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Synthesis and structure of $[NEt_4]Fe(CO)_3(\mu\text{-}SPh)_2Mo(CO)_3(SPh)$: a heterodinuclear compound with bridging and terminal thiolate ligands

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Abstract

A new heterodinuclear compound, $[NEt_4]Fe(CO)_3(\mu\text{-}SPh)_2Mo(CO)_3(SPh)$, has been prepared from the reaction of $Fe(CO)_4Br_2$ with $[NEt_4]SPh$ and molybdenum carbonyl starting materials. The compound has been characterized spectroscopically and by X-ray diffraction.

Introduction

Synthesis of heteronuclear metal complexes has been a goal of much current research [1]. We have been interested in the synthesis of thiolate-bridged mixed-metal compounds and have explored the possibility of using metal carbonyl-thiolate starting materials in such preparations. Metal-thiolate reagents with cyclopentadienyl ligands rather than carbonyls have previously been found to act as precursors to polynuclear compounds [2].

We have previously established that bis-thiolate compounds of the type $[NEt_4]_2Mo(CO)_4(SR)_2$ can be isolated and used as starting materials for trinuclear compounds of the form $(CO)_4Mo(SR)_2M(SR)_2Mo(CO)_4^{2-/0}$ (M = Fe, Co; R = Ph, Bz) [3]. A dinuclear form is not obtained from these reactions regardless of the stoichiometry. In this paper we report on an alternate approach to forming such compounds based on the use of $Fe(CO)_4Br_2$. This easily obtained compound, which has not received much attention as an organometallic starting material, reacts with thiolates in an as yet poorly defined way. However, from this and appropriate molybdenum-containing reagents, a new iron–molybdenum–thiolate compound has been obtained.

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Results and discussion

Reaction of $Fe(CO)_4Br_2$ with $[NEt_4]SPh$ at low temperature followed by addition of $C_7H_8Mo(CO)_4$ or $Mo(CO)_3(CH_3CN)_3$ results in a complex reaction from which the compound $[NEt_4]Fe(CO)_3(\mu\text{-}SPh)_2Mo(CO)_3(SPh)$ is the isolated product, in 34% yield:

$$Fe(CO)_4Br_2 + 3[NEt_4]SPh + Mo(CO)_3(CH_3CN)_3 \rightarrow$$

$$[NEt_4]Fe(CO)_3(\mu\text{-}SPh)_2Mo(CO)_3(SPh) + 2[NEt_4]Br + 3CH_3CN$$

The formulation is supported by analytical and infrared data, and a structural determination has been carried out (Fig. 1). Selected bond distances and angles are summarized in Tables 1 and 2.

The bromide ions are displaced from iron in the course of the reaction, as is one of the carbonyl ligands. The anion has a "butterfly" shape with iron and molybdenum bridged by two thiolates. The Fe–Mo distance of 2.749 Å indicates a metal–metal bond. The metal–sulfur core departs considerably from planarity, as indicated by a torsional angle between the Fe–Mo–S planes of 94°. (The non-bonding S $\cdots$ S distance is 2.92 Å.) The structure thus more closely resembles that of $Fe_2(CO)_6(SMe)_2$ [4], which has a torsional angle of 103°, than it does $Mo_2(CO)_8(S\text{-}^tBu)_2$ [5], which has a planar core. The Fe–Mo distance is nearly the mean of the metal–metal bond lengths in these homodinuclear compounds.

The sulfur-bridged Fe–Mo bond, which is predicted for this compound on the basis of the 18-electron rule, is similar in length to the relatively few other such bonds that have been characterized by X-ray diffraction [6]. Their values fall in the range of 2.7–2.8 Å. In contrast, the compound $Cp_2Mo(\mu\text{-}S\text{-}^nBu)_2FeCl_2$ [7], where no metal–metal bond is required by electron counting, has an Fe–Mo distance of 3.66 Å. Similarly, in the compounds $[Mo(CO)_4(\mu\text{-}SPh)_2Fe(\mu\text{-}SPh)_2Mo(CO)_4]^{0/2-}$,

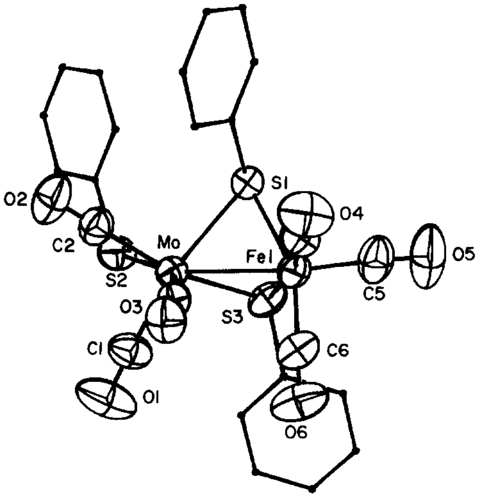

Fig. 1. ORTEP drawing for the anion of $[NEt_4]Fe(CO)_3(\mu\text{-}SPh)_2Mo(CO)_3(SPh)$ showing non-hydrogen atoms with 50% probability ellipsoids (phenyl carbons shown without ellipsoids).

Table 1

Selected bond lengths (Å) for $[\mathrm{NEt_4}]\mathrm{Fe(CO)_3}(\mu\text{-SPh})_2\mathrm{Mo(CO)_3(SPh)}$ (e.s.d.s in parentheses)

Mo-Fe(1)	2.7488(5)	Fe(1)-S(3)	2.293(1)
Mo-S(1)	2.5274(9)	Fe(1)-C(4)	1.774(4)
Mo-S(2)	2.5110(9)	Fe(1)-C(5)	1.791(5)
Mo-S(3)	2.5088(9)	Fe(1)-C(6)	1.780(4)
Mo-C(1)	1.946(4)	S(1)-C(11)	1.783(3)
Mo-C(2)	1.989(4)	S(2)-C(21)	1.764(4)
Mo-C(3)	1.950(4)	S(3)-C(31)	1.789(4)
Fe(1)-S(1)	2.3038(9)		

the average Fe–Mo distances are 2.77 and 3.40 Å for the oxidized and reduced forms, respectively, indicating the loss of the metal–metal bonds upon reduction [8]. (It is interesting to note that compounds such as $[\mathrm{NEt_4}]_2[(\mathrm{PhS})_2\mathrm{FeMoS_4}]$ [9] with an $\mathrm{FeMoS_2}$ core, where S is the simple sulfido ligand, have Fe–Mo distances close to the Fe–$(\mathrm{SR})_2$–Mo bonding range given above. The nature of the metal–metal interaction is not fully established but a bond is not usually proposed [10]. The shorter distances observed for this class of compounds are likely attributable to the tetrahedral geometry around the metal atoms.)

Rather unusually for metal carbonyl-thiolate compounds of this type, the anion has a terminal thiolate group that (when $\mathrm{C_7H_8Mo(CO)_4}$ is used) has replaced one of the carbonyls on molybdenum. This formulation would appear to be quite

Table 2

Selected bond angles (deg) for $[\mathrm{NEt_4}]\mathrm{Fe(CO)_3}(\mu\text{-SPh})_2\mathrm{Mo(CO)_3(SPh)}$ (e.s.d.s in parentheses)

Fe(1)-Mo-S(1)	51.57(2)	S(3)-Mo-C(3)	111.3(1)
Fe(1)-Mo-S(2)	138.77(3)	C(1)-Mo-C(2)	95.1(2)
Fe(1)-Mo-S(3)	51.46(2)	C(1)-Mo-C(3)	78.2(2)
Fe(1)-Mo-C(1)	117.1(1)	C(2)-Mo-C(3)	81.4(1)
Fe(1)-Mo-C(2)	129.5(1)	Mo-Fe(1)-S(1)	59.25(2)
Fe(1)-Mo-C(3)	69.6(1)	Mo-Fe(1)-S(3)	58.86(3)
S(1)-Mo-S(2)	101.93(3)	Mo-Fe(1)-C(4)	109.7(1)
S(1)-Mo-S(3)	69.89(3)	Mo-Fe(1)-C(5)	149.2(1)
S(1)-Mo-C(1)	166.9(1)	Mo-Fe(1)-C(6)	97.6(1)
S(1)-Mo-C(2)	97.8(1)	S(1)-Fe(1)-S(3)	77.75(3)
S(1)-Mo-C(3)	101.0(1)	S(1)-Fe(1)-C(4)	92.8(1)
S(2)-Mo-S(3)	92.48(3)	S(1)-Fe(1)-C(5)	103.2(1)
S(2)-Mo-C(1)	83.1(1)	S(1)-Fe(1)-C(6)	156.7(1)
S(2)-Mo-C(2)	78.9(1)	S(3)-Fe(1)-C(4)	167.8(1)
S(2)-Mo-C(3)	151.5(1)	S(3)-Fe(1)-C(5)	94.3(1)
S(3)-Mo-C(1)	98.0(1)	S(3)-Fe(1)-C(6)	92.8(1)
S(3)-Mo-C(2)	163.4(1)	C(4)-Fe(1)-C(5)	95.3(2)
C(4)-Fe(1)-C(6)	93.1(2)	Fe(1)-S(3)-C(31)	112.7(1)
C(5)-Fe(1)-C(6)	98.7(2)	Mo-C(1)-O(1)	174.9(4)
Mo-S(1)-Fe(1)	69.18(3)	Mo-C(2)-O(2)	179.0(3)
Mo-S(1)-C(11)	114.8(1)	Mo-C(3)-O(3)	170.1(3)
Fe(1)-S(1)-C(11)	114.7(1)	Fe(1)-C(4)-O(4)	177.9(4)
Mo-S(2)-C(21)	115.4(1)	Fe(1)-C(5)-O(5)	175.9(4)
Mo-S(3)-Fe(1)	69.68(3)	Fe(1)-C(6)-O(6)	178.5(4)
Mo-S(3)-C(31)	119.7(1)		

favorable since it occurs even when $C_7H_8Mo(CO)_4$ is used as the starting material; attempts to make a simpler iron carbonyl–molybdenum carbonyl–bis-thiolate bridged species have thus far been unsuccessful.

Cyclic voltammetric study revealed two irreversible redox processes: an oxidation at $+0.35$ V and a reduction at -1.30 V, referenced to an Ag/AgCl electrode in CH_3CN at -30°C. The potential required for oxidation is relatively high for a thiolate-rich anionic compound, perhaps contributing to the somewhat surprising stability of the compound in the solid state towards air, compared to some other similar compounds.

The conditions for the synthesis are mild. The terminal thiolate suggests the possibility of thermal rearrangements; for instance, intramolecular conversion to form a third bridge, with or without loss of CO. Heating to 60°C in CH_3CN produces a mixture of products whose identity is under investigation.

The synthetic method, employing $Fe(CO)_4Br_2$, is noteworthy, since it suggests the possibility of extension to other compounds. Attempts at simple reaction of $Fe(CO)_4Br_2$ with thiolate at room temperature result in a green, neutral, evidently not mononuclear iron–carbonyl–thiolate compound which appears pure but which has resisted complete characterization so far. The available data suggest a tentative formulation of $[Fe(CO)_2(SPh)_2]_x$. This compound does not react with $C_7H_8Mo(CO)_4$. Thus, the success of the reaction described in this report depends on a reaction between $Fe(CO)_4Br_2$ and SPh^- at reduced temperatures at which an unstable intermediate, perhaps $Fe(CO)_4(SPh)_2$, is formed which can then be trapped by addition of an easily substituted reagent such as the molybdenum compounds used here, to form a dinuclear complex. When the order of addition is reversed, that is, $Fe(CO)_4Br_2$ is added last after allowing $Mo(CO)_3(CH_3CN)_3$ and three equivalents of $[NEt_4]SPh$ to react at low temperature, the complex can be obtained but in reduced yield. Reaction of $[NEt_4]_2Mo(CO)_4(SPh)_2$ [3] and $Fe(CO)_4Br_2$ did not produce this complex, nor did it produce the simple bromide displacement product, $Mo(CO)_4(SPh)_2Fe(CO)_4$. Further work is planned to obtain more information about the mechanism of the reaction and to investigate extension of the use of $Fe(CO)_4Br_2$ to form other heteronuclear compounds.

Experimental

Reactions were conducted under an argon atmosphere using Schlenk line techniques, and solid compounds were stored under nitrogen. Acetonitrile was distilled over CaH_2 prior to use; other solvents were stored over molecular sieves. Infrared and visible spectra were obtained with Beckman IR-10 and Cary 5 spectrophotometers, respectively. Cyclic voltammetry was performed using a Bioanalytical Systems CV-1B potentiostat. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

$[NEt_4]Fe(CO)_3(\mu\text{-}SPh)_2Mo(CO)_3(SPh)$

$Fe(CO)_4Br_2$ [11] (2.0 g, 6.10 mmol) was dissolved in 20 mL of CH_3CN and cooled immediately to -25°C to -30°C. $[NEt_4]SPh$[3b] (4.36 g, 18.2 mmol) was added as a solid to this mixture and stirred for 10 min, during which time the color deepened to a dark red. To this mixture, 1.84 g (6.1 mmol) $Mo(CO)_3(CH_3CN)_3$ [12] was added as a solid and the resulting mixture was stirred for 1.5 h, during which time the temperature was allowed to rise to −15°C. The solvent was then evaporated at room temperature and 20 mL of $CHCl_3$ was added to extract the product. Filtration of this solution resulted in a slightly impure fraction of product which can be recrystallized from CH_3CN/CH_3OH to give 0.80 g. Hexane was added to the original filtrate to obtain a mass of impure solid upon cooling which was then collected by filtration and recrystallized twice from CH_3CN/CH_3OH to obtain 0.81 g of the same product. The combined yield was 34%. (Use of $C_7H_8Mo(CO)_4$ [13] and two equivalents of $[NEt_4]SPh$ required purification of the crude product by chromatography and resulted in a lower yield, but did provide the same product as the only isolable compound.) IR (as KBr pellet): $\nu(CO)$ 2040s, 1980sh, 1950sh, 1920sh, 1875s, 1830s cm^{-1}. VIS (CH_3CN): 485 nm (1.56×10^4 cm^{-1} M^{-1}).

Reaction of $Fe(CO)_4Br_2$ with NaSPh

$Fe(CO)_4Br_2$ (4.0 g, 12.2 mmol) and NaSPh (3.20 g, 24.2 mmol) were stirred in 150 mL of toluene for 4 h. Gas was evolved and the solution became green-brown. The solution was filtered and the solid residue was washed with additional toluene until the washes were not deeply colored. The filtrate was evaporated to 50 mL, treated with 50 mL of hexane and cooled to −15°C. The dark green product was collected by filtration, washed with hexane and dried under vacuum (3.0 g, 75% yield, based on $[Fe(CO)_2(SPh)_2]$). This material can be recrystallized from CH_2Cl_2 to give a purified microcrystalline product. Anal. Found: C, 50.45; H, 3.36; S, 19.97; Fe, 15.29. $Fe(CO)_2(SPh)_2$ calc.: C, 50.91; H, 3.05; S, 19.41; Fe, 16.91%. IR (as KBr pellet): $\nu(CO)$ 2078, 2019 cm^{-1}. VIS (toluene): 442 (sh, 4100 mL g^{-1} cm^{-1}), 600 (sh, 640 mL g^{-1} cm^{-1}). (Absorption coefficients given in parentheses on a mass concentration basis.) Repeated attempts at obtaining diffraction-quality crystals were unsuccessful.

Table 3

Crystallographic data for $[NEt_4]Fe(CO)_3(\mu\text{-}SPh)_2Mo(CO)_3(SPh)$

Formula weight	777.62
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	12.244(1)
b (Å)	14.644(2)
c (Å)	20.215(1)
α (deg)	90
β (deg)	105.14(7)
γ (deg)	90
V (Å^3)	3498(1)
Z	4
$d_{calc.}$ (g/cm^3)	1.476
2θ (deg)	4–45
No. unique reflections	4784
Observed data ($I \geqslant 3\sigma$)	3616
μ (cm^{-1})	9.76
Number of parameters	397
R	0.027
R_w	0.035

Crystallography

Details of crystal structure and data collection parameters are listed in Table 3 and refined data for $[NEt_4]Fe(CO)_3(\mu\text{-}SPh)_2Mo(CO)_3(SPh)$ are summarized in Tables 1, 2 and 4. Measurements were made on an Enraf–Nonius CAD4 computer

Table 4

Fractional coordinates of non-hydrogen atoms for $[NEt_4]Fe(CO)_3(\mu\text{-}SPh)_2Mo(CO)_3(SPh)$ (e.s.d.s in parentheses)

Atom	*x*	*y*	*z*	*B* (Å^2) [a]
Mo	0.25152(2)	0.24411(2)	0.49122(1)	3.599(6)
Fe(1)	0.25424(4)	0.40728(3)	0.55885(2)	3.99(1)
S(1)	0.35470(7)	0.38965(6)	0.47791(4)	3.66(2)
S(2)	0.38863(8)	0.12404(6)	0.47496(5)	4.84(2)
S(3)	0.37758(8)	0.29206(7)	0.60478(4)	4.62(2)
O(1)	0.1284(3)	0.0839(2)	0.5412(2)	9.28(9)
O(2)	0.1575(2)	0.1983(2)	0.3354(1)	7.27(8)
O(3)	0.0011(2)	0.3045(2)	0.4674(1)	5.61(6)
O(4)	0.0971(2)	0.5357(2)	0.4739(2)	6.93(7)
O(5)	0.3794(3)	0.5459(2)	0.6528(2)	10.1(1)
O(6)	0.0951(2)	0.3565(3)	0.6377(1)	7.66(8)
C(1)	0.1787(3)	0.1411(3)	0.5232(2)	5.7(1)
C(2)	0.1910(3)	0.2155(3)	0.3922(2)	4.70(8)
C(3)	0.0979(3)	0.2895(2)	0.4790(2)	4.22(8)
C(4)	0.1570(3)	0.4843(2)	0.5066(2)	4.71(8)
C(5)	0.3325(3)	0.4933(3)	0.6145(2)	6.2(1)
C(6)	0.1582(3)	0.3765(3)	0.6077(2)	5.17(9)
C(11)	0.2979(3)	0.4495(2)	0.3997(2)	3.66(7)
C(12)	0.3715(3)	0.5057(3)	0.3776(2)	4.66(8)
C(13)	0.3342(3)	0.5527(3)	0.3158(2)	5.7(1)
C(14)	0.2251(4)	0.5452(3)	0.2777(2)	5.7(1)
C(15)	0.1520(3)	0.4899(3)	0.3000(2)	5.7(1)
C(16)	0.1876(3)	0.4411(2)	0.3601(2)	4.75(9)
C(21)	0.4490(3)	0.1425(2)	0.4059(2)	4.22(8)
C(22)	0.5108(3)	0.0706(3)	0.3883(2)	5.55(9)
C(23)	0.5674(4)	0.0832(4)	0.3383(2)	7.5(1)
C(24)	0.5627(3)	0.1645(4)	0.3045(2)	7.7(1)
C(25)	0.5013(4)	0.2360(3)	0.3211(2)	6.4(1)
C(26)	0.4439(3)	0.2249(3)	0.3709(2)	5.09(9)
C(31)	0.3540(3)	0.2469(3)	0.6821(2)	5.20(9)
C(32)	0.3807(4)	0.3002(4)	0.7398(2)	8.4(1)
C(33)	0.3712(5)	0.2638(4)	0.8012(2)	9.4(2)
C(34)	0.3357(4)	0.1783(4)	0.8054(2)	8.9(2)
C(35)	0.3107(7)	0.1273(4)	0.7493(3)	13.4(2)
C(36)	0.3215(6)	0.1624(4)	0.6873(2)	11.3(2)
N(100)	0.2225(2)	0.8302(2)	0.4152(1)	4.66(7)
C(111)	0.2490(4)	0.8858(3)	0.4805(2)	5.9(1)
C(112)	0.1730(4)	0.8675(3)	0.5273(2)	7.3(1)
C(121)	0.1045(4)	0.8491(4)	0.3723(2)	7.2(1)
C(122)	0.0817(5)	0.9492(4)	0.3503(3)	9.9(2)
C(131)	0.3126(4)	0.8565(3)	0.3787(2)	6.9(1)
C(132)	0.3002(5)	0.8099(4)	0.3107(3)	9.8(2)
C(141)	0.2270(3)	0.7293(3)	0.4313(2)	5.6(1)
C(142)	0.3371(4)	0.6970(3)	0.4787(3)	7.2(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter.

controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. Preliminary examination and data collection were performed on a red rhomboid of dimensions 0.47 × 0.39 × 0.35 mm with Mo-K_α radiation. Lorentz and polarization corrections were applied to the data. The structure was solved with the structure solution program SHELX-86E.

Complete tables of structure factors, positional parameters for hydrogen atoms, anisotropic thermal parameters and bond distances are available from the author.

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