S−C and C−H Bond Activations as well as C−C Couplings in C5H5FeC5H4C≡CSC≡CSiMe3 Promoted by the Cluster Os3(CO)10(NCMe)2[§]

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The new compounds [Os3(CO)9(μ-CO){μ-η^2-(Fc)CCSC≡CSiMe3}] (**1**), [Os3(CO)10(μ-η^1-SC≡CSiMe3)-(μ-η^2-C≡CFc)] (**2**), [Os3(CO)9(μ-η^1-SC≡CSiMe3)(μ_3-η^2-C≡CFc)] (**3**), [Os3(CO)9(μ_3-η^2,η^3,η^3-{C5H5-FeC5H3CCC(S)C(SiMe3)CHO}] (**4**), and [Os3(CO)9(μ_3-S){μ_3-η^2-(Me3Si)CCC≡CFc}] (**5**) were obtained from the reaction of FcC≡CSC≡CSiMe3 with the activated cluster Os3(CO)10(NCMe)2, as a result of S−C and C−H bond activation as well as C−C coupling reactions in the thioether. The crystal structures of all of them were determined by X-ray diffraction analysis.

Introduction

Studies on cleavage and formation of S−C bonds applying transition metal compounds, clusters among others, are of interest from the hydrodesulfurization (HDS) processes point of view as well as that of the organic synthesis.[1] On the other hand, the coordination chemistry of alkyne thioethers has been poorly developed, although they present multiple metal binding sites. Studies of reactivity of these organosulfur compounds indicate the propensity for cleavage of the S−C bonds, although the compounds [(CuCl)4·2S{C≡CC(CH3)3}2]$_n$ and (CuOSO2CF3)2·S{C≡CC(CH3)3}2, in which the thioether binds to the copper atoms toward the C−C triple bond, have been described.[2] In previous papers, we have reported[3] that the reactions between Ru3(CO)12 and the thioethers RC≡CSC≡CR′ (R = R′ = Fc; R = Fc, R′ = SiMe3; R = R′ = SiMe3; R = SiMe3, R′ = Si^{i}Pr3) yielded different types of derivatives depending on the presence of the organometallic C5H5FeC5H4 (Fc) substituent. Thus, the compounds [Ru3(CO)9(μ_3-η^2,η^4,η^3-{RCC(C2Fc)SC(Fc)CSC≡CR})] R = Fc or SiMe3), which contain the Ru2(CO)6 and Ru(CO)3 fragments linked to one dithioether, were isolated, while the open triangular clusters [Ru3(CO)9(μ_3-η^2-C≡CR)(μ-SC≡CR′}] (R = R′ = SiMe3, R = SiMe3, R′ = Si^{i}Pr3) were formed using organic thioether. Recently, a great deal of research has been devoted to carbonyl clusters whose metal centers are connected to an unsaturated

polycarbon chain due to their implications in materials science.[4] The rupture of S−C bonds followed by C−C coupling reactions in thioethers containing acetylenic groups may also be used as a synthetic strategy to construct these chains. Thus, we have prepared tri- and tetranuclear clusters containing a bridging C4 chain[5] by reaction of the thioethers RC≡CSC≡CR′ (R = R′ = SiMe3; R = SiMe3, R′ = Si^{i}Pr3) in the presence of M3(CO)12 (M = Fe, Ru). The chemistry of coordinated alkynes with trinuclear carbonyl clusters is well documented. Studies on the reactivity of 1,3-diynes and polyalkynes with M3(CO)10(NCMe)2 (M = Ru, Os) have confirmed the formation of compounds such as [M3(CO)9(μ-CO)(μ_3-η^1,η^1,η^2-R(C≡C)$_n$R′] [M = Ru, R = H, R′ = W(CO)3Cp, n = 2,[6] R = R′ = Ph, n = 2,[7] R = H, R′ = Fc, n = 1 or 2;[8] M = Os, R = R′ = SiMe3 n = 3;[9] R = R′ = C4H4S, n = 2,[10] R = R′ = Me, n = 2[11]], in which the coordinative preference of the clusters for one of the C≡C groups depends on electronic and steric constraint factors. Subsequent reactions may result in either cleavage of the central C−C single bond to form bis(alkynyl) clusters[12] or carbon−carbon bond formation between two alkyne molecules with or

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Scheme 1

i = CH₂Cl₂, rt, 3h;
ii = toluene, 65°C, 1h
•— = CO
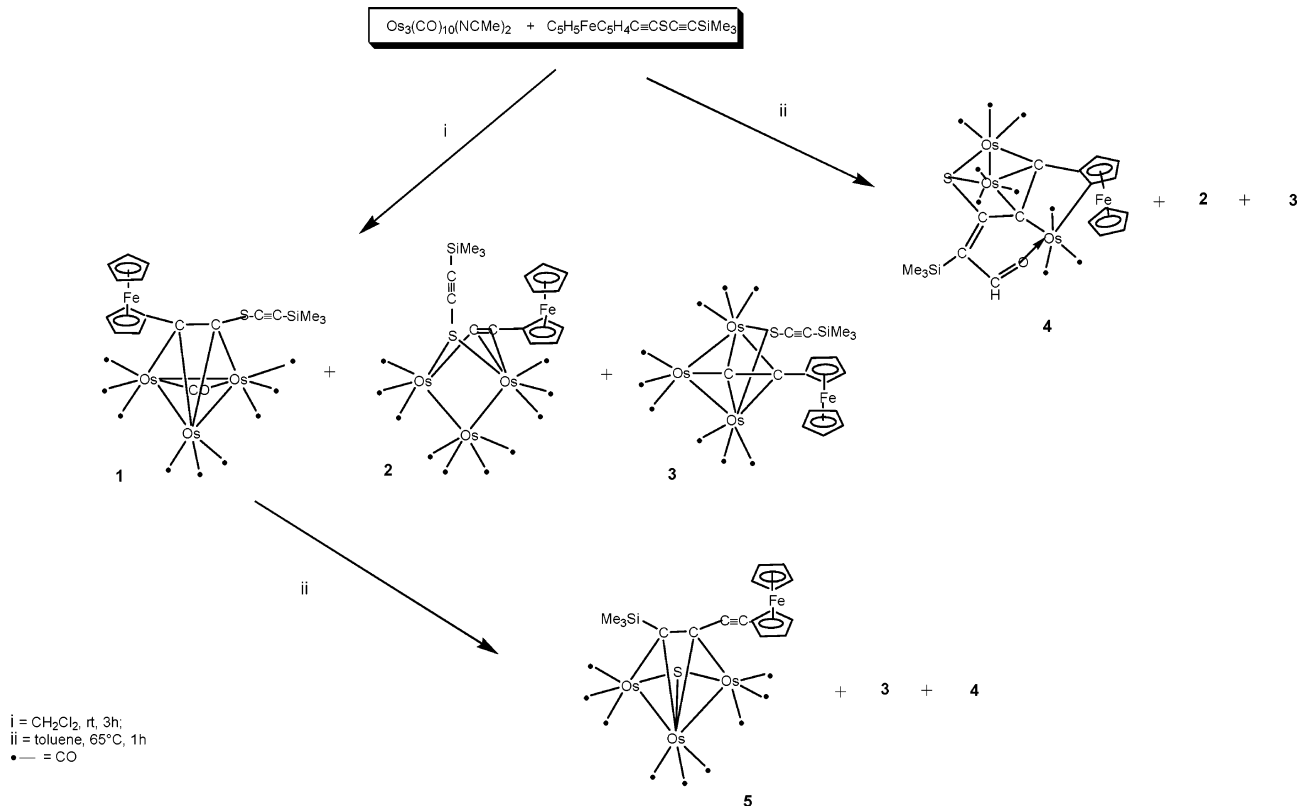
without incorporation of CO groups.[11,13] Also, well known is the mono- or disubstitution of acetonitrile molecules in Os$_3$(CO)$_{10}$(NCMe)$_2$ by SR$_2$ (R = Et, Pr) or S(CH$_2$)$_5$[14] or the formation of [Os$_3$(CO)$_{10}$(μ-η^2-SCH(Ph)CH$_2$CH(Ph)] by cleavage of one S–C bond in the thietane SCH(Ph)CH$_2$CH(Ph) in the presence of this osmium-activated derivative.[15] Here, we report the synthesis and characterization of new compounds obtained by S–C and C–H bond activations as well as C–C coupling reactions in FcC≡CSC≡CSiMe$_3$ using Os$_3$(CO)$_{10}$(NCMe)$_2$.

Results and Discussion

An excess of FcC≡CSC≡CSiMe$_3$ was added to a dichloromethane solution of Os$_3$(CO)$_{10}$(NCMe)$_2$, and the mixture was left stirring at room temperature for 3 h. After removing the solvent, the residue was purified by TLC to form the new compounds [Os$_3$(CO)$_9$(μ-CO)(μ_3-η^2-FcCCSC≡CSiMe$_3$)] (**1**), as main product, [Os$_3$(CO)$_{10}$(μ-η^1-SC≡CSiMe$_3$)(μ-η^2-C≡CFc)] (**2**), and [Os$_3$(CO)$_9$(μ-η^1-SC≡CSiMe$_3$)(μ_3-η^2-C≡CFc)] (**3**) (Scheme 1). All these compounds have been characterized by spectroscopic, analytical, and crystallographic data.

Compound **1** showed in the IR spectrum bands corresponding to terminal and bridging carbonyl ligands, whose pattern was similar to those observed in compounds M$_3$(CO)$_9$(μ-CO)L (M = Ru, Os; L = four-electron-donor ligand).[7,9,10,16] The analytical and mass spectrometric data were in agreement with this formula (L = FcC≡CSC≡CSiMe$_3$). Due to the fact that the thioether ligand presents two different C≡C groups as well as one sulfur

atom, the next question was to determine its coordinative preference, which was inferred from the absence in its IR spectrum of one of the two νC≡C bands of the free thioether[3a] together with a bigger shifting of the signals corresponding to the Fc than the SiMe$_3$ group, in its ^{1}H NMR spectrum. The substitution of the two acetonitrile molecules in Os$_3$(CO)$_{10}$-(NCMe)$_2$ by FcC≡CSC≡CSiMe$_3$ to form compound **1** was also suggested by the absence of resonances corresponding to NCMe in its proton NMR spectrum. The coordination of the thioether to the osmium cluster is similar to that observed in alkynes. This structure was confirmed by X-ray diffraction (see Figure 1 and Table 1).
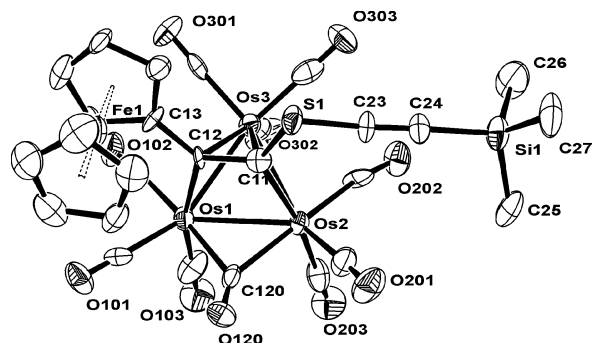

Figure 1. Molecular structure of [Os$_3$(CO)$_9$(μ-CO)(μ_3-η^2-FcCCSC≡CSiMe$_3$)], **1**.

Two crystallographically independent molecules appear in the unit cell. The molecule consists of a triangular arrangement of osmium atoms with averaged metal–metal bond distances of 2.786(1) Å, which are in the range found in the analogous compounds [Os$_3$(CO)$_9$(μ-CO){μ-η^1,η^1,η^2-R(C≡C)$_n$R'}] [R = R' = SiMe$_3$, n = 3;[9] R = R' = Fc, n = 2;[17] R = R' = SC$_4$H$_4$[10]]. The thioether exhibits a μ_3-II coordination where the FcC≡C

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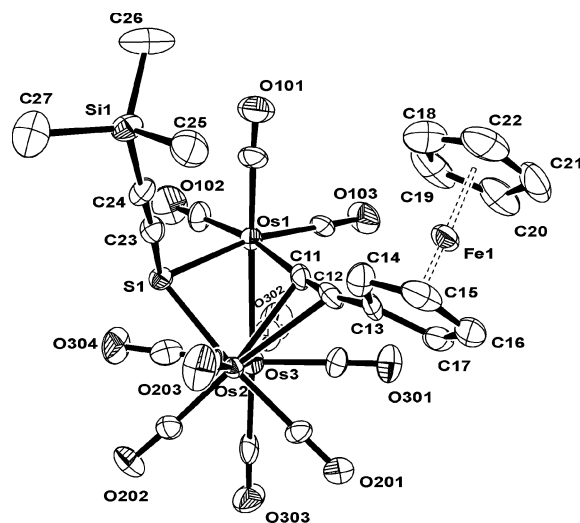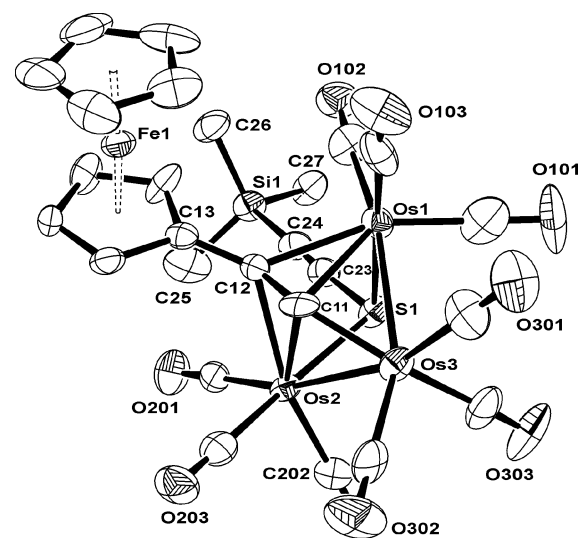
Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 1

C(11)−C(12)	1.413(19)	C(31)−C(32)	1.440(20)
C(11)−S(1)	1.808(14)	C(31)−S(2)	1.802(16)
C(11)−Os(2)	2.136(14)	C(31)−Os(4)	2.150(14)
C(11)−Os(3)	2.269(14)	C(31)−Os(6)	2.264(15)
C(12)−C(13)	1.510(18)	C(32)−C(33)	1.425(19)
C(12)−Os(1)	2.121(13)	C(32)−Os(5)	2.150(15)
C(12)−Os(3)	2.283(14)	C(32)−Os(6)	2.347(14)
C(23)−C(24)	1.217(19)	C(43)−C(44)	1.230(20)
C(23)−S(1)	1.706(14)	C(43)−S(2)	1.685(16)
Os(1)−Os(2)	2.814(1)	Os(4)−Os(5)	2.812(1)
Os(1)−Os(3)	2.773(1)	Os(4)−Os(6)	2.787(1)
Os(2)−Os(3)	2.769(1)	Os(5)−Os(6)	2.762(1)
C(12)−C(11)−S(1)	122.3(10)	C(32)−C(31)−S(2)	120.2(11)
C(12)−C(11)−Os(2)	110.7(10)	C(32)−C(31)−Os(4)	111.4(11)
C(12)−C(11)−Os(3)	72.4(8)	C(32)−C(31)−Os(6)	75.0(8)
S(1)−C(11)−Os(2)	126.4(8)	S(2)−C(31)−Os(4)	127.1(8)
S(1)−C(11)−Os(3)	124.0(7)	S(2)−C(31)−Os(6)	124.3(7)
Os(2)−C(11)−Os(3)	77.8(4)	Os(4)−C(31)−Os(6)	78.3(5)
C(11)−C(12)−C(13)	126.6(12)	C(33)−C(32)−C(31)	127.4(14)
C(11)−C(12)−Os(1)	107.7(9)	C(31)−C(32)−Os(5)	105.7(10)
C(11)−C(12)−Os(3)	71.4(8)	C(31)−C(32)−Os(6)	68.7(8)
C(13)−C(12)−Os(1)	125.5(9)	C(33)−C(32)−Os(5)	126.9(11)
C(13)−C(12)−Os(3)	120.3(9)	C(33)−C(32)−Os(6)	121.9(9)
Os(1)−C(12)−Os(3)	78.0(5)	Os(5)−C(32)−Os(6)	75.6(5)
C(24)−C(23)−S(1)	176.0(14)	C(44)−C(43)−S(2)	174.6(15)
Os(3)−Os(1)−Os(2)	59.4(1)	Os(6)−Os(4)−Os(5)	59.1(1)
Os(3)−Os(2)−Os(1)	59.6(1)	Os(6)−Os(5)−Os(4)	60.0(1)
Os(2)−Os(3)−Os(1)	61.0(1)	Os(5)−Os(6)−Os(4)	60.9(1)

group is acting as a four-electron donor. The coordinated C(11)−C(12) triple bond [1.413(19) Å] has increased in length as a result of the coordination compared to the free ligand [1.185 Å], while the C−C distance of the pendant C≡CSiMe$_3$ group [1.217(19) Å] is similar to that exhibited in the free thioether [1.189(4) Å]. The framework is completed with one bridging CO in addition to nine terminal carbonyl ligands.

The IR spectra of [Os$_3$(CO)$_{10}$(μ-η^1-SC≡CSiMe$_3$)(μ-η^2-C≡CFc)] (**2**) and [Os$_3$(CO)$_9$(μ-η^1-SC≡CSiMe$_3$)(μ_3-η^2-C≡CFc)] (**3**) show the expected pattern for an open trinuclear complex bearing ten[18] and nine terminal carbonyl groups,[18c,19] respectively. Although the acetylide ligand shows σ,π coordination in both complexes, it behaves as a three-electron donor in compound **2** (μ-η^2 bonding mode), while in compound **3** it is one σ and two π bonded to the three osmium atoms. The coordination mode exhibited in **2** is the less common in cluster chemistry, and only a few examples of this are reported.[20] The corresponding signals for Fc and SiMe$_3$ were shown in the ^{1}H NMR spectra, and their ^{13}C NMR spectra have been recorded to identify the different carbon atoms. The molecular ion m/z (1190 and 1162, respectively) was observed in the MALDI spectrum. An X-ray study of compounds **2** and **3** confirmed that they are formed by the oxidative addition of the thioether FcC≡CSC≡CSiMe$_3$ to the osmium cluster, as a consequence of the rupture of only one S−C bond. We have previously observed this type of reaction using iron and ruthenium carbonyls instead and also acetylenic derivatives such as RC≡CH, Ph$_2$PC≡CR, or RC≡CX (X = halogen), which are known to be oxidatively added to carbonyl clusters.[21]

The ORTEP diagrams of compounds **2** and **3** are shown in Figures 2 and 3, while selected bond distances and angles of **2**

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Figure 2. Molecular structure of [Os$_3$(CO)$_{10}$(μ-η^1-SC≡CSiMe$_3$)-(μ-η^2-C≡CFc)], **2**.

Figure 3. Molecular structure of [Os$_3$(CO)$_9$(μ-η^1-SC≡CSiMe$_3$)-(μ_3-η^2-C≡CFc), **3**.

and the two independent molecules of **3** are given in Table 2. The crystal structures confirmed that the C≡CFc group interacts with the osmium atoms via one σ bond with Os(1) and one π bond with Os(2) in compound **2** or through one σ bond with Os(3) and two π bonds with Os(1) and Os(2) in compound **3**. Thus, the C(11)−C(12) distance [1.322(18) Å] of the μ-C$_2$Fc unit in compound **3** corresponds to a single C−C bond and is similar to that reported for the compounds [(H)Os$_3$(CO)$_9$-(C≡CR)] (R = SiPh$_3$, CMe$_3$),[22a] [Ru$_3$(CO)$_9$(μ_3-η^2-C≡CSiMe$_3$)-(μ-SC≡CFc)],[3a] and [AuRu$_3$(CO)$_9$P(tol)$_3${μ_3-η^2-C$_2$C≡CAuP-(tol)$_3$].[22b] On the other hand, the length of 1.265(14) Å observed in compound **2** for the same ligand corresponds to a double

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 2 and 3

2		3			
C(11)−C(12)	1.266(14)	C(11)−C(12)	1.322(18)	C(31)−C(32)	1.333(18)
C(11)−Os(1)	2.049(10)	C(11)−Os(1)	2.265(13)	C(31)−Os(4)	2.298(12)
C(11)−Os(2)	2.359(9)	C(11)−Os(2)	2.274(12)	C(31)−Os(5)	2.263(13)
C(12)−C(13)	1.408(14)	C(11)−Os(3)	1.958(14)	C(31)−Os(6)	1.934(14)
C(12)−Os(2)	2.593(9)	C(12)−C(13)	1.427(18)	C(32)−C(33)	1.452(17)
C(23)−C(24)	1.214(12)	C(12)−Os(2)	2.363(12)	C(32)−Os(5)	2.360(13)
C(23)−S(1)	1.698(9)	C(12)−Os(1)	2.301(13)	C(32)−Os(4)	2.273(12)
Os(1)···Os(2)	3.321(1)	C(23)−C(24)	1.186(19)	C(43)−C(44)	1.191(18)
Os(1)−Os(3)	2.880(1)	C(23)−S(1)	1.723(16)	C(43)−S(2)	1.714(15)
Os(2)−Os(3)	2.884(1)	Os(1)···Os(2)	3.408(1)	Os(4)···Os(5)	3.406(1)
Os(1)−S(1)	2.465(2)	Os(1)−Os(3)	2.872(1)	Os(4)−Os(6)	2.878(1)
Os(2)−S(1)	2.458(2)	Os(2)−Os(3)	2.863(1)	Os(5)−Os(6)	2.853(1)
		Os(1)−S(1)	2.454(3)	Os(4)−S(2)	2.453(3)
		Os(2)−S(1)	2.453(3)	Os(5)−S(2)	2.445(3)
Os(1)−C(11)−C(12)	172.5(8)	C(11)−C(12)−C(13)	146.0(12)	C(31)−C(32)−C(33)	142.6(12)
C(11)−C(12)−C(13)	169.9(10)	Os(1)−C(12)−C(13)	133.8(9)	Os(4)−C(32)−C(33)	133.7(10)
Os(1)−C(11)−Os(2)	97.5(4)	Os(2)−C(12)−C(13)	120.0(9)	Os(5)−C(32)−C(33)	121.2(9)
Os(2)−C(12)−C(13)	124.7(7)	Os(3)−C(11)−C(12)	150.9(10)	Os(6)−C(31)−C(32)	149.2(10)
Os(1)−Os(3)−Os(2)	70.4(1)	Os(1)−C(11)−Os(2)	97.3(5)	Os(4)−C(31)−Os(5)	96.6(5)
Os(1)−S(1)−Os(2)	84.8(1)	Os(1)−C(11)−Os(3)	85.4(5)	Os(4)−C(31)−Os(6)	85.3(4)
Os(1)−S(1)−C(23)	106.2(3)	Os(2)−C(11)−Os(3)	84.8(4)	Os(5)−C(31)−Os(6)	85.3(5)
Os(2)−S(1)−C(23)	106.8(4)	Os(1)−C(12)−Os(2)	93.9(4)	Os(4)−C(32)−Os(5)	94.6(4)
C(24)−C(23)−S(1)	176.4(10)	Os(1)−Os(3)−Os(2)	72.9(1)	Os(4)−Os(6)−Os(5)	72.9(1)
		Os(1)−S(1)−Os(2)	88.0(1)	Os(4)−S(2)−Os(5)	88.1(1)
		Os(1)−S(1)−C(23)	106.2(5)	Os(4)−S(2)−C(43)	105.1(4)
		Os(2)−S(1)−C(23)	105.3(5)	Os(5)−S(2)−C(43)	108.7(5)
		C(24)−C(23)−S(1)	175.6(13)	C(44)−C(43)−S(2)	174.5(13)

bond and is close to the distances found in the compounds [Os₃(H)(CO)₁₀(C≡CSiMe₃)],[22c] [Os₃(H)(CO)₉(PPh₃)(C≡CCMe₂-PPh₃)]BF₄,[20b] and [Os₃(CO)₇(C≡C^{i}Pr)₂(PPh₂)₂].[20c] As expected for complex **2**, the C(11)−Os(2) [2.359(9) Å] and C(12)−Os(2) [2.593(9) Å] distances are not equivalent.

The thioalkyne ligand is bridging the two end metals of the open triangular cluster. The S(1)−Os(1) and S(1)−Os(2) distances [2.465(2) and 2.458(2) Å for **2**, 2.458(2) and 2.465-(2) for **3**] are quite similar, indicating that this ligand acts as three-electron donor between both metals.

The Os−S and Os−Os distances in both compounds are in the range found in the clusters [Os₃(CO)₉(μ₃-MeC₂Me)(μ₃-SPh)-(μ-H)] and Os₃(CO)₉(μ₃-η²-C₂CH₂CH₂)(μ-SPh)(μ-H)[18d] and other related compounds.[16,23] Three terminal carbonyls around each metal in an open triangular core, in addition to one more CO attached to the unbridged osmium atom in compound **2**, complete the structures. Both compounds are electron precise according to the 18-electron rule.

The reaction of FcC≡CSC≡CSiMe₃ with Os₃(CO)₁₀(NCMe)₂ results in the formation of the compound [Os₃(CO)₉(μ-η¹-SC≡CSiMe₃)(μ₃-η²-C≡CFc)] (**3**), while the reaction using Ru₃(CO)₁₂ instead leads to [Ru₃(CO)₉(μ-η¹-SC≡CFc)(μ₃-η²-C≡CSiMe₃)]. These results seem to suggest that the preference for the cleavage of one of the two S−C bonds in the asymmetric thioether FcC≡CSC≡CSiMe₃ depends on the type of metal carbonyl used as precursor. Thus, the presence of labile ligands in Os₃(CO)₁₀-(CNMe)₂ has initially allowed the easy coordination of this thioether to the C−C triple bond of the SC≡CFc group before its conversion to [Os₃(CO)₉(μ-η¹-SC≡CSiMe₃)(μ-η²-C≡CFc)], while a different mechanism must take place in the formation of [Ru₃(CO)₉(μ-η¹-SC≡CFc)(μ₃-η²-C≡CSiMe₃)] using Ru₃(CO)₁₂ as a consequence of the higher difficulty to remove the CO ligands.

When the reaction between FcC≡CSC≡CSiMe₃ and Os₃(CO)₁₀(NCMe)₂ was carried out in toluene at 65 °C for 1 h, in addition to compounds **2** and **3** the interesting complex

[Os₃(CO)₉(μ₃-η²,η³,η³-{C₅H₅FeC₅H₃CCC(S)C(SiMe₃)CHO}] (**4**) was obtained. This compound is made up of two osmium carbonyl fragments, Os₂(CO)₆ and Os(CO)₃, linked to a complex thiolate ligand that is derived from the cleavage of one S−C bond and C−C coupling between the C$_α$ atoms of the SC≡CSiMe₃ and C≡CFc fragments in the thioether. We may speculate that a further oxidative addition of a hydride ligand to an osmium atom as a consequence of the C−H bond activation in the Fc substituent followed by the insertion of one CO into the Os−H bond yields a formyl group. Finally, another C−C coupling between the carbon atom bearing the trimethylsilyl substituent and the formyl group takes place.

Our previous research on FcC≡CSC≡CSiMe₃ in the presence of Ru₃(CO)₁₂ under the same conditions (65 °C, excess of thioether) afforded the compound [Ru₃(CO)₉(μ₃-η²,η⁴,η³-{Me₃-SiCC(C₂Fc)SC(Fc)CSC≡CSiMe₃})]. The formation of both osmium and ruthenium complexes have in common the cleavage of two M−M bonds in the cluster precursor, affording M₂(CO)₆ and M(CO)₃ (M = Ru, Os) fragments and the breaking of one S−C bond together with a C−C coupling between the two generated fragments. At this stage, only in the ruthenium case the new thiolate is converted into a dithioether by forming a new S−C bond with another molecule of FcC≡CSC≡CSiMe₃, while C−H bond activation in one Cp ring of the Fc substituent as well as coupling of a formyl group with the thiolate chain is observed only in the osmium compound. The IR spectrum in the carbonyl region of [Os₃(CO)₉(μ₃-η²,η³,η³-{C₅H₅FeC₅H₃-CCC(S)C(SiMe₃)CHO}] (**4**) displayed a more complex pattern than that found in the related compound [Ru₃(CO)₉(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)SC(Fc)CSC≡CSiMe₃})],[3a] as a consequence of a lower symmetry. The νCO observed at 1560 cm⁻¹ was assigned to the CHO group. Its ¹H NMR spectrum (see Experimental Section) shows two signals corresponding to the C₅H₃ group, which are deshielded due to the orthometalation, and the formyl group appears as a singlet resonance at δ 8.43 ppm. The presence of the CHO group in the compound Os₃H-
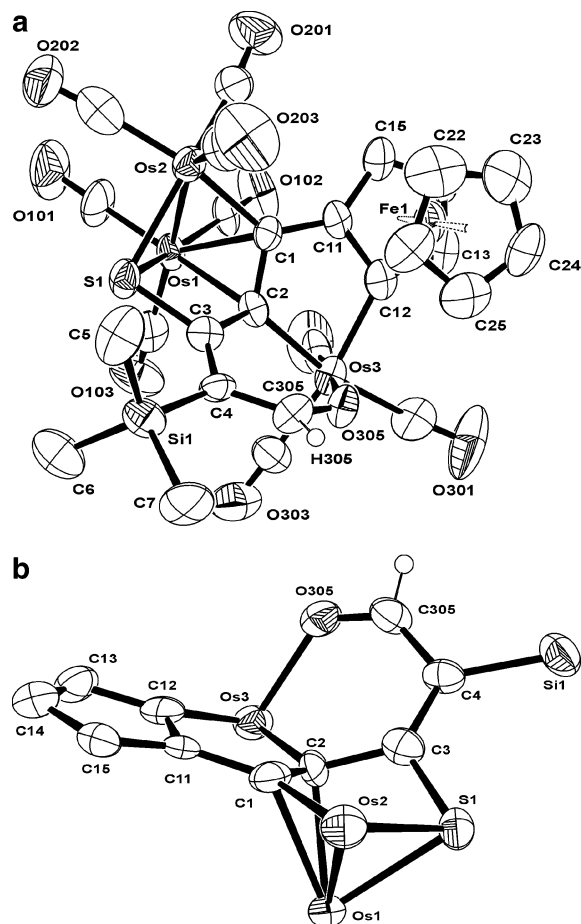
(23) Adams, R. D.; Huang, W. *J. Organomet. Chem.* **1999**, *573*, 14.

Figure 4. Molecular structure of $[Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^3,\eta^3\text{-}\{C_5H_5\text{-}FeC_5H_3CCC(S)C(SiMe_3)CHO\}]$, **4**.

$(CO)_9(CH_2=CCHO)$ has been confirmed[24a] by IR [νCO 1515 cm^{-1}] and ^{1}H NMR [δ 9.5 ppm]. Although a few clusters of the iron triad bearing organic ligands coordinated to an oxygen atom of the formyl or acyl groups are known,[24] crystallographic studies on these derivatives are scarce.

The structure of **4** has been confirmed by X-ray diffraction and is shown in Figure 4a, while a detailed view of the core bonding system is presented in Figure 4b. Selected bonds and angles are given in Table 3. The Os(1)−Os(2) distance of 2.728(1) Å is in the range expected for a osmium−osmium bond, but shorter than those collected in this paper for compounds **1**, **2**, **3**, and **5**. The sulfur atom is symmetrically bonded to Os(1) and Os(2) atoms, as derived by the equal Os(1)−S(1) and Os(2)−S(1) distances [2.433(5) Å]. In compound **4** the thiolate forms two metallacycles with the unbonded metal−metal Os(CO)$_3$ fragment. The distance of 2.15(2) Å for Os(3)−O(305) indicates that the oxygen atom of the formyl group is coordinated to this osmium atom, and the value of 1.22-(2) Å for the C(305)−O(305) bond justifies its double-bond character. Analogous data have been reported for compounds $[Os_3(H)(Ph_3PCCHO)(CO)_9]$,[25a] $[Os_3(H)_2(C_6H_4Ph_2PCCHO)\text{-}(CO)_8]$,[25a] and $[Os_3(H)(CHCHO)(CO)_{10}]$.[25b]

Taking into account the above results, it is possible to think that the reaction of the activated osmium cluster and this

(24) (a) Arce, A. J.; De Sanctis, Y.; Deeming, A. J. *Polyhedron* **1988**, *7*, 979. (b) Johnson, B. F. G.; Lewis, J.; Odiaca, T. I. *J. Organomet. Chem.* **1986**, *307*, 61. (c) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Chem. Soc., Dalton Trans.* **1996**, 3151.

(25) (a) Deeming, A. J.; Nuel, D.; Powell, N. I.; Whittaker, C. *J. Chem. Soc., Dalton Trans.* **1992**, 757. (b) Arce, A. J.; Deeming, A. J.; Hursthouse, M. B.; Walker, N. P. C. *J. Chem. Soc., Dalton Trans.* **1987**, 1861.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

C(1)−C(2)	1.47(3)	C(1)−C(11)	1.44(2)
C(1)−Os(1)	2.36(2)	C(1)−Os(2)	2.10(2)
C(2)−C(3)	1.48(2)	C(2)−Os(1)	2.32(2)
C(2)−Os(3)	2.11(2)	C(3)−C(4)	1.39(2)
C(3)−S(1)	1.80(2)	C(4)−C(305)	1.43(3)
C(4)−Si(1)	1.88(2)	C(11)−C(12)	1.48(3)
C(12)−Os(3)	2.10(2)	C(305)−Os(3)	2.15(2)
C(305)−O(305)	1.22(2)	O(305)−Os(3)	2.15(2)
Os(1)−Os(2)	2.728(1)	Os(1)−S(1)	2.433(5)
Os(2)−S(1)	2.433(5)		
C(11)−C(1)−C(2)	109.4(17)	C(11)−C(1)−Os(2)	130.7(15)
C(11)−C(1)−Os(1)	127.2(12)	C(2)−C(1)−Os(2)	119.9(12)
C(2)−C(1)−Os(1)	70.0(9)	Os(2)−C(1)−Os(1)	75.2(5)
C(1)−C(2)−C(3)	109.4(17)	C(1)−C(2)−Os(3)	120.4(12)
C(3)−C(2)−Os(3)	119.7(14)	C(3)−C(2)−Os(1)	96.0(11)
C(1)−C(2)−Os(1)	73.5(10)	Os(3)−C(2)−Os(1)	128.0(8)
C(4)−C(3)−C(2)	128.6(18)	C(4)−C(3)−S(1)	123.1(15)
C(2)−C(3)−S(1)	108.0(13)	C(3)−C(4)−C(305)	115.2(17)
C(3)−C(4)−Si(1)	123.8(15)	C(305)−C(4)−Si(1)	120.2(13)
O(305)−C(305)−C(4)	131.4(18)	C(305)−O(305)−Os(3)	126.4(13)
C(3)−S(1)−Os(2)	95.2(6)	C(3)−S(1)−Os(1)	84.0(6)
Os(2)−S(1)−Os(1)	68.2(1)		

thioether at room temperature may lead to the compound $[Os_3\text{-}(CO)_9(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}FcCSC\equiv CSiMe_3)]$ (**1**), by the easy shifting of the two acetonitrile molecules. A solution of **1**, at this temperature, should generate the compound $[Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}SC\equiv CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C\equiv CFc)]$ (**2**) by cleavage of only one S−C bond and opening of one Os−Os bond, although the 10 CO ligands remain. The loss of one carbonyl in compound **2** should yield the compound $[Os_3(CO)_9(\mu\text{-}\eta^1\text{-}SC\equiv CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C\equiv CFc)]$, **3**. This sequential transformation should be faster if the reaction is carried out at higher temperature. Hovever, no conversion of compound **2** into **3** was observed by heating a solution of the former compound in toluene at 65 °C. In addition, the compound $[Os_3(CO)_9(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}FcCCSC\equiv CSiMe_3)]$ (**1**) was heated at the same temperature for 1 h to determine if it was a precursor of the compound $[Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}SC\equiv CSiMe_3)\text{-}(\mu_3\text{-}\eta^2\text{-}C\equiv CFc)]$ (**2**), but the new derivative $[Os_3(CO)_9(\mu_3\text{-}S)\text{-}\{\mu_3\text{-}\eta^2\text{-}(Me_3Si)CCC\equiv CFc\}]$ (**5**) (Scheme 1) and compounds **3** and **4** were the only products obtained in this reaction. In conclusion, the compounds $[Os_3(CO)_9(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}FcCCSC\equiv CSiMe_3)]$ (**1**) and $[Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}SC\equiv CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C\equiv CFc)]$ (**2**) are formed through different routes, and compound **2** is not a precursor of **3**.

$[Os_3(CO)_9(\mu_3\text{-}S)\{\mu_3\text{-}\eta^2\text{-}(Me_3Si)CCC\equiv CFc\}]$ (**5**) is also formed, in an amount to run the IR only, from the reaction between $FcC\equiv CSC\equiv CSiMe_3$ and $Os_3(CO)_{10}(NCMe)_2$ in toluene at 65 °C. The IR spectrum of $[Os_3(CO)_9(\mu_3\text{-}S)\{\mu_3\text{-}\eta^2\text{-}(Me_3Si)CCC\equiv CFc\}]$ (**5**) in the carbonyl region compared well with the related iron or ruthenium derivatives and also other open triangular clusters containing nine carbonyl ligands.[26] All protons corresponding to the ferrocenyl and trimethylsilyl groups were present in the ^{1}H NMR. The analytical data as well as the presence of the molecular peak in the MALDI-TOF spectrum of compound **5** were in agreement with its formulation. Although analogous clusters $[M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(RCCC\equiv CR')(\mu_3\text{-}S)]$ (M = Ru, R = R′ = SiMe_3; M = Fe, R = SiMe_3, R′ = $^iPr_3$) have been previously prepared using $M_3(CO)_{12}$ (M = Fe, Ru) as precursors, compound **5** is the first of this type of compound whose crystal structure has been solved. Suitable crystals for X-ray studies of **5** were grown from hexane at room temperature. As can be discerned by the crystallographic data, $[Os_3(CO)_9(\mu\text{-}S)\{\mu_3\text{-}\eta^2\text{-}(Me_3Si)CCC\equiv CFc\}]$ (**5**) is an open triangular cluster containing

(26) (a) Adams, R. D.; Dawoodl, Z. D.; Foust, D. F.; Segmüller, B. E. *Organometallics* **1983**, *2*, 5. (b) Adams, R. D.; Qu, X.; Wu, W. *Organometallics* **1994**, *13*, 1272.
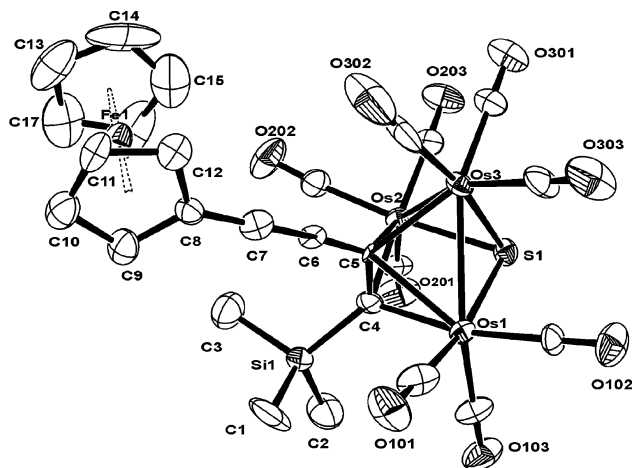
Figure 5. Molecular structure of $[Os_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}\{SiMe_3\}\text{-}CCC\equiv CFc)]$, **5**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 5

C(4)−C(5)	1.381(18)	C(4)−Si(1)	1.885(13)
C(4)−Os(1)	2.209(14)	C(4)−Os(2)	2.190(11)
C(5)−C(6)	1.338(16)	C(5)−Os(1)	2.386(12)
C(5)−Os(2)	2.391(13)	C(5)−Os(3)	2.213(13)
C(6)−C(7)	1.286(17)	C(7)−C(8)	1.427(19)
Os(1)−S(1)	2.408(3)	Os(2)−S(1)	2.418(3)
Os(3)−S(1)	2.411(3)	Os(1)−Os(3)	2.872(1)
Os(2)−Os(3)	2.848(1)	Os(1)···Os(2)	
C(5)−C(4)−Si(1)	127.7(10)	C(5)−C(4)−Os(2)	80.6(7)
Si(1)−C(4)−Os(2)	124.6(7)	C(5)−C(4)−Os(1)	79.7(8)
Si(1)−C(4)−Os(1)	124.8(6)	Os(2)−C(4)−Os(1)	104.6(5)
C(4)−C(5)−Os(1)	65.6(7)	C(4)−C(5)−Os(2)	64.6(7)
C(4)−C(5)−Os(3)	122.6(9)	C(6)−C(5)−C(4)	125.0(12)
C(6)−C(5)−Os(1)	136.4(9)	C(6)−C(5)−Os(2)	130.0(8)
C(6)−C(5)−Os(3)	112.2(9)	Os(1)−C(5)−Os(2)	93.5(4)
Os(1)−C(5)−Os(3)	77.2(4)	Os(2)−C(5)−Os(3)	76.3(4)
C(5)−C(6)−C(7)	171.2(12)	C(6)−C(7)−C(8)	176.5(13)
Os(1)−Os(3)−Os(2)	75.0(1)	Os(1)−S(1)−Os(3)	73.2(1)
Os(1)−S(1)−Os(2)	92.3(1)	Os(2)−S(1)−Os(3)	72.3(1)

the coordinated Me₃SiCCC≡CFc ligand, formed by the cleavage of the S−C bond in the SC≡CSiMe₃ fragment, followed by a C−C coupling between the Me₃SiC≡C and C≡CFc groups. The extruded sulfur is located as a bridging ligand between the three osmium atoms. The nine carbonyls divided uniformly around each metal completed the structure. The ORTEP diagram of **5** is shown in Figure 5, and selected bonds and distances are given in Table 4. The Os(1)−Os(3) (2.872(1) Å) and Os(2)−Os(3) (2.848(1) Å) bond lengths are similar to those found in the open triangular clusters **2** and **3**. The C(4)−C(5) (1.381-(18) Å) and C(6)−C(7) (1.286(17) Å) bond distances are in the range expected for single and triple bonds, respectively.

Experimental Section

General Procedures. All reactions were performed under an argon atmosphere. Reagent grade solvents were dried by standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer 1650 FTIR spectrophotometer. ¹H and ¹³C NMR spectra were recorded on Bruker AMX-300 and DRX-500 instruments, respectively. $Os_3(CO)_{10}(NCMe)_2$[27] and $FcC\equiv CSC\equiv CSiMe_3$[3a] were prepared according to published procedures. Product separations were performed by TLC using silica plates.

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with $C_5H_5FeC_5H_4C\equiv CSC\equiv CSiMe_3$. Method A. $FcC\equiv CSC\equiv CSiMe_3$ (65.2 mg, 0.193 mmol)

(27) King, R. B.; Eisch, J. J. *Organomet. Synth.* **1988**, *4*, 235.

was added to a solution of $Os_3(CO)_{10}(NCMe)_2$ (90 mg, 0.096 mmol) in CH_2Cl_2 (40 mL). The resulting mixture was stirred at room temperature (rt) for 3 h. The color of the mixture changed from orange to deep red. The solvent was removed under reduced pressure, and the products were separated on TLC using hexane−CH_2Cl_2 (10:1) as eluent. The first band yielded the orange compound $[Os_3(CO)_9(\mu\text{-}\eta^1\text{-}SC\equiv CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C\equiv CFc)]$ (**3**) (traces), followed by a second pink band of $[Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}SC\equiv CSiMe_3)\text{-}(\mu\text{-}\eta^2\text{-}C\equiv CFc)]$ (**2**) (0.021 g, 19%), while the third band gave the red compound $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}FcCCSC\equiv CSiMe_3)]$ (**1**) as the main product (0.060 g, 53%). The three compounds were crystallized by hexane at −20 °C.

Spectral data for **1**: IR (hexane) cm⁻¹: $\nu_{C\equiv C}$ 2100 (m); ν_{CO} 2068 (vs), 2055 (s), 2029 (s), 2012 (sh, w), 2006 (m), 1979 (sh, w), 1840 (w). ¹H NMR (CDCl₃, 300 MHz, 22 °C): δ 4.35 (t, 2H, C₅H₄, J = 1.9 Hz), 4.30 (t, 2H, C₅H₄, J = 1.9 Hz), 4.24 (s, 5H, C₅H₅), 0.27 (s, 9H, SiMe₃). MS-MALDI (ditranol): m/z 1190 [M⁺ + H], 1162 [M⁺ + H − CO]. Anal. Calc for $C_{27}H_{18}O_{10}SSiFeOs_3$ (found): C, 27.27 (27.44); H, 1.52 (1.62); S, 2.70 (2.64).

Spectral data for **2**: IR (hexane) cm⁻¹: $\nu_{C\equiv C}$ 2100 (w); ν_{CO} 2072 (s), 2056 (m), 2016 (vs), 2004 (m), 1996 (sh, w), 1981 (w). ¹H NMR (CDCl₃, 300 MHz, 22 °C): δ 4.58 (t, 2H, C₅H₄, J = 1.9 Hz), 4.42 (t, 2H, C₅H₄, J = 1.9 Hz), 4.29 (s, 5H, C₅H₅), 0.25 (s, 9H, SiMe₃). ¹³C NMR (CDCl₃, 500 MHz, 22 °C): 179.9, 178.1, 177.8, 175.9 (CO's), 117.1 (*C*-CFc), 105.4 (S*C*-C), 95.5 (C-*C*Fc), 85.8 (SC-*C*), 72.4, 71.0, 70.1 (C₅H₄), 70.64 (C₅H₅), 0.09 (SiMe₃). MS-MALDI (ditranol): m/z 1190 [M⁺ + H], 1162−1134 [M⁺ + H − nCO, n = 1, 2]. Anal. Calc for $C_{27}H_{18}O_{10}SSiFeOs_3$ (found): C, 27.27 (27.58); H, 1.52 (1.62); S, 2.70 (2.67).

Spectral data for **3**: IR (hexane) cm⁻¹: $\nu_{C\equiv C}$ 2106 (vw); ν_{CO} 2094 (w), 2074 (vs), 2049 (s), 2016 (s), 2006 (vs), 1982 (sh, w), 1977 (m). ¹H NMR (CDCl₃, 300 MHz, 22 °C): δ 4.69 (t, 2H, C₅H₄, J = 1.9 Hz); 4.45 (t, 2H, C₅H₄, J = 1.9 Hz); 4.26 (s, 5H, C₅H₅); 0.24 (s, 9H, SiMe₃). ¹³C NMR (CDCl₃, 500 MHz, 22 °C): 177.4, 174.4, 172.3 (CO's), 124.1 (*C*-CFc), 104.1 (S*C*-C), 85.8 (SC-*C*), 83.5 (C-*C*Fc), 70.6, 70.4, 69.3 (C₅H₄), 69.7 (C₅H₅), −0.03 (SiMe₃). MS-MALDI (ditranol): 1162 [M⁺ + H], 1134 [M⁺ + H − CO]. Anal. Calc for $C_{26}H_{18}O_9SSiFeOs_3$ (found): C, 27.10 (26.85); H, 1.64 (1.55); S, 2.75 (2.75).

Method B. A mixture of $Os_3(CO)_{10}(NCMe)_2$ (90 mg, 0.086 mmol) and $FcC\equiv CSC\equiv CSiMe_3$ (58.2 mg, 0.171 mmol) in toluene (35 mL) was stirred at 65 °C for 1 h. The color of the mixture changed from orange to brown. The solvent was then removed in vacuo, and the products were separated by TLC on silica gel using hexane−CH_2Cl_2 (10:1) as eluent. The first band gave an orange mixture of two compounds, $[Os_3(CO)_9(\mu\text{-}\eta^1\text{-}SC\equiv CSiMe_3)(\mu_3\text{-}\eta^2\text{-}C\equiv CFc)]$ (**3**) (0.041 g, 42%) together with the above-mentioned compound $[Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}SC\equiv CSiMe_3)(\mu\text{-}\eta^2\text{-}C\equiv CFc)]$ (**2**) (0.011 g, 11%), which were separated by a further repurification by TLC with a hexane−diethyl ether (20:1) solvent mixture. The second band yielded the green compound $[Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^3,\eta^3\text{-}\{C_5H_5FeC_5H_3CCC(S)C(SiMe_3)CHO\}]$ (**4**) (0.034 g, 34%), which was crystallized at −20 °C by hexane.

Spectral data for **4**: IR (hexane) cm⁻¹: ν_{CO} 2089 (m), 2074 (vs), 2054 (s), 2047 (sh, w), 2011 (vs), 1996 (s), 1986 (w), 1977 (m). ¹H NMR (CDCl₃, 300 MHz, 22 °C): δ 8.43 (s, 1H, CHO), 5.12 (d, 1H, CH of C₅H₃, J = 1.8 Hz), 4.73 (m, 2H, CH of C₅H₃), 4.04 (s, 5H, C₅H₅), 0.39 (s, 9H, SiMe₃). ¹³C NMR (CDCl₃, 500 MHz, 22 °C): 190.9 [C(O)H], 179.2, 177.9, 173.8, 172.3 (CO's), 131.3, 127.0, 124.0, 112.6 [(Si*C*=*C*(S)*C*-C], 93.9, 78.5, 77.8, 75.8, 71.5 (C₅H₃), 69.3 (C₅H₅), −0.36 (SiMe₃). MS-MALDI (ditranol): 1190 [M⁺ + H], 1162 [M⁺ + H − CO]. Anal. Calc for $C_{27}H_{18}O_{10}SSiFeOs_3$ (found): C, 27.27 (27.60); H, 1.52 (1.78); S, 2.70 (2.61).

Thermolysis of $[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{-}(Fc)CCSC\equiv CSiMe_3\}]$, 1. A solution of compound **1** (55 mg, 0.046 mmol) in toluene (30 mL) was stirred at 65 °C for 1 h. The color of the reaction mixture

Table 5. Crystallographic Data for Complexes 1−5

	1	**2**	**3**	**4**	**5**
empirical formula	$C_{27}H_{18}FeO_{10}Os_3SSi$	$C_{27}H_{18}FeO_{10}Os_3SSi$	$C_{26}H_{18}FeO_9Os_3SSi$	$C_{27}H_{18}FeO_{10}Os_3SSi$	$C_{26}H_{18}FeO_9Os_3SSi$
fw	1189.01	1189.01	1161.00	1189.01	1161.00
temperature [K]	200(2)	200(2)	200(2)	293(2)	200(2)
λ(Mo Kα) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$Pbca$	$P2_1/n$	$P2_1/c$
a [Å]; α [deg]	13.757(1); 116.8(1)	10.395(1); 70.1(1)	9.565(2)	10.875(1)	17.749(3)
b [Å]; β [deg]	16.676(2); 104.4(1)	11.737(1); 80.7(1)	32.852(2)	17.721(2); 100.1(1)	10.782(1); 118.4(1)
c [Å]; γ [deg]	16.838(2); 99.6(1)	14.941(1); 71.6(1)	39.838(6)	16.601(1)	18.093(1)
volume [Å^3]; Z	3158.3(5); 4	1623.5(2); 2	12518(3); 16	3149.2(5); 4	3046.5(6); 4
ρ_{calcd} [g cm^{-3}]	2.501	2.432	2.464	2.508	2.531
μ [mm^{-1}]	12.637	12.292	12.747	12.674	13.095
F(000)	2176	1088	8480	2176	2120
cryst size [mm]	$0.10 \times 0.10 \times 0.10$	$0.24 \times 0.15 \times 0.08$	$0.10 \times 0.10 \times 0.10$	$0.34 \times 0.16 \times 0.05$	$0.31 \times 0.27 \times 0.25$
θ range [deg]	5 to 25	3 to 27.5	5 to 27.5	3 to 25	3 to 27.5
index ranges	−15 to 16, −19 to 20, −20 to 20	−13 to 13, −15 to 15, −18 to 19	−12 to 12, −42 to 42, −51 to 51	−12 to 12, −21 to 21, −19 to 18	−23 to 23, −12 to 14, −23 to 23
no. of collected reflns	20 448	14 090	88 150	45 227	23 149
no. of indep reflns	11 327 [$R_{int} = 0.076$]	7450 [$R_{int} = 0.081$]	14298 [$R_{int} = 0.165$]	5475 [$R_{int} = 0.200$]	6968 [$R_{int} = 0.140$]
no. of reflns [$F > 4\sigma(F)$]	7568	5213	8018	3811	4498
goodness-of-fit on F^2	0.978	0.962	0.921	1.112	1.091
final R indices	R1 = 0.055, wR2 = 0.120	R1 = 0.045, wR2 = 0.092	R1 = 0.059, wR2 = 0.130	R1 = 0.069, wR2 = 0.146	R1 = 0.056, wR2 = 0.124
R indices (all data)	R1 = 0.097, wR2 = 0.138	R1 = 0.079, wR2 = 0.101	R1 = 0.126, wR2 = 0.150	R1 = 0.109, wR2 = 0.168	R1 = 0.098, wR2 = 0.145
largest diff peak hole [e Å^{-3}]	2.233/−3.081	2.718/−2.586	3.165/−2.471	2.239/−2.160	3.302/−2.122

changed from deep red to brown. The solvent was removed in vacuo, and the products were separated by TLC on silica gel using hexane−CH_2Cl_2 (10:1) as eluent. The first orange band gave compound **3** (0.009 g, 16%), followed by a second orange band of $[Os_3(CO)_9(\mu_3$-S)\{μ_3-η^2-\{SiMe$_3$\}CCC≡CFc\}] (**5**) (0.016 g, 29%), which was crystallized at room temperature by hexane. Finally, the third band lead to compound **4** as the main product (0.026 g, 47%).

Spectral data for **5**: IR (hexane) cm^{-1}: $\nu_{C≡C}$ 2186 (vw); ν_{CO} 2096 (w), 2069 (vs), 2064 (s), 2017 (sh, w), 2010 (m), 2004 (s), 1991 (w). ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 4.41 (t, 2H, C$_5$H$_4$, J = 1.9 Hz), 4.30 (t, 2H, C$_5$H$_4$, J = 1.9 Hz), 4.18 (s, 5H, C$_5$H$_5$), 0.35 (s, 9H, SiMe$_3$). MS-MALDI (dithranol): 1162 (M$^+$ + H calculated 1162), 1134 [M$^+$ + H − CO]. Anal. Calc for $C_{26}H_{18}O_9SSiFeOs_3$ (found): C, 26.85 (27.49); H, 1.55 (1.75); S, 2.75 (2.69).

X-ray Structure Determinations for Complexes 1−5. X-ray crystals of **1−5** were grown as described in the Experimental Section. Crystals of **4** were randomly mounted in a glass capillary and transferred to the diffractometer for characterization and data collection at room temperature. The rest of the complexes were covered with a layer of a viscous perfluoropolyether (Fomblin Y). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer at 200 K. The intensity data sets were collected on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for all the complexes are presented in Table 1.

The structures were solved, using the WINGX package,[28] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[29] Complexes **1** and **3** crystallized with two independent molecules in the unit cell. Absorption correction procedures were carried out using the multiscan SORTAV program[30] for complexes **1−3** and **5**, while a numerical method[31] was used for **4**. In all the cases the largest difference peaks and holes were located close ($\approx$1 Å) to the osmium atoms or the iron atom (peak of complex **2**).

All the non-hydrogen atoms were refined anisotropically, except C(601) in complex **1**, and C(6) in complex **4**, which could be only isotropically refined. All the hydrogen atoms were included, positioned geometrically, and refined by using a riding model except H(305) in complex **4**, which was located in the Fourier difference map and isotropically refined.

X-ray crystallographic files in CIF format for **1−5** have been deposited with the Cambridge Crystallographic Data Center.

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