Synthesis, characterization and reactivity studies of the new compound [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_5$FeC$_5$H$_3$CCC(S)C(Fc)CHO}]

Esther Delgado [a,*], Elisa Hernández [a], Ángel Nievas [a], María Villa [a],
Avelino Martín [b], Beatriz Alonso [a]

[a] *Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain*
[b] *Departamento de Química Inorgánica, Edificio de Farmacia, Universidad de Alcalá de Henares, 28871 Madrid, Spain*

Abstract

Processes such as S–C and C–H bond activations as well as C–C coupling reactions have taken place in the synthesis of the new compound [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_5$FeC$_5$H$_3$CCC(S)C(Fc)CHO}] (Fc = C$_5$H$_4$FeC$_5$H$_5$), which contains an aldehyde oxametallacycle. A reactivity study of it has been carried out. In addition, other new triosmium clusters such as [Os$_3$(CO)$_9$(μ_3,η^2-C≡CFc)(μ,η^1-SC≡CFc)], [Os$_3$(CO)$_{10}$(μ,η^2-C≡CFc)(μ,η^1-SC≡CFc)] and [Os$_3$(CO)$_9$(μ-CO)(μ_3,η^2-FcCCSC≡CFc)] have been prepared from the reaction of [Os$_3$(CO)$_{10}$(NCMe)$_2$] and FcC≡CSC≡CFc. All the compounds have been characterized by analytical and spectroscopic techniques. The crystal structures of [Os$_3$(CO)$_9$(μ_3,η^2-C≡CFc)(μ,η^1-SC≡CFc)] and [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_5$FeC$_5$H$_3$CCC(S)C(Fc)CHO}] have been determined by X-ray crystallography and some electrochemical studies have also carried out.
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Keywords: Triosmium carbonyls; Bis(ferrocenyl) thioether; Osmium thiolates

1. Introduction

During the last years, our research has been focussed on the reactivity of organosulfur compounds containing unsaturated C–C bonds, such as alkyne thioethers or dithioacetals of α,β-unsaturated ketones, in the presence of carbonyl clusters of metals of the iron triad [1]. Recently, we have observed that the presence of one ferrocenyl group in the thioether FcC≡CSC≡CSiMe$_3$ (Fc = C$_5$H$_4$FeC$_5$H$_5$) yields a more interesting reactivity than that showed by the analogous alkyne thioethers bearing organic groups RC≡CSC≡CR′ (R = R′ or R ≠ R′). Also, this reactivity depends on the metal nature. Thus, conversion of two FcC≡CSC≡CSiMe$_3$ molecules into the new dithioether SiMe$_3$CC(C$_2$Fc)SC(Fc)CSCCSiMe$_3$ by formation of a new S–C bond, has been confirmed in the preparation of the compound [Ru$_3$(CO)$_9${μ_3-η^2,η^4,η^3-Me$_3$SiCC(C$_2$Fc)SC-

(Fc)CSCCSiMe$_3$}] [1d], while the triosmium derivative [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_5$FeC$_5$H$_3$CCC(S)C(SiMe$_3$)-CHO}] [1f] containing the CHO end-capping thiolate C$_5$H$_5$FeC$_5$H$_3$CCC(S)C(SiMe$_3$)CHO has been obtained in the osmium case. On the basis of these results, we considered it to be of interest to explore the reactivity of the compound FcC≡CSC≡CFc with the activated cluster [Os$_3$(CO)$_{10}$(NCMe)$_2$]. These results are herein described.

2. Results and discussion

In a previous paper [1f], we described the synthesis of the compound [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_5$FeC$_5$H$_3$-CCC(S)C(SiMe$_3$)CHO}] by thermolysis of the cluster [Os$_3$(CO)$_9$(μ-CO)(μ_3,η^2-FcCCSC≡CFc)]. With the aim of extending this study to the analogous cluster [Os$_3$(CO)$_9$-(μ-CO)(μ_3,η^2-FcCCSC≡CFc)], we have carried out the following reactions. Initially, [Os$_3$(CO)$_{10}$(NCMe)$_2$] was treated with FcC≡CSC≡CFc in CH$_2$Cl$_2$ at room temperature and the compounds [Os$_3$(CO)$_{10}$(μ,η^2-C≡CFc)-

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* Corresponding author. Tel.: +34 914975268; fax: +34 914974833.
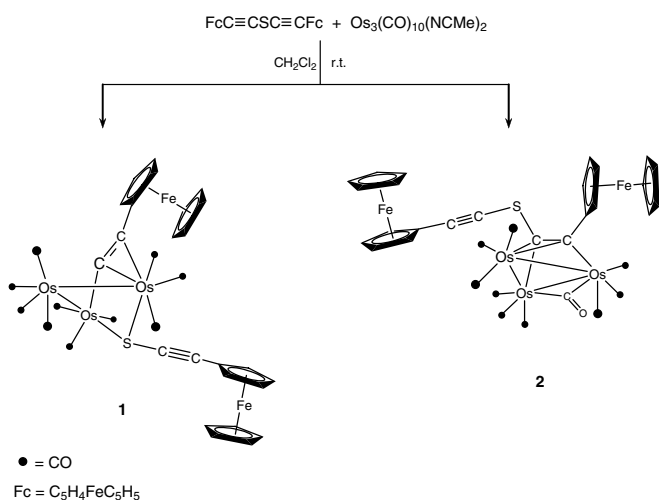*E-mail address:* esther.delgado@uam.es (E. Delgado).

$(\mu,\eta^1\text{-SC}\equiv\text{CFc})]$ **1** and $[\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3,\eta^2\text{-FcCC-}$
$\text{SC}\equiv\text{CFc})]$ **2** were obtained from the reaction by using a TLC separation (Scheme 1).

Further heating of compound **2** in toluene, gave compounds $[\text{Os}_3(\text{CO})_9(\mu_3,\eta^2\text{-C}\equiv\text{CFc})(\mu,\eta^1\text{-SC}\equiv\text{CFc})]$ **3** and $[\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2,\eta^3,\eta^3\text{-}\{\text{C}_5\text{H}_5\text{FeC}_5\text{H}_3\text{CCC}(\text{S})\text{C}(\text{Fc})\text{CHO}\}]$ **4** (Scheme 2).
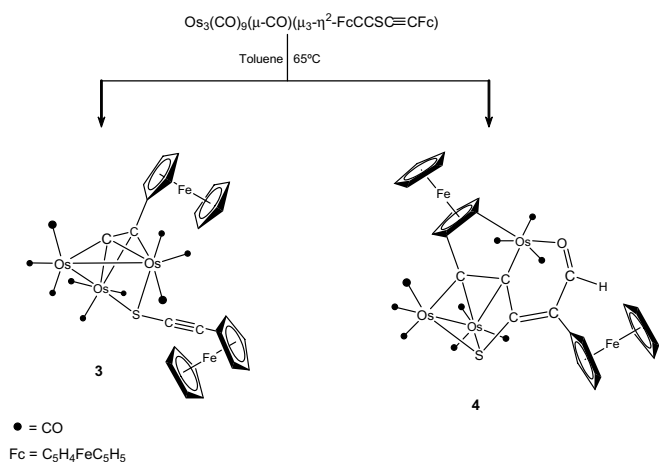
Spectroscopic data (^{1}H NMR, IR) of compound $[\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3,\eta^2\text{-FcCCSC}\equiv\text{CFc})]$ **2** are related to those of the cluster $[\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3,\eta^2\text{-FcCCSC}\equiv\text{C-}\text{SiMe}_3)]$ [1f]. Also, the carbonyl bands pattern in the IR spectrum is similar to those observed in other compounds $[\text{M}_3(\text{CO})_9(\mu\text{-CO})\text{L}]$ (M = Ru, Os; L = four-electron donor ligand) [2]. Resonances corresponding to the presence of two non-equivalent Fc groups, slightly shifted as compared with those of the free thioether [4], are exhibited in its ^{1}H NMR spectrum. In the FAB-MS of **2** appears the molecular ion as well as the fragmentation peaks corresponding to the loss of ten CO groups. We have found that the open triangular clusters $[\text{Os}_3(\text{CO})_{10}(\mu,\eta^2\text{-C}\equiv\text{CFc})(\mu,\eta^1\text{-SC}\equiv\text{C-}$

Fc)] **1** and $[\text{Os}_3(\text{CO})_9(\mu_3,\eta^2\text{-C}\equiv\text{CFc})(\mu,\eta^1\text{-SC}\equiv\text{CFc})]$ **3**, are formed via the cleavage of one Os–Os bond in the activated cluster $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ and an oxidative addition to the osmium atoms of the alkynethiolate and the acetylide fragments derived from the rupture across one S–C bond in the thioether FcC≡CSC≡CFc, respectively. The most remarkable difference between both compounds is centered on the coordination mode of the acetylide ligand, which is acting as a three-electron donor being σ coordinated to one Os and π coordinated to another Os atom in compound **1** and as a five-electron donor towards a σ, π, π coordination in compound **3**. The IR spectra of $[\text{Os}_3(\text{CO})_{10}(\mu,\eta^1\text{-SC}\equiv\text{CFc})(\mu,\eta^2\text{-C}\equiv\text{C-}$
Fc)] **1** and $[\text{Os}_3(\text{CO})_9(\mu,\eta^1\text{-SC}\equiv\text{CFc})(\mu_3,\eta^2\text{-C}\equiv\text{CFc})]$ **3** show the expected pattern for other similar open trinuclear clusters containing ten and nine CO ligands, respectively [1f,3]. Resonances corresponding to the two inequivalent ferrocenyl groups are observed in their ^{1}H NMR spectra. The analytical data as well as the FAB mass spectra are in agreement with their formula. An X-ray diffraction study of $[\text{Os}_3(\text{CO})_9(\mu_3,\eta^2\text{-C}\equiv\text{CFc})(\mu,\eta^1\text{-SC}\equiv\text{CFc})]$ **3** confirms the proposed structure. An ORTEP drawing of **3** is shown in Fig. 1.

Selected bond lengths and angles are given as figure caption. The Os(1)–Os(3) and Os(1)–Os(2) distances of 2.8804(7) and 2.8946(8), respectively, are within the range expected for metal–metal bond, but there is no bond between Os(2) and Os(3). The sulfur atom of the thiolate bridges the two non-bonded osmium atoms. The S(1)–Os(2) and S(1)–Os(3) distances, being almost identical, are indicating that the three electrons donated by the sulfur atom are located between both osmium metals. The C(1)–C(2) distance of 1.306(11) Å is in agreement with a σ, π, π coordination of the acetylide C≡CFc. In addition to the

FcC≡CSC≡CFc + Os₃(CO)₁₀(NCMe)₂

$\underset{\text{CH}_2\text{Cl}_2}{}$ r.t.

1

2

● = CO

Fc = C₅H₄FeC₅H₅

Scheme 1.

Os₃(CO)₉(μ-CO)(μ₃-η²-FcCCSC≡CFc)

Toluene | 65°C

3

4

● = CO
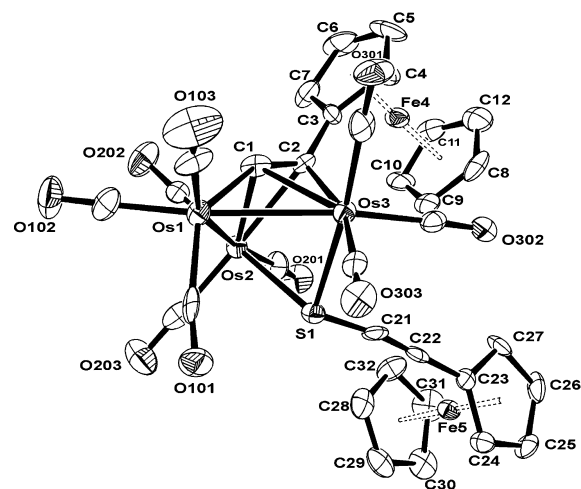
Fc = C₅H₄FeC₅H₅

Scheme 2.

Fig. 1. View of the crystal structure of compound **3** (thermal ellipsoids at the 50% probability level). Selected bond distances (Å) and angles (°). C(1)–C(2) 1.306(11), C(21)–C(22) 1.222(12), S(1)–Os(2) 2.451(2), S(1)–Os(3) 2.457(2), Os(1)–Os(3) 2.8804(7), Os(1)–Os(2) 2.8946(8), Os(3)–Os(1)–Os(2) 72.20(2), C(1)–C(2)–C(3) 135.8(8).

clusters **1**–**3**, one interesting compound has been obtained, this being proposed to be $[Os_3(CO)_9(\mu_3-\eta^2,\eta^3,\eta^3-\{C_5H_5FeC_5H_3CCC(S)C(Fc)CHO\}]$ **4** on the basis of analytical and spectroscopic data as compared with the previously prepared compound $[Os_3(CO)_9(\mu_3-\eta^2,\eta^3,\eta^3-\{C_5H_5FeC_5H_3CCC(S)C(SiMe_3)CHO\}]$ [1f]. Thus, the ^1H NMR data allows us to establish that the $C_5H_3FeC_5H_5$ fragment is η^1-bonded to the unit $Os(CO)_3$ [δ 4.67 (1H, C_5H_3), 4.70 (1H, C_5H_3), 5.10 (1H, C_5H_3)] and to confirm the presence of the aldehyde [δ 9.07, CHO]. In its positive FAB mass spectrum appears the peak corresponding to the molecular ion [m/z: 1302]. The structure of compound **4** has been determined by X-ray crystallography. A view of the molecule is depicted in Fig. 2.

According to X-ray data, compound $[Os_3(CO)_9(\mu_3-\eta^2,\eta^3,\eta^3-\{C_5H_5FeC_5H_3CCC(S)C(Fc)CHO\}]$ **4** is made up of the $Os_2(CO)_6$ [$Os(2)$–$Os(3)$ distance of 2.7442(7) Å] and $Os(CO)_3$ units linked by the CHO end-capping thiolate $\{C_5H_5FeC_5H_3CCC(S)C(Fc)CHO\}]$, which is acting as a ten-electron donor. Although trinuclear osmium compounds containing $Os_2(CO)_6$ and $Os(CO)_3$ fragments are frequently formed by rupture of Os–Os bonds in the cluster precursor, however, the most interesting aspect of **4** is that a consequence of the C–H bond activation in a C_5H_4 ring of one of the two $C_5H_4FeC_5H_5$ groups, a five-membered metallacycle as well as a six-membered aldehyde oxametallacycle have been formed around the same carbonyl osmium fragment. The C_{sp2}–H bond activation in the presence of transition metals is of great interest in chemical processes [4]. On the other hand, the reactions between ketones and ruthenium or osmium carbonyl clusters yield compounds containing oxametallacycles. For instance, $[Ru_3(CO)_6\{\mu_3-\eta^2,\eta^2,\eta^2-O=C(CH=CHPh)-CH=CPh\}_2]$ [5], $[Ru_3(CO)_7\{\eta^2-O=C(CH=CHPh)CH=CPh\}\{\mu-\eta^1,\eta^4-O-C(CH=CHPh)CH-CPh-CH(CH_2Ph)C(O)(CH=CHPh)\}$-

$\{\mu_3-\eta^1,\eta^1,\eta^4-(CH_2Ph)-CH=C(O)-CH=CHPh\}$ [5]. However, as far as we know, the use of aldehydes as reactants generate acylhydroderivatives $[Os_3(CO)_{10}(\mu-H)\{\mu-C(O)-R\}]$ ($R = C_5Me_4FeC_5Me_5$, $C_5H_4FeC_5H_5$) [6], ($R = Me$, n-C_5H_{11}, n-C_6H_{13}, $PhCH_2$, Me_2CH, Ph) [7], ($R = C_4H_3NH$, C_4H_3O, C_4H_3S) [8]. The scarce examples of aldehyde oxametallacycle derivatives reported have been obtained *in situ* towards different reaction processes. Thus, compound $[Os_3(CO)_{10}(\mu-H)(\mu_3,\eta^2-CHC(O)H)]$ [9] has been detected in a ^1H NMR experiment from the reaction between $Os_3(CO)_{10}(\mu-H)_2$ and 1-pentyne and a WRu_3 cluster containing an aldehyde oxametallacycle has been obtained from the reaction of $[Ru_3(CO)_{10}(NCMe)_2]$ and $[W(C\equiv CC\equiv CH)(CO)_3Cp]$ [10].

A possible explanation for the formation of compound $[Os_3(CO)_9(\mu_3-\eta^2,\eta^3,\eta^3-\{C_5H_5FeC_5H_3CCC(S)C(Fc)CHO\}]$ **4** could be as follows: initially, the C–H bond activation in a C_5H_4 ring yields the oxidative addition of a hydride ligand at the $Os(CO)_3$ fragment. Further insertion of a CO in the Os–H bond generates a CHO group that suffers a C–C coupling reaction with the carbon atom carrying the Fc substituent. Finally, the coordination through the oxygen atom gives the aldehyde oxametallacycle.

A sample of compound **4** was heated at 80 °C in toluene for 6 h to give a new triosmium derivative **5**. In the ^1H NMR spectrum, the absence of the resonance corresponding to one C_5H_5 group and the presence in the FAB-MS of the molecular ion peak, which value indicates the loss of the fragment $Fe(\eta^5-C_5H_5)$, allow us to formulate it as $[Os_3(CO)_9(\mu_3-\eta^2,\eta^3,\eta^3-\{C_5H_4CCC(S)C(Fc)CHO\}]$ **5** (Scheme 3).

Compounds in which one ferrocenyl group has been demetalated are known. For example, the synthesis of the compounds $[M(CO)_3(\eta^5-C_5H_4R)]$ ($M = Tc$, Re; R = ketone, ester, amide) [11] has been achieved by reaction of $C_5H_5FeC_5H_4R$ with MO_4^- ($M = Tc$, Re) in the presence of $CrCl_3$ and $Cr(CO)_6$, as a consequence of the loss of a $Fe(\eta^5-C_5H_5)$ fragment and the transference of the C_5H_4R ligand to the technetium or rhenium atom.
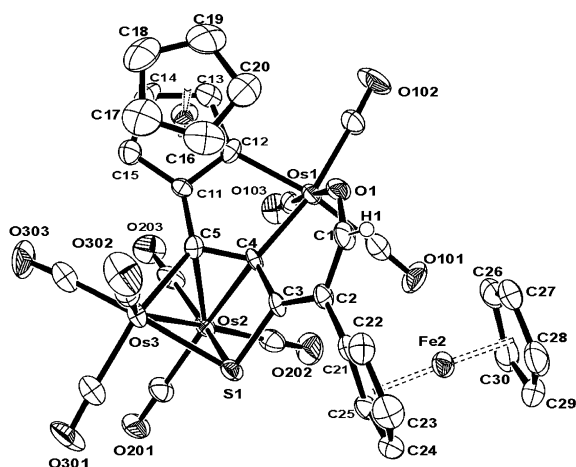
Fig. 2. View of the crystal structure of compound **4** (thermal ellipsoids at the 50% probability level). Selected bond distances (Å) and angles (°). C(1)–O(1) 1.270(10), C(12)–Os(1) 2.137(8), O(1)–Os(1) 2.179(6), Os(2)–Os(3) 2.7442(7), C(101)–Os(1)–C(12) 170.1(3), C(103)–Os(1)–O(1) 176.4(3), C(102)–Os(1)–C(4) 164.7(4).

$[Os_3(CO)_9(\mu_3-\eta^2,\eta^3,\eta^3-\{C_5H_5FeC_5H_3CCC(S)C(Fc)CHO\}]$

Toluene 80 °C

PPh$_2$H Toluene, 65 °C

5

6

● = CO
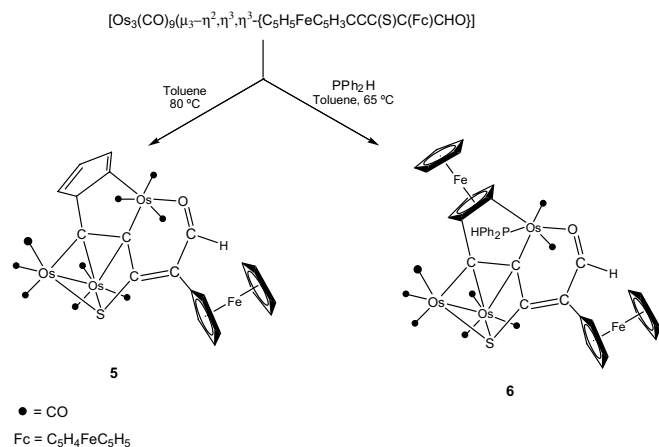
Fc = $C_5H_4FeC_5H_5$

Scheme 3.

Also, it has been reported the loss of one or two Fe(η^5-C$_5$H$_5$) fragments in the compound [Mn(CO)$_3$(η^5-C$_5$R$_5$)] (R = C$_5$H$_4$FeC$_5$H$_5$) [12].

In addition to the loss of the Fe(η^5-C$_5$H$_5$) fragment, the formation of compound [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_4$-CCC(S)C(Fc)CHO}] 5 implies as well the protonation of the remaining C$_5$H$_3$ ring, probably due to some moisture. Taking into account that the PPh$_2$H may afford H$^+$ and PPh$_2^-$, we have considered of interest to explore the thermolysis of compound 4 in the presence of PPh$_2$H. After 1.5 h at 80 °C, the ^{31}P NMR data indicated that several compounds were present in the reaction. Using a TLC separation, the only compound we were able to identify by spectroscopic data (see Section 5) was [Os$_3$(CO)$_8$-(PPh$_2$H)(μ_3-η^2,η^3,η^3-{C$_5$H$_5$FeC$_5$H$_3$CCC(S)C(Fc)CHO}] 6. This formula is in agreement with the value of the molecular ion peak observed in the positive FAB mass spectrum. In addition, a doublet signal (δ 8.72) corresponding to the proton of the aldehyde seems to indicate that the substitution of a CO by the phosphine has taken place in a *trans* position to the CHO group. An increase of the yield of compound 6 (8%), but still low is obtained when the reaction is carried out at lower temperature. Thus, the same reaction at 65 °C, affords compound 6 (20%) and another compound which decomposes in the TLC.

3. Electrochemical studies

Compounds containing a redox active group joined to another metal fragment or metal cluster via an unsaturated carbon chain, capable of allowing electronic communication between metal centers, are of interest from material science point of view. Due to the thioether FcC≡CSC≡CFc contains two ferrocenyl groups in the molecule, initially we were interested in exploring its electrochemical behavior. Its cyclic voltammogram shows only one two-electron oxidation for the ferrocenyl groups at $E_{1/2}$ = +0.620 V vs. SCE, indicating that both fragments are equivalent without electronic communication. In contrast, it has been reported that the compound FcC≡CC≡CFc shows two one-electron oxidations for the ferrocenyl group, as a consequence of a moderate degree of electronic communication between both redox groups [13]. Also, the electrochemical behavior observed for the disulfide complex MesSC$_5$H$_4$FeC$_5$H$_4$SSC$_5$H$_4$FeC$_5$H$_4$Mes is consistent with the existence of significant interactions between the two ferrocenyl units [14]. According to these results, we suggest that the presence of a sulfur atom as spacer between the two alkynyl fragments in compound FcC≡CC≡CFc may enlarge the distance enough to avoid any electronic communication. In addition, we have also analyzed how the coordination of this thioether to the triosmium core in the cluster [Os$_3$(CO)$_9$(μ-CO)(μ_3,η^2-FcCCSC≡CFc)] 2 may affect to its electrochemical behavior. Thus, we have observed a shift in the standard redox potential to a more negative voltage as compared

to FcC≡CSC≡CFc which indicates that the formation of the complex makes the oxidation easier. The cyclic voltammogram of 2 also shows only one two-electron redox process at $E_{1/2}$ = +0.609 V. This wave exhibited significant peak broadening as well as a large ΔE_p value, suggesting the occurrence of two closely spaced redox processes.

4. Conclusions

Compound [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_5$FeC$_5$H$_3$CCC-(S)C(Fc)CHO}] 4, which contains an aldehyde oxametallacycle, has been obtained from the reaction of FcC≡CSC≡CFc with Os$_3$(CO)$_{10}$(NCMe)$_2$ towards several processes such as S–C bond cleavage, C–C coupling reactions and C$_{sp2}$–H bond activation.

Thermal treatment of the compound [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_5$FeC$_5$H$_3$CCC(S)C(Fc)CHO}] 4 favours the demetallation of one Fe(η^5-C$_5$H$_5$) fragment to generate [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_4$CCC(S)C(Fc)CHO}] 5.

Electronic communication has not been observed between the two Fc groups either in the thioether FcC≡CSC≡CFc or in the cluster [Os$_3$(CO)$_9$(μ-CO)(μ_3,η^2-FcCCSC≡CFc)] 2.

5. Experimental

5.1. General procedures

All reactions were carried out under argon atmosphere. Solvents were dried using standard methods. IR spectra were recorded on a Perkin–Elmer Spectrum BX FT-IR spectrophotometer using NaCl cells. ^{1}H and ^{31}P NMR spectra were registered on a Bruker AMX-300 instrument. Elemental analyses were performed on a Perkin–Elmer 240-B microanalyzer. FAB mass spectra were carried out on a WG Autospect Spectrometer using 3-nitrobenzyl alcohol as matrix. [Os$_3$(CO)$_{10}$(NCMe)$_2$] [15] and [FcC≡CSC≡CFc] [1d] were prepared according to published procedures. Product separations were performed by TLC using silica plates.

5.2. Reaction of [Os$_3$(CO)$_{10}$(NCMe)$_2$] with [FcC≡CSC≡CFc]

A mixture of Os$_3$(CO)$_{10}$(NCMe)$_2$ (100 mg, 0.107 mmol) and FcC≡C–S–C≡CFc (48 mg, 0.107 mmol) in dichloromethane (60 mL) was stirred under argon at room temperature for 3.5 h. The color of the mixture changed from orange to brown. The solvent was removed under reduced pressure and the products were separated by TLC using hexane–CH$_2$Cl$_2$ (10:3) as eluent. The first orange band gave compound [Os$_3$(CO)$_{10}$(μ,η^1-SC≡CFc)(μ,η^2-C≡CFc)] 1 (19 mg, 0.014 mmol, 14%) followed by a red band of [Os$_3$(CO)$_9$(μ-CO)(μ_3,η^2-FcCCSC≡CFc)] 2 (74 mg, 0.056 mmol, 53%).

Spectral data for 1: IR (hexane) cm^{-1} ν_{CO} 2101 m, 2070 s, 2056 m, 2016 vs, 2002 m, 1980 w. ^{1}H NMR (CDCl$_3$,

300 MHz, 22 °C) δ 4.24 (t, $J = 1.9$ Hz, 2H, C_5H_4), 4.26 (s, 5H, C_5H_5), 4.30 (s, 5H, C_5H_5), 4.41 (t, $J = 1.9$ Hz, 2H, C_5H_4), 4.46 (t, $J = 1.9$ Hz, 2H, C_5H_4), 4.63 (t, $J = 1.9$ Hz, 2H, C_5H_4). MS (FAB$^+$) m/z: 1302 [M$^+$+H], 1245–1020 [M$^+$−nCO, $n = 2$–10]. Anal. Calc. for $C_{34}H_{18}Fe_2O_{10}Os_3$-S · C_6H_{14}: C, 34.63; H, 2.33; S, 2.31. Found: C, 34.27; H, 2.29; S, 2.42%.

Spectral data for **2**: IR (hexane) cm^{-1} ν_{CO} 2099 m, 2068 vs, 2055 s, 2029 s, 2007 s, 1996 sh, 1840 w. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C) δ 4.26 (s, 5H, C_5H_5), 4.28 (s, 5H, C_5H_5), 4.30–4.32 (m, 4H, C_5H_4), 4.40 (t, $J = 1.9$ Hz, 2H, C_5H_4), 4.53 (t, $J = 1.9$ Hz, 2H, C_5H_4). MS (FAB$^+$) m/z: 1302 [M$^+$+H], 1273–1022 [M$^+$−nCO, $n = 1$–10]. Anal. Calc. for $C_{34}H_{18}Fe_2O_{10}Os_3S$ · 1/2C_6H_{14}: C, 33.06; H, 1.87; S, 2.31. Found: C, 33.02; H, 2.08; S, 2.24%.

5.3. Thermolysis of [Os$_3$(CO)$_9$(μ-CO)(μ_3,η^2-FcCCSC≡CFc)] 2

A solution of compound **2** (148 mg, 0.114 mmol) in toluene (60 mL) was stirred at 65 °C for 2 h. The color of the reaction changed from deep red to brown. The solvent was removed in vacuo and the products were separated by TLC using hexane/CH$_2$Cl$_2$ (10:3) as eluent. The first orange band afforded compound [Os$_3$(CO)$_9$(μ,η^1-SC≡CFc)-(μ_3,η^2-C≡CFc)] **3** (45 mg, 0.035 mmol, 31%). The second band yielded the green compound [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_5$FeC$_5$H$_3$CCC(S)C(Fc)CHO}] **4** (18 mg, 0.014 mmol, 12%). Crystals of **3** and **4** suitable for X-ray studies were obtained in hexane/dichloromethane and hexane/THF at −20 °C, respectively.

Spectral data for **3**: IR (hexane) cm^{-1} ν_{CO} 2094 w, 2073 vs, 2048 s, 2015 s, 2005 vs, 1977 m. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C) δ 4.24 (s, 5H, C_5H_5), 4.25 (m, 2H, C_5H_4), 4.29 (s, 5H, C_5H_5), 4.45 (t, $J = 1.9$ Hz, 2H, C_5H_4), 4.47 (t, $J = 1.9$ Hz, 2H, C_5H_4), 4.73 (t, $J = 1.9$ Hz, 2H, C_5H_4). MS (FAB$^+$) m/z: 1274 [M$^+$+H], 1245–1019 [M$^+$−nCO, $n = 1$–9]. Anal. Calc. for $C_{33}H_{18}Fe_2O_9Os_3$-S · C_6H_{14}: C, 34.46; H, 2.37; S, 2.36. Found: C, 34.62; H, 2.21; S, 2.72%.

Spectral data for **4**: IR (hexane) cm^{-1} ν_{CO} 2088 s, 2073 vs, 2052 s, 2009 vs, 2006 sh, 1996 s, 1983 w, 1976 w. IR (KBr) cm^{-1} $\nu_{C=O}$ 1648 w. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C) δ 4.07 (s, 5H, C_5H_5), 4.22 (s, 5H, C_5H_5), 4.38–4.40 (m, 1H, C_5H_4), 4.41–4.45 (m, 2H, C_5H_4), 4.57 (td, $J = 1.3$ Hz, $J = 2.5$ Hz, 1H, C_5H_4), 4.67 (dd, $J = 0.9$ Hz, $J = 2.5$ Hz, 1H, C_5H_3), 4.70 (t, $J = 2.5$ Hz, 1H, C_5H_3), 5.10 (dd, $J = 0.9$ Hz, $J = 2.5$ Hz, 1H, C_5H_3), 9.07 (s, 1H, CHO). MS (FAB$^+$) m/z: 1302 [M$^+$+H], 1273 [M$^+$−CO]. Anal. Calc. for $C_{34}H_{18}Fe_2O_{10}Os_3S$ · C_6H_{14}: C, 34.63; H, 2.33; S, 2.31. Found: C, 34.85; H, 2.33; S, 2.30%.

5.4. Thermolysis of [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_5$FeC$_5$H$_3$CCC(S)C(Fc)CHO}] 4

A solution of compound **4** (18 mg, 0.014 mmol) was stirred in toluene (20 mL) at 80 °C for 6 h. The color of the

reaction changed from dark green to brown. The solvent was removed under reduced pressure and the product was separated by TLC using hexane–dichloromethane (10:3) as eluent, affording the dark green compound [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_4$CCC(S)C(Fc)CHO}] **5** (3 mg, 0.0025 mmol, 18%).

Spectral data for **5**: IR (hexane) cm^{-1} ν_{CO}: 2093 m, 2076 vs, 2056 s, 2013 sh, 2007 vs, 2002 vs, 1989 w, 1982 w. IR (KBr) cm^{-1} $\nu_{C=O}$ 1647 w. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C) δ 3.81 (m, 1H, C_5H_4), 4.21 (s, 5H, C_5H_5), 4.35 (td, $J = 1.3$ Hz, $J = 2.5$ Hz, 1H, Fe-η^5-C_5H_4), 4.37 (dt, $J = 1.3$ Hz, $J = 2.6$ Hz, 1 H, Fe-η^5-C_5H_4), 4.44 (dt, $J = 1.3$ Hz, $J = 2.5$ Hz, 1H, Fe-η^5-C_5H_4), 4.58 (td, $J = 1.3$ Hz, $J = 2.6$ Hz, 1H, Fe-η^5-C_5H_4), 6.56 (td, $J = 0.8$ Hz, $J = 2.5$ Hz, 1H, C_5H_4), 6.59 (ddd, $J = 0.6$ Hz, $J = 2.5$ Hz, $J = 4.7$ Hz, 1H, C_5H_4), 7.09 (td, $J = 1.2$ Hz, $J = 4.8$ Hz, 1H, C_5H_4), 9.02 (s, 1H, CHO). MS (FAB$^+$) m/z: 1182 [M$^+$+H], 1154–901 [M$^+$−nCO, $n = 1$–10].

5.5. Reaction of [Os$_3$(CO)$_9$(μ_3-η^2,η^3,η^3-{C$_5$H$_5$FeC$_5$H$_3$CCC(S)C(Fc)CHO}] 4 with PPh$_2$H

A stoichiometric amount of the secondary phosphine PPh$_2$H (0.013 mmol, 2.3 μL) was added to a solution of compound **4** (17 mg, 0.013 mmol) in toluene (20 mL) at 65 °C. The mixture was stirred for 3 h. Then, the solvent was removed in vacuo and the green compound [Os$_3$(CO)$_8$(PPh$_2$H)(μ_3-η^2,η^3,η^3-{C$_5$H$_5$FeC$_5$H$_3$CCC(S)C(Fc)-CHO}] **6** was obtained, as main product (4 mg, 0.0027 mmol, 20%), by TLC using hexane–CH$_2$Cl$_2$ (10:3) as eluent.

Spectral data for **6**: IR (hexane) cm^{-1} ν_{CO}: 2078 s, 2049 vs, 2017 s, 2004 s, 1987 sh, 1981 m, 1969 m, 1954 s. IR (KBr) cm^{-1} $\nu_{C=O}$ 1651 w. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C) δ 4.02 (s, 5H, C_5H_5), 4.09 (s, 5H, C_5H_5), 4.20 (m, 1H, C_5H_4), 4.33 (m, 2H, C_5H_4), 4.63–4.69 (m, 2H, C_5H_3, C_5H_4), 4.79 (m, 1H, C_5H_3), 5.12 (m, 1H, C_5H_3), 6.65 (d, $J_{H-P} = 346.5$ Hz, 1H, H-P), 7.65–7.15 (m, 10H, C_6H_5), 8.72 (d, $^4J_{H-P} = 1.9$ Hz, 1H, CHO). ^{31}P{^{1}H} NMR (CDCl$_3$, 300 MHz, 22 °C) δ −1.46. MS (FAB$^+$) m/z: 1460 [M$^+$+H], 1274 [M$^+$−PPh$_2$H], 1105–1021 [M$^+$−PPh$_2$-H−nCO, $n = 6$–9].

5.6. Electrochemical studies

The experiments were performed on 10^{-3} M dichloromethane solutions of either the thioether FcC≡CSC≡CFc and compound [Os$_3$(CO)$_9$(μ-CO)(μ_3,η^2-FcCCSC≡CFc)] **2**, with supporting electrolyte 0.1 M ^{n}Bu$_4$NPF$_6$, using SCE as the reference electrode, along with platinum working and auxiliary electrodes, and a scan rate of 100 mV s^{-1}.

5.7. X-ray diffraction analysis of 3 and 4

Crystals of complexes **3** and **4** were grown from saturated hexane/dichloromethane and hexane/THF solutions at −20 °C, respectively, removed from the Schlenks and

Table 1
Crystal data and details of the structure of compounds **3** and **4**

Compound	3	4
Empirical formula	$C_{33}H_{18}Fe_2O_9Os_3S$	$C_{34}H_{18}Fe_2O_{10}Os_3S \cdot C_4H_8O \cdot 1/2C_6H_{14}$
Formula weight	1272.83	1416.03
Temperature (K)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	$Pbca$	$\bar{P}$
a (Å)	10.341(4)	10.453(2)
b (Å)	22.173(5)	12.157(1)
c (Å)	28.817(7)	17.961(4)
α (°)		108.22(1)
β (°)		92.55(2)
γ (°)		98.04(1)
V (Å^3)	6607(3)	2137.3(7)
Z	8	2
D_{calc} (mg/m^3)	2.559	2.199
Absorption coefficient (mm^{-1})	12.47	9.65
$F(000)$	4672	1324
Crystal size (mm^3)	$0.43 \times 0.34 \times 0.17$	$0.10 \times 0.10 \times 0.10$
Theta range for data collection (°)	3.04–27.7	3.14–27.5
Index ranges	−13 to 13, −28 to 28, −37 to 21	−13 to 13, −15 to 15, −23 to 23
Reflections collected	42 593	43 528
Independent reflections [R(int)]	7671 [0.166]	9786 [0.055]
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	0.927	0.993
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.045$, $wR_2 = 0.075$	$R_1 = 0.054$, $wR_2 = 0.128$
R indices (all data)	$R_1 = 0.105$, $wR_2 = 0.086$	$R_1 = 0.069$, $wR_2 = 0.136$
Largest difference in peak and hole	1.644 and −2.052	2.694 and −4.614

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. The intensity data sets were collected at 200 K 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 [16], by direct methods (SHELXS-97) and refined by least-squares against F2 (SHELXL-97) [17].

Each molecule of complex **4** crystallized together with a molecule of tetrahydrofuran and half of hexane. All non-hydrogen atoms of **3** and **4** were anisotropically refined. The hydrogen atoms were positioned geometrically and refined by using a riding model.

6. Supplementary data

CCDC 654361 and 654362 contain the supplementary crystallographic data for compounds **3** and **4**. These data

can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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