# Synthesis and Structure of Heterobimetallic Compounds with a Single Thiolato-Bridged Ligand

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Reactions between $CpFe(CO)_2SPh$ and $M(CO)_5THF$ (M = Cr, Mo, and W) in a mixture of benzene and THF at room temperature afforded compounds of the type $CpFe(CO)_2(\mu\text{-}SPh)M(CO)_5$ (**1**) [M = Cr (**1a**), Mo (**1b**), and W (**1c**)] in high yield. However, migration of the thiolato ligand occurred during reactions between $CpM(CO)_xSPh$ (M = Fe, x = 2; M = Mo and W, x = 3) and $Fe_2(CO)_9$ forming compounds $[Fe(\mu\text{-}SPh)(CO)_3]_2$ and $[CpM(CO)_x]_2$ (M = Fe, x = 2; M = Mo and W, x = 3). Single-crystal X-ray diffraction analyses reveal that **1c** is a single thiolato-bridged hererobimetallic compound without a metal–metal bond. Metal–metal bond formation in compounds **1** by decarbonylation under thermal or photolytic condition was not observed. Reactions between compounds **1** and $PPh_3$ produced $CpFe(CO)_2SPh$ and $PPh_3M(CO)_5$ (M = Cr, Mo, and W) by M–S bond cleavage in **1**.

## Introduction

Recent investigations of the chemical properties of phosphido-bridged bimetallic complexes have revealed several interesting cooperative effects between metals in these bimetallic complexes.[1] The dative metal−metal bond between metals can activate the substitution of the carbonyl ligands [1b−1f] and transfer the substitution site from one metal to the other.[1e] Interestingly, having a similar dative metal−metal bond, sulfido-bridged $CpW(CO)_2(\mu\text{-}SMe)W(CO)_5(W-W)$ and phosphido-bridged $CpW(CO)_2(\mu\text{-}PPh_2)W(CO)_5(W-W)$ complexes behave differently on substitution towards phosphanes. Thus, reaction between $CpW(CO)_2(\mu\text{-}SMe)W(CO)_5(W-W)$ and phosphanes formed $CpW(PR_3)(CO)_2(\mu\text{-}SMe)W(CO)_5$ [2] while its phosphido-bridged analogue $CpW(CO)_2(\mu\text{-}PPh_2)W(CO)_5(W-W)$ gave $CpW(CO)_2(\mu\text{-}PPh_2)W(PR_3)(CO)_4(W-W)$.[1c] In addition, compounds with thiols as a ligand are significantly related to catalysts and biological activity.[3−8] Many of them are bimetallic complexes.[3,4,5a,6,7] As thiols having strong bridging abilities in coordination, enormous numbers of bimetallic compounds containing $(\mu\text{-}SR)_2$ bridges are reported.[9] For complexes with only one (μ-SR) bridge, only a small number of heterobimetallic compounds, without a metal−metal bond, have been synthesized.[10,11] Thus, evaluation of the influence of the thiolate ligands in the chemical behavior of bimetallic complexes could be valuable in order to compare those with phosphido-bridged analogues.

In continuing our interest in the search for cooperative effects in phosphido-bridged heterobimetallic compounds, we attempted to synthesize thiolato-bridged heterobimetallic compounds with and without metal−metal bonds. Herein, we report the synthesis and characterization of single thiolato-bridged heterobimetallic compounds $CpFe(CO)_2(\mu\text{-}SPh)M(CO)_5$ (M = Cr, Mo, and W). Removal of CO to form their metal−metal-bonded analogues $CpFe(CO)(\mu\text{-}SPh)M(CO)_5(Fe-M)$ (M = Cr, Mo, and W) was unsuccessful. The M−S bond cleavage in compounds **1** by $PPh_3$ as well as thiolato ligand transfer from the metallothiolates $CpM(CO)_xSPh$ (M = Fe, $x$ = 2; M = Mo and W, $x$ = 3) to $Fe_2(CO)_9$ to form $[Fe(\mu\text{-}SPh)(CO)_3]_2$ at ambient temperature is also described.

## Results and Discussion

### Synthesis of Compound 1 and Structure of 1c

Stirring of a benzene solution of $CpFe(CO)_2SPh$ with a THF solution of $M(CO)_5THF$ (M = Cr, Mo, and W) at room temperature afforded compounds **1a**, **1b**, and **1c** in high yield [Equation (1)]. The compound $[W(\mu\text{-}SPh)(CO)_4]_2$ [12] was also obtained in trace amounts during isolation of compound **1c**. Compounds **1a**, **1b**, and **1c** can also be prepared in good yield by using $M(NBD)(CO)_4$ (NBD = norbornadiene; M = Cr, Mo, and W)[13] instead of $M(CO)_5THF$, but formation of the heterobimetallic compounds is comparatively slow. They are reddish-orange solids, soluble in common organic solvents, and are air-stable.

$$CpFe(CO)_2SPh + M(CO)_5THF \rightarrow CpFe(CO)_2(\mu\text{-}SPh)M(CO)_5 + THF \quad (1)$$

M = Cr (**1a**), Mo (**1b**), W (**1c**)

Single-crystal X-ray diffraction analysis of compound **1c** revealed that two independent molecules crystallized in the asymmetric unit cell. The independent two molecules are crystallographically nonidentical, where they are distinguished by the chirality of the S atom. The molecular struc-

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tures are shown in Figures 1 and 2. Selected bond lengths and bond angles are listed in Table 1.

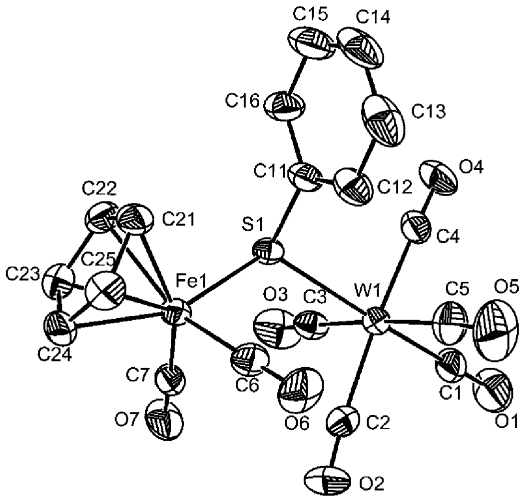

Figure 1. ORTEP drawing of **1c** (molecule 1); hydrogen atoms are omitted

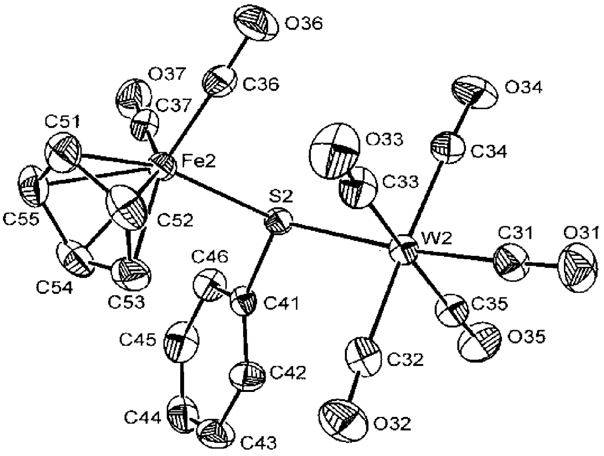

Figure 2. ORTEP drawing of **1c** (molecule 2); hydrogen atoms are omitted

Table 1. Selected bond lengths [Å] and bond angles [°] in compound **1c**.

| Molecule 1 | | Molecule 2 | |
|---|---|---|---|
| Bond lengths | | | |
| Fe1W1 | 4.2236(9) | Fe2W2 | 4.1987(9) |
| W1−S1 | 2.5772(13) | W2−S2 | 2.5865(12) |
| W1−C1 | 1.952(7) | W2−C31 | 1.959(5) |
| W1−C2 | 2.025(6) | W2−C32 | 2.021(6) |
| W1−C3 | 2.027(6) | W2−C33 | 2.030(6) |
| W1−C4 | 2.045(6) | W2−C34 | 2.046(6) |
| W1−C5 | 2.047(7) | W2−C35 | 2.060(5) |
| Fe1−S1 | 2.3007(15) | Fe2−S2 | 2.3166(14) |
| Fe1−C6 | 1.766(6) | Fe2−C36 | 1.770(6) |
| Fe1−C7 | 1.784(6) | Fe2−C37 | 1.778(6) |
| Fe1−C21 | 2.103(6) | Fe2−C51 | 2.094(6) |
| Fe1−C22 | 2.106(5) | Fe2−C52 | 2.110(6) |
| Fe1−C23 | 2.109(5) | Fe2−C53 | 2.112(5) |
| Fe1−C24 | 2.089(5) | Fe2−C54 | 2.096(5) |
| Fe1−C25 | 2.101(6) | Fe2−C55 | 2.091(5) |
| S1−C11 | 1.781(5) | S2−C41 | 1.790(5) |
| C1−O1 | 1.152(9) | C31−031 | 1.154(7) |
| C2−O2 | 1.139(8) | C32−032 | 1.140(7) |
| C3−O3 | 1.134(8) | C33−033 | 1.135(7) |
| C4−O4 | 1.133(8) | C34−034 | 1.131(7) |
| C5−O5 | 1.139(9) | C35−035 | 1.128(7) |
| C6−O6 | 1.133(7) | C36−036 | 1.142(7) |
| C7−O7 | 1.130(8) | C37−037 | 1.134(7) |
| Bond angles | | | |
| W1−S1−Fe1 | 119.86(5) | W2−S2−Fe2 | 117.71(5) |
| W1−S1−C11 | 109.52(19) | W2−S2−C41 | 115.14(16) |
| Fe1−S1−C11 | 106.44(18) | Fe2−S2−C41 | 104.24(15) |
| S1−W1−C1 | 172.77(24) | S2−W2−C31 | 173.68(16) |
| S1−W1−C2 | 97.05(18) | S2−W2−C32 | 98.72(15) |
| S1−W1−C3 | 85.78(17) | S2−W2−C33 | 94.46(6) |
| S1−W1−C4 | 87.11(17) | S2−W2−C34 | 84.29(15) |
| S1−W1−C5 | 97.07(21) | S2−W2−C35 | 89.02 (14) |
| C1−W1−C2 | 87.4(3) | C31−W2−C32 | 87.58(22) |
| C1−W1−C3 | 88.5(3) | C31−W2−C33 | 86.21(23) |
| C1−W1−C4 | 89.5(3) | C31−W2−C34 | 89.41(22) |
| C1−W1−C5 | 88.8(3) | C31−W2−C35 | 90.39(22) |
| C2−W1−C3 | 90.03(25) | C32−W2−C33 | 88.46(24) |
| C2−W1−C4 | 175.83(24) | C32−W2−C34 | 176.99(21) |
| C2−W1−C5 | 87.4(3) | C32−W2−C35 | 90.53(21) |
| C3−W1−C4 | 90.67(24) | C33−W2−C34 | 91.37(24) |
| C3−W1−C5 | 176.4(3) | C33−W2−C35 | 176.49(21) |
| C4−W1−C5 | 91.7(3) | C34−W2−C35 | 89.47(21) |
| C6−Fe1−C7 | 95.2(3) | C36−Fe2−C37 | 92.1(3) |
| S1−Fe1−C6 | 90.22(19) | S2−Fe2−C36 | 89.77(17) |
| S1−Fe1−C7 | 90.56(19) | S2−Fe2−C37 | 89.48(17) |

There is no metal−metal bond present in any of the molecules as the bond lengths Fe1−W1 [4.2236(9) Å] and Fe2−W2 [4.1987(8) Å] are longer than the sum the covalent radii of the metal atoms. The tungsten atom has a distorted octahedral geometry, coordinated to five carbonyl groups and a bridging thiolato ligand. The W1−C1 [1.952(7) Å] and W2−C31 [1.959(5) Å] distances *trans* to the bridging thiolato ligand are shorter than the four equatorial W−C distances 2.036(7) Å (av.) and 2.039(6) Å (av.), respectively. This indicates that the thiolato ligand is a better σ-donor but a poorer π-acceptor compared to the CO ligand. The bond lengths Fe1−S1 [2.3007(15) Å], Fe2−S2 [2.3166(14) Å], W1−S1 [2.5772(13) Å], and W2−S2 [2.5865(12) Å] are comparable to the reported values.[10a] The bond angles W1−S1−Fe1 [119.86(5)°] and W2−S2−Fe2 [117.71(5)°] are also within the range of other reported M−S−M bond angles.[10a,11]

### Thiolato Ligand Transfer from CpM(CO)$_x$SPh (M = Fe, $x$ = 2; M = Mo and W, $x$ = 3) to Fe(CO)$_4$ by Fe$_2$(CO)$_9$

The reaction between Fe$_2$(CO)$_9$ and CpFe(CO)$_2$SPh in THF at room temperature leads to the formation of [CpFe(CO)(μ-CO)]$_2$ [14] and [Fe(μ-SPh)(CO)$_3$]$_2$ [15] in good yield. Metallothiolates of the type CpM(CO)$_3$SPh (M = Mo and W) also react with Fe$_2$(CO)$_9$ in a similar way and give the compounds [Fe(μ-SPh)(CO)$_3$]$_2$ and their respective dimers Cp$_2$M$_2$(CO)$_6$ (M = Mo and W).[16,17] The above transformation indicates that instead of obtaining any bimetallic compound like those of compounds **1,** the thiolato ligand is transferred from the CpM unit to the $Fe(CO)_4$ moiety during the reaction by M−S bond cleavage. The exact mechanism is not clear but it is believed to proceed via an associative pathway forming a bimetallic intermediate with the bridging thiolato ligand (Scheme 1).[18,19]

$$Fe_2(CO)_9 + THF \rightarrow Fe(CO)_4THF + Fe(CO)_5 \quad (a)$$

$$Fe(CO)_4THF + CpFe(CO)_2SPh \rightarrow CpFe(CO)_2(\mu\text{-}SPh)Fe(CO)_4 + THF \quad (b)$$

$$CpFe(CO)_2(\mu\text{-}SPh)Fe(CO)_4 \rightarrow CpFe(CO)_2 + Fe(CO)_4SPh \quad (c)$$

$$2CpFe(CO)_2 \rightarrow [CpFe(\mu\text{-}CO)(CO)]_2 \quad (d)$$

$$2Fe(CO)_4SPh \rightarrow [Fe(\mu\text{-}SPh)(CO)_3]_2 + 2CO \quad (e)$$

Scheme 1

$Fe_2(CO)_9$ can exist in THF solution as $Fe(CO)_4THF$ [Scheme 1, (a)].[20] Then $Fe(CO)_4THF$ can easily release the solvent molecule during the reaction, and the resultant reactive fragment $Fe(CO)_4$ coordinates to the sulfur lone pair of $CpFe(CO)_2SPh$ to generate the bimetallic intermediate $CpFe(CO)_2(\mu\text{-}SPh)Fe(CO)_4$ [Scheme 1, (b)].[18,19] It is then fragmented to $CpFe(CO)_2$ and $Fe(CO)_4SPh$ units by cleavage of the CpFe−S bond [Scheme 1, (c)]. Compound $[Fe(\mu\text{-}SPh)(CO)_3]_2$ is then formed by decarbonylation and dimerization of $Fe(CO)_4SPh$ according to Scheme1, (e).[21] Thiolato ligand transfer and formation of $[Fe(\mu\text{-}SPh)(CO)_3]_2$ in the case of $CpM(CO)_3SPh$ (M = Mo and W) is most likely to follow similar reaction paths.

Thiolato ligand transfer is reported for a few cases, these are the early to late transition metals such as titanium to cobalt,[22] rhodium,[23] or platinum.[18] It is due to the hard and soft mismatching of coordination between the titanium and thiolato ligand.[18] Thiolato ligand transfer from late to late transition metals is rare, but when it does occur it is between two different metals and under thermal conditions.[24] Thus, thiolate ligand transfer from iron to iron at ambient temperature in the above reaction is notable.

### Reactivities of Compound 1

Reactions of compounds **1** with $PPh_3$ generate $CpFe(CO)_2SPh$ and $M(CO)_5PPh_3$ (M = Cr, Mo, and W).[25] This indicates that substitution of the metallothiolate with phosphane occurs on the W center in compounds **1**. It also suggests that $PPh_3$ is not only a stronger Lewis base, but also π-acceptor, in contrast to $CpFe(CO)_2SPh$. Interestingly, the reaction of $CpW(CO)_3(\mu\text{-}SMe)W(CO)_5$ and $CpW(CO)_3(\mu\text{-}SPh)W(CO)_5$ with hexafluorobut-2-yne produced $CpW(CO)(\eta^2\text{-}CF_3C_2CF_3)(\mu\text{-}SMe)W(CO)_5$ and $CpW(CO)(\eta^2\text{-}CF_3C_2CF_3)(SPh)$, respectively.[10a] In addition, the CO on Fe in $CpFe(CO)_2(\mu\text{-}PPh_2)W(CO)_5$ can be replaced by $PMe_3$ to produce $CpFe(CO)(PMe_3)(\mu\text{-}PPh_2)W(CO)_5$ under mild conditions.[1e] This indicates that the carbonyl ligands on the CpM moieties in these two compounds are labile towards substitution.

Under thermolytic or photolytic conditions, the CO ligand cannot be removed from compounds **1** to form $CpFe(CO)(\mu\text{-}SPh)M(CO)_5$(*Fe−M*) (M = Cr, Mo, and W). Instead, decomposition of the complex was observed. This indicates that the CO ligand on Fe cannot be substituted by the M−Fe bond formation under the reaction conditions. This observation is consistent with the results of the reaction between compounds **1** and phosphane discussed in the previous paragraph.

## Conclusions

Reactions between $CpFe(CO)_2SPh$ and $M(CO)_5THF$ (M = Cr, Mo, and W) or $M(CO)_4(NDB)$ (M = Cr, Mo, and W) produce $CpFe(CO)_2(\mu\text{-}SPh)M(CO)_5$ (M = Cr, Mo, and W) in good yield. However, reactions of metallothiolates $CpFe(CO)_2SPh$ and $CpM(CO)_3SPh$ (M = Mo and W) with $Fe_2(CO)_9$ resulted in the transfer of SR from metallothiolates to $Fe_2(CO)_9$ to produce $[Fe(\mu\text{-}SPh)(CO)_3]_2$. Attempts to remove CO from $CpFe(CO)_2(\mu\text{-}SPh)M(CO)_5$ (M = Cr, Mo, and W) to form the metal−metal-bonded $CpFe(CO)(\mu\text{-}SPh)M(CO)_5$(*Fe−M*) were unsuccessful. The fact that the carbonyl ligands are inert towards substitution by the metal−metal dative-bond formation is proposed as a reason. Replacement of the metallothiolate moiety $CpFe(CO)_2SPh$ from $CpFe(CO)_2(\mu\text{-}SPh)M(CO)_5$ (M = Cr, Mo, and W) by $PPh_3$ and formation of $M(CO)_5(PPh_3)$ supports the above argument.

## Experimental Section

**General Procedures:** All reactions and other manipulations were performed using standard Schlenk techniques under nitrogen at ambient temperature. Commercially available chemicals were purchased and used without further purification. All solvents were dried and distilled immediately prior to use. The compounds $CpFe(CO)_2SPh$,[26] $M(NBD)(CO)_4$ (M = Cr, Mo, and W),[13] and $CpM(CO)_3SPh$ (M = Cr, Mo, and W)[27] were prepared according to the reported procedures. − A 450-W Hanovia medium-pressure quartz mercury lamp (Ace-Glass) and a pyrex Schlenk tube, used as a reaction vessel, were used in the photoreactions. − Infrared spectra were recorded with a Perkin−Elmer 882 infrared spectrophotometer. − The $^1H$ NMR spectra were recorded with a Bruker Ac-200 spectrometer. − Electron impact (EI) and fast-atom bombardment (FAB) mass spectra were recorded with a VG 70−2505 or a JEOL JMS-HX 100 mass spectrometer. − Microanalyses were performed using a Perkin−Elmer 2400 CHN analyzer.

**Synthesis of Compounds 1:** To a benzene solution (50 mL) of $CpFe(CO)_2SPh$ (0.50 g, 1.75 mmol), a THF solution (250 mL) of $M(CO)_5THF$ (M = Cr, Mo, and W) [prepared by photolysis of $M(CO)_6$ (2.0 mmol)] was added, and the solution was stirred for 0.5 h at room temperature. The reaction mixture was concentrated to dryness. The residue was dissolved in dichloromethane/hexane (1:10) and then filtered using Celite. The filtrate was concentrated to10 mL and subjected to silica gel chromatography using dichloromethane/hexane (1:2) as the eluent. The reddish-orange bands were collected and dried. Compounds **1** were recrystallized from the mixture of dichloromethane and hexane in high yield. − **Compound 1a:** Yield 0.66 g (79%). − $C_{18}H_{10}CrFeO_7S$ (477.89): calcd. C 45.19, H 2.09; found C 45.09, H 2.08. − IR (hexane, νCO): $\tilde{\nu}$ = 2064 m, 2039 s, 2005 s, 1988 w, 1937 vs, 1915 vs cm$^{-1}$. − $^1$H NMR ($CD_3COCD_3$): δ = 7.40−7.249 (m, 5 H, $C_6H_5$), 5.20 (s, 5 H, $C_5H_5$). − MS (FAB): *m/z* = 478 [M$^+$], 450 [M$^+$ − CO], 422 [M$^+$ − 2 CO], 366 [M$^+$ − 4 CO], 282 [M$^+$ − 7 CO]. − **Compound 1b:** Yield 0.467 g (51%). − $C_{18}H_{10}FeMoO_7S$ (523.85): calcd. C 41.38, H 1.92; found C 41.46, H 2.11. − IR (hexane, νCO): $\tilde{\nu}$ = 2072m, 2041 s, 2006 s, 1989 m, 1942 vs, 1933 sh. 1916 vs cm$^{-1}$. − $^1$H NMR ($CD_3COCD_3$): δ = 7.52−7.159 (m, 5 H, $C_6H_5$), 5.30 (s, 5 H, $C_5H_5$). − MS (FAB): *m/z* = 524 [M$^+$], 468 [M$^+$ − 2 CO], 412 [M$^+$ − 4 CO], 356 [M$^+$ − 6 CO], 328 [M$^+$ − 7 CO]. − **Compound 1c:** Yield 0.789 g (74%). − $C_{18}H_{10}FeO_7SW$ (610.02): calcd. C 35.41, H 1.64; found C 35.48, H 1.83. − IR (hexane, νCO): $\tilde{\nu}$ = 2068 m, 2041 s, 2006 s, 1981 m, 1965 w, 1933 vs, 1912 vs cm$^{-1}$. − $^1$H NMR ($CD_3COCD_3$): δ = 7.62−7.299 (m, 5 H, $C_6H_5$), 5.23 (s, 5 H, $C_5H_5$). − MS (FAB): *m/z* = 610 [M$^+$], 554 [M$^+$ − 2 CO], 526 [M$^+$ − 3 CO], 470 [M$^+$ − 5 CO], 442 [M$^+$ − 6 CO], 414 [M$^+$ − 7CO].

**Synthesis of Compounds 1 from M(NBD)(CO)$_4$ (M = Cr, Mo, and W; NBD = Norbornadiene):** To a solid mixture of $CpFe(CO)_2SPh$ (0.5 g, 1.75 mmol) and $M(NBD)(CO)_4$ (2.5 mmol) (M = Cr, Mo, and W) 50 mL of THF was added and stirred for 2 d at room temperature. The resulting reaction mixture was concentrated to dryness. The residue was dissolved in dichloromethane and filtered through Celite. The filtrate was concentrated to 5 mL and subjected to chromatography on a silica gel column using dichloromethane/hexane (1:3) as the eluent. The reddish-orange bands were collected and dried. Recrystallization of the residues from a mixture of dichloromethane and hexane afforded compounds **1**. Yield 0.594 g (71%) (**1a**), 0.449 g (49%) (**1b**), 0.715 g (67%) (**1c**).

**Reactions of CpM(CO)$_x$SPh (M = Fe, *x* = 2; M = Mo and W, *x* = 3) with Fe$_2$(CO)$_9$:** To a THF (50 mL) solution of $CpM(CO)_xSPh$ (M = Fe, $x$ = 2; M = Mo and W, $x$ = 3) (0.5 mmol) $Fe_2(CO)_9$ (0.728 g, 2.0 mmol) was added and stirred for 2 d at room temperature. The reaction mixture was concentrated to dryness. The residue was dissolved in dichloromethane and filtered through Celite. The filtrate was concentrated to 5 mL. Silica gel chromatography of each filtrate using dichloromethane/hexane (1:3) as the eluent gave the dimers $[CpM(CO)_x]_2$ (M = Fe, $x$ = 2; M = Mo and W, $x$ = 3) and $[Fe(\mu\text{-}SPh)(CO)_3]_2$ (**A**).[15] Yield 0.041 g (23%) ([FeCp(μ-CO)(CO)]$_2$),[14] 0.102 g (41%) (**A**); 0.046 g (19%) ([CpMo(CO)$_3$]$_2$),[16] 0.117 g (47%) (**A**); 0.070 g (21%) ([CpW(CO)$_3$]$_2$),[17] 0.112 g (45%) (**A**).

**Reactions of CpFe(CO)$_2$(μ-SPh)M(CO)$_5$ (M = Cr, Mo, and W) with PPh$_3$:** To a THF solution of CpFe(CO)$_2$(μ-SPh)M(CO)$_5$ (0.5 mmol) [M = Cr (0.240 g), Mo (0.264 g) and W (0.305 g)] PPh$_3$ (0.262 g, 1.0 mmol) was added and the mixture stirred for 2 d at room temperature. The reaction mixture was concentrated to dryness. The residue was dissolved and then filtered through Celite. The filtrate was concentrated to 5 mL and subjected to chromatography on a silica gel column using dichloromethane and hexane as the eluent. The compounds M(CO)$_5$PPh$_3$ (M = Cr, Mo, and W)[25] and CpFe(CO)$_2$SPh (B) were obtained by removing solvents from the first pale yellow band and the third reddish-orange band, respectively. The second reddish-orange band is unchanged starting materials CpFe(CO)$_2$(μ-SPh)M(CO)$_5$ (M = Cr, Mo, and W). Yield 0.045 g (19%) [CpFe(CO)$_2$(μ-SPh)Cr(CO)$_5$], 0.129 g (69%) [Cr(CO)$_5$PPh$_3$], 0.085 g (73%) (**B**); 0.062 g (24%) [CpFe(CO)$_2$(μ-SPh)Mo(CO)$_5$], 0.134 g (71%) [Mo(CO)$_5$PPh$_3$] 0.083 g, (77%) (**B**); 0.095 g (29%) [CpFe(CO)$_2$(μ-SPh)W(CO)$_5$] 0.159 g (79%) [W(CO)$_5$PPh$_3$], 0.079 g (81%) (**B**). Yields of the products are calculated based on that of the reacted CpFe(CO)$_2$(μ-SPh)M(CO)$_5$.

**Crystal Structure Determination of Compound 1c:** Single crystals of compound **1c** were grown by slow vapor diffusion of hexane into a dichloromethane solution of **1c** at 0 °C. A lath yellow crystal (0.25 × 0.18 × 0.34 mm) was mounted on a glass fiber for data collection using Mo-$K_\alpha$ radiation of an Enraf−Nonius CAD4 diffractometer at room temperature. Detailed data collection parameters are given in Table 2. Cell parameters were refined from 25 reflections with the 2θ range 20−36°. Three standard reflections were monitored every hour throughout the data collection. The variation was within 6%. Lorentz and polarization corrections were applied. A semiempirical absorption correction was applied based on azimuthal scans of three reflections. The structure was solved by direct methods. The atomic and isotropic thermal parameters for all hydrogen atoms were fixed. Structure refinement was performed by using the NRCSDP[28] program and a VAX workstation machine. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158994. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Summary of crystal data for compound **1c**

| | |
|---|---|
| Empirical formula | $C_{18}H_{10}FeO_7SW$ |
| Formula mass | 610.02 |
| Space group | $P\bar{1}$ |
| *a* [Å] | 9.1039(13) |
| *b* [Å] | 14.1232(15) |
| *c* [Å] | 16.3126(16) |
| α [°] | 92.586(8) |
| β [°] | 100.8470(10) |
| γ [°] | 103.909(10) |
| *V* [Å$^3$] | 1990.5(4) |
| ρ(calcd.) [Mg·m$^{-3}$] | 2.036 |
| *Z* | 4 |
| Crystal dimensions [mm] | 0.25 × 0.18 × 0.34 |
| Temperature | room temperature |
| λ(Mo-$K_\alpha$) [Å] | 0.70930 |
| 2θ range [°] | 50.0 |
| Scan type | ω |
| No. of reflections | 7044 |
| No. of observed reflections | 5617 [> 2.5σ(*I*)] |
| No. of parameters refined | 506 |
| *R* | 0.025 |
| $R_w$ | 0.028 |
| GoF | 1.31 |
| $D_{\text{map}}$ min., max. [e/ Å$^3$] | −1.080, 1.200 |

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