −78°C was treated with a slurry of $[Me_2SSMe]BF_4$ (0.196 g, 1.00 mmol) by slow incremental additions. The solution was allowed to warm up slightly to help dissolve the iron reagent. After 15 min, an IR spectrum showed new bands at 2040vs (weak shoulder at 2045) and 2000 cm^{-1} as well as unreacted starting material. Another equivalent of $[Me_2SSMe]BF_4$ was added. No starting material remained but 2040vs, 2000m cm^{-1} bands were still present. The 2000 cm^{-1} absorption could indicate the presence of a 17-electron cation $[Fe(CO)_3(PPh_3)_2]^+$ although we actually doubt this (see Discussion). Still keeping the solution at −78°C, the solvent was partially evaporated by flushing with nitrogen. Ethyl acetate was then added, producing a mixture of a red-purple and white solid. An infrared spectrum of the solid showed ν(CO) 2095w, 2060sh, 2040vs cm^{-1}. The sample decomposed rapidly at room temperature. At room temperature ^1H NMR showed that the only methyl signal was that of $[Ph_3PSMe]BF_4$ (characteristic doublet at δ 2.56 (SCH_3, J(P–SMe) = 15.0 Hz), 7.70–8.10 (m, C_6H_5)).

Reaction of $Fe(CO)_3(AsPh_3)_2$ and $[Me_2SSMe]BF_4$

A similar reaction was attempted between $Fe(CO)_3(AsPh_3)_2$ and $[Me_2SSMe]BF_4$. Infrared spectra indicated conversion to $Fe(CO)_4(AsPh_3)$ ν(CO) at 2052, 1979, and 1945 cm^{-1}) within 20 min.

Reduction of $[Fe(CO)_3(PPh_2Me)_2(SMe)]BF_4$ by Na/Hg

A THF slurry of $Fe(CO)_3(PPh_2Me)_2(SMe)]BF_4$ (0.208 g, 0.31 mmol) was added to a cooled sodium amalgam made from Na (0.03 g, 1.3 mmol) in about 1 mL of Hg. The red color quickly faded as a white-gray precipitate formed. The solution was filtered, the solvent evaporated, and the residue recrystallized from CH_2Cl_2/pentane to give a yellow crystalline solid, 0.107 g, identified by its infrared spectrum to be $Fe(CO)_3(PPh_2Me)_2$, 64% yield.

Discussion

The weak nucleophilic character of iron pentacarbonyl is known based on its protonation in strong acid [9] and by the formation of $[FeX(CO)_5]^+$ in reactions with halogens [10,11]. It seemed unlikely that $Fe(CO)_5$ was a strong enough nucleophile to react with $[Me_2SSMe]BF_4$, as does its isoelectronic analogue $[Mn(CO)_5]^-$ [1]; indeed, this was verified in this study.

By substituting good donor ligands for CO, the nucleophilicity of a metal center can be enhanced. This fact is at least qualitatively evident in protonation [9,12] and halogenation studies on $M(CO)_{5-n}(L)_n$ species (M = Fe, Ru, Os, L = phosphines) [13,14]; moreover, it is in keeping with predictions based on the donor-acceptor characteristics of these non-carbonyl ligands.

Thus, we carried out reactions between $[Me_2SSMe]BF_4$ and several phosphine and phosphite disubstituted iron and ruthenium carbonyl species and two trisubstituted species. Successful reactions are portrayed below (eqs. 2 and 3):

$$Fe(CO)_3(L)_2 + [Me_2SSMe]BF_4 \rightarrow [Fe(CO)_3(L)_2SMe]BF_4 + Me_2S \qquad (2)$$

$(L = PPh_2Me, PPhMe_2, P(OMe)_3$; also $Ru(CO)_3(PPh_3)_2)$;

$$Fe(CO)_2[P(OMe)_3]_3 + [Me_2SSMe]BF_4 \rightarrow [Fe(CO)_2\{P(OMe)_3\}_3SMe]BF_4 + Me_2S \qquad (3)$$

These reactions, run using CH_2Cl_2 as solvent, occurred within minutes as noted by a definitive color change. The progress was also monitored by recording infrared spectra on aliquots of the reaction mixture. The appearance of new $\nu(CO)$ absorptions at higher frequency and the decrease in intensity of $\nu(CO)$ absorptions for the starting material were easily followed and gave clear evidence of a completed reaction. Generally, good yields of product were obtained by evaporation of the solvent followed by recrystallization of the residue.

While one might expect this to be a general reaction, several notable exceptions were encountered. Monosubstituted iron carbonyls, and $Fe(CO)_5$ itself, are unreactive toward $[Me_2SSMe]BF_4$; presumably this reflects their low nucleophilicity. The reaction of $Fe(CO)_3(PPh_3)_2$, in contrast to its ruthenium analog, gave no isolable adduct upon reaction with $[Me_2SSMe]BF_4$. Two equivalents of $[Me_2SSMe]BF_4$ were required to consume all the starting material and the reaction gave the organometallic species $Fe(CO)_4(PPh_3)$ along with $[PPh_3SMe]BF_4$ as isolable products. A similar result occurs with $Fe(CO)_3(AsPh_3)_2$. The reaction of $Fe(CO)_2[P(OMe)_3]_2(PPh_3)$ also required two equivalents of $[Me_2SSMe]BF_4$ and produced $[Fe(CO)_3\{P(OMe)_3\}_2SMe]BF_4$ along with $[PPh_3SMe]BF_4$. The dissociation of a triphenylphosphine ligand and its further reaction with $[Me_2SSMe]BF_4$ appears to be the common denominator in these results. Also, the organometallic products from both reactions require that some decomposition occurs so that CO could be scavenged into the eventual organometallic species.

At this time we cannot definitely establish a mechanism for these reactions. One possible explanation for these results is that the metal complex is initially oxidized to a 17 electron complex that then decomposes. The $[Me_2SSMe]BF_4$ can act as an oxidizing agent [2], and if oxidation did occur, the products expected are the ones actually isolated in these experiments. Unstable $[Fe(CO)_3(PR_3)_2]^+$ [15] is known to degrade in solution to give $Fe(CO)_4(PR_3)$ and the phosphine released would then consume $[Me_2SSMe]BF_4$ to form $[R_3PSMe]BF_4$ [15]. This mechanism explains the need for more than one equivalent of the sulfur reagent; there is one equivalent for oxidation, one to react with the phosphine. The argument against this mechanism is that complexes with phosphines other than triphenylphosphine would be expected to behave similarly; indeed since they are more easily oxidized [15], it would appear that this route should, if anything, be more likely for some of the other systems we looked at.

An alternative mechanism assuming that phosphine dissociation as the first step avoids the need for oxidation. Free phosphine would, of course, be scavenged by the sulfur reagent and the coordinatively unsaturated iron complex, would then be converted to $Fe(CO)_4(L)$, partial decomposition occurring to generate the needed CO and more phosphine. One equivalent of $[Me_2SSMe]BF_4$ would be consumed by the first phosphine (giving $[R_3PSMe]BF_4$) while additional sulfur reagent would be used to scavenge additional phosphine and oxidize any free metal. This mechanism avoids explaining the fact that other complexes do not react in this fashion. The tendency for a phosphine to dissociate is generally related to the ligand size rather than to its donor/acceptor properties [16]. Dissociation of triphenylphosphine, a large ligand, is a reasonable hypothesis. It is possible that dissociation is actually promoted by initial $[MeS]^+$ addition since crowding in a 6-coordinate intermediate would further encourage this process.

When $[SMe]^+$ addition reactions do occur a 1:1 stoichiometry is sufficient. In the cases when this did not occur, a greater than 1:1 ratio of $[Me_2SSMe]BF_4$ to complex is needed to consume all of the starting material. The presence of a significant amount of starting material after addition of one equivalent of $[Me_2SSMe]BF_4$ is a clear diagnostic for the failure to carry out the $[SMe]^+$ addition reaction.

Using the traditional oxidation state formalism, the observed $[SMe]^+$ addition to a metal complex involves an oxidation of the metal center. Thus the zero-valent iron center in $Fe(CO)_3(L)_2$ is converted to an iron(+2) center in $[Fe(CO)_3(L)_2SMe]^+$. Not surprisingly, then, a reducing agent (Na/Hg) can serve to effect the reverse reaction, namely,

$$[Fe(CO)_3(PPh_2Me)_2SMe]BF_4 + Na/Hg \rightarrow Fe(CO)_3(PPh_2Me)_2\ (+NaSMe + NaBF_4)$$

References

1 P.M. Treichel and P.C. Nakagaki, Organometallics, 5 (1986) 711.
2 P.M. Treichel and E.K. Rublein, J. Organomet. Chem., 359 (1989) 195.
3 P.M. Treichel, M.S. Schmidt, P.C. Nakagaki and E.K. Rublein, J. Organomet. Chem., 311 (1986) 193.
4 B.M. Trost and S.J. Martin, J. Am. Chem. Soc., 106 (1984) 4263, and cited references.
5 S.H. Smallcombe and M.C. Caserio, J. Am. Chem. Soc., 93 (1971) 5826.
6 A.F. Clifford and A.K. Mukherjee, Inorg. Synth., 8 (1965) 185.
7 N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Utley, Inorg. Synth., 15 (1974) 50.
8 W. Hieber and J. Muschi, Chem. Ber., 98 (1965) 3931.
9 A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, J. Chem. Soc., (1902) 3653.
10 Z. Iqbal and T.C. Waddington, J. Chem. Soc. A, (1968) 2958.

11 K. Noack, J. Organomet. Chem., 13 (1968) 411.
12 K.R. Laing and W.R. Roper, J. Chem. Soc. A, (1969) 1889.
13 J.P. Collman and W.R. Roper, J. Am. Chem. Soc., (1966) 3504.
14 H.B. Kuhnhen, J. Organomet. Chem., 105 (1976) 357.
15 P.K. Baker, N.G. Connelly, B.M.R. Jones, J.P. Maher and K.R. Somers, J. Chem. Soc., Dalton Trans., (1980) 579.
16 C.A. Tolman, J. Am. Chem. Soc., 92 (1970) 2956.