

Triosmium compounds containing the oxametallacycle [Os(CO)₃{C(R)=CHC(O)CH=C(H)C₅H₄FeC₅H₅}] moiety. Synthesis and electrochemical studies

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Dedicated to Professor Victor Riera for his contribution to Organometallic Chemistry.

Abstract

The compounds [Os₃(CO)₁₀{μ,η³-(SCH₂CH₂SC=CHC(O)CH=CH(C₅H₄)Fe(C₅H₅)}] (2), [Os₃(CO)₉{μ,η³-(SCH₂CH₂SC=CHC(O)CH=CH(C₅H₄)Fe(C₅H₅)}] (3) and [Os₃(CO)₈{μ₃,η²-(C=CHC(O)CH=CH(C₅H₄)Fe(C₅H₅))(SCH₂CH₂S)}] (4) have been obtained by rupture of S–C bonds in the ketene dithioacetal [C₅H₅FeC₅H₄CH=CHC(O)CH=C(SCH₂CH₂S)], in their reaction with the activated cluster [Os₃(CO)₁₀(NCMe)₂]. The presence of an oxametallacycle in these derivatives has been confirmed by an X-ray diffraction analysis. The electrochemical study has indicated the ability of these compounds to modify the electrode surfaces.

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1. Introduction

Metal complexes containing α,β-unsaturated ketone systems are useful intermediates in the synthesis of organic compounds [1]. Previous reports on [M₃(CO)₁₂] (M = Fe, Ru) chemistry with this type of ligand has confirmed the formation of di-, tri-, penta- and hexanuclear derivatives which have in common at least one five-membered oxametallacycle [2]. The synthesis of compounds with nuclearity higher than two is favoured by the propensity of the oxametallacycle to associate with another metal with the lone electron pair of the oxygen atom of the C=O group as well as the C=C bond

i.e. [Ru₃(CO)₆{μ₃-η²,η²,η³-OC(CH=CHPh)CH=CPh}₂, {Ru₅(CO)₁₁(μ₄-O)(μ₃-H)(p-MeC₆H₄C(O)C(H)=CPh)₃} and {Ru₆(CO)₁₂(μ-CO)₂(μ-H)₂(μ₄-O)(μ-RCOCH=CPh)₂}] [3]. The coordination chemistry of α,β-unsaturated ketones containing β-positioned heteroatoms, such as the ketene dithioacetals, is very interesting due to the multifunctional coordination sites they show. However, studies on their reactivity with transition metals are very limited. The chemistry of ring opening in heterocyclic containing sulphur atoms is of great interest from the hydrodesulphurization (HDS) processes point of view [4]. On the other hand, although compounds containing vinylidene ligands bonded to several metals have been considered as models in processes that imply rearrangements between different hydrocarbons chemisorbed on metal surfaces, as far as we know, not many homopolynuclear derivatives of the iron triad containing this type of ligands have been prepared [5]. Although most of the vinylidene derivatives described have been generated

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by modifications of cluster-bounded ligands such as CO, alkylidene, alkynyl, ketenylidenes, in recent years, we have found a new route to prepare them [2e]. Thus, $\text{Ru}_3(\text{CO})_{12}$ reacts with $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{CH}=\text{C}(\text{SCH}_2\text{CH}_2\text{S})$, in the presence of Me_3NO , to yield the tetraruthenium vinylidene compound $[\text{Ru}_4(\text{CO})_{10}\{\mu_3\text{-(SCH}_2\text{CH}_2\text{S)}\}\{\mu_4,\eta^3\text{-(C}=\text{CHC}(\text{O})\text{CH}=\text{CHC}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)\}]$ by cleavage of the two S–C bonds in the dithioacetal. In contrast, mono and binuclear species, $[\text{Fe}(\text{CO})_3\{\eta^4\text{-(C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{CH}=\text{C}(\text{SCH}_2\text{CH}_2\text{S)})\}]$ and $[\text{Fe}_2(\text{CO})_5\{\mu,\eta^4\text{-(SCH}_2\text{CH}_2\text{SC}=\text{CHC}(\text{O})\text{CH}=\text{CHC}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)\}]$, were isolated using $\text{Fe}_3(\text{CO})_{12}$ instead. In the iron mononuclear compound the C=C and C=O bonds of the dithioacetal act as a π,π -coordinated ligand, while a metallacycle is formed in the dinuclear derivative as a consequence of the cleavage of one S–C bond. On the basis of these results, it appears that the presence of sulphur atoms in the dithioacetal as compared with the ketones before mentioned, which do not have these heteroatoms in the β position, does not affect to the tendency to generate stable oxametallacycles. However, the lone electron pair on these chalcogenide atoms give them a preferential position, to act as bridging ligands related to the olefinic group present in the metallacycle. Our interest now, consists of exploring the reactivity of the compound $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{CH}=\text{C}(\text{SCH}_2\text{CH}_2\text{S})]$ **1** in the presence of the activated cluster $\text{Os}_3\text{-(CO)}_{10}(\text{NCMe})_2$ in order to complete the study on this organo-sulphur compound towards the iron triad metals. Furthermore, the interest was the study of the potential electronic communication between the ferrocenyl (Fc) group and the osmium atoms. Herein we report the synthesis, characterization and electrochemical studies of a series of new osmium compounds.

2. Results and discussion

We have previously described [2e] the synthesis and spectroscopic characterization of compound **1** and here we present its crystal structure. Single crystals for X-ray diffraction were obtained from CH_2Cl_2 /hexane at -20°C .

Two enantiomers are present in the crystal in a 93–7% (major/minor) ratio. The Fig. 1 depicts a view of the molecule of the major enantiomer. The C(11)–C(12) [1.341(5) Å] and C(14)–C(15) [1.355(5) Å] distances are in the expected range for a double bond [6]. The distances of 1.748(3) Å for C(15)–S(1) and 1.743(3) Å for C(15)–S(2) compare well with another dithioacetals [7]. The 1,3-dithiolane ring adopts an envelope shape, in which the C(16) atom acts as a flat with a mean plane deviation of 0.566 Å.

The compound $[\text{Os}_3(\text{CO})_{10}\{\mu,\eta^3\text{-(SCH}_2\text{CH}_2\text{SC}=\text{CHC}(\text{O})\text{CH}=\text{CH}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)\}]$ (**2**) has been obtained from the reaction of the activated osmium cluster $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ and $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{CH}=\text{C}(\text{SCH}_2\text{CH}_2\text{S})]$ in CH_2Cl_2 at 45°C , after TLC purification (Scheme 1).

The carbonyl pattern in its IR spectrum [2109 (m), 2071 (vs), 2030 (sh), 2028 (s), 2005 (s), 1985 (m), 1975 (w), 1962 (w)] compares well with analogous open triangular clusters such as $[\text{Os}_3(\text{CO})_{10}\{\mu\text{-(SCH}_2\text{CMe}_2\text{CH}_2)_3\}]$ [8] and $[\text{HOs}_3\text{-(CO)}_{10}(\eta^3,\eta^1,\eta^1\text{-OC}_4\text{H}_2\text{CCHCHPh})]$ [9]. The coordination to one osmium atom of the ketonic group to generate a metallafurene, was observed by IR spectroscopy in KBr pellets ($\nu_{\text{C}=\text{O}}$ 1618 cm^{-1}). The ^1H NMR spectrum of compound **2** showed all resonances corresponding to the organic groups present in the molecule, the most important of which are four resonances for the $\text{SCH}_2\text{CH}_2\text{S}$ fragment (δ 3.77, 3.17, 2.93 and 2.58) indicating their

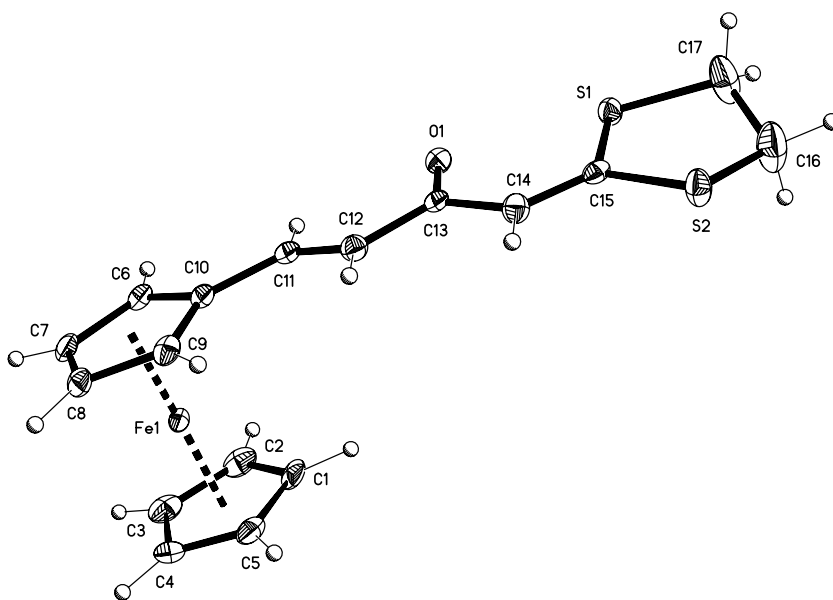
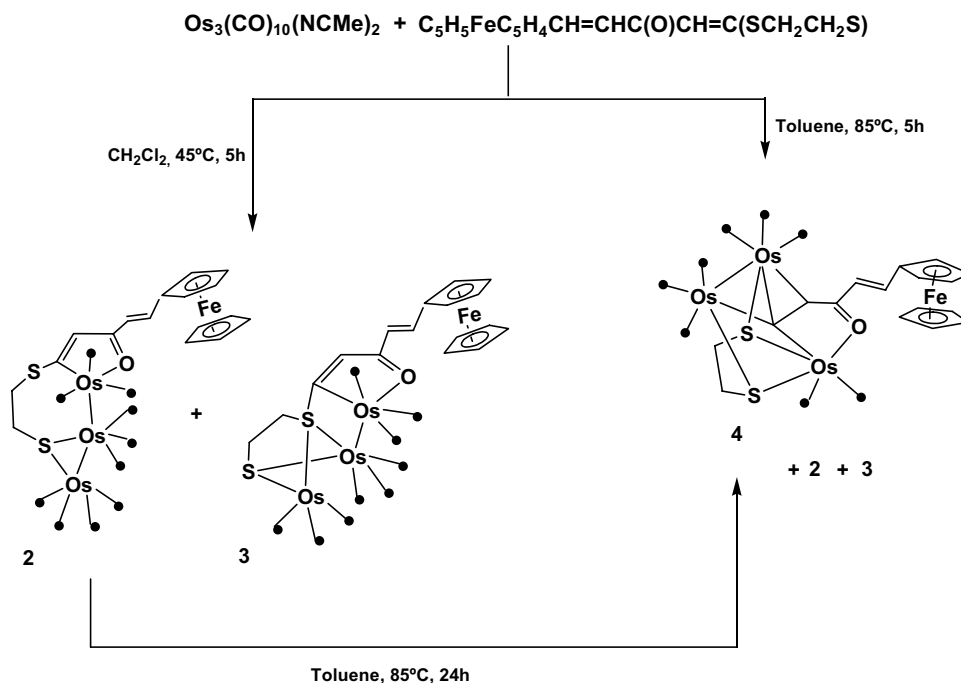


Fig. 1. Molecular structure of **1**. Selected bond lengths (Å) and angles ($^\circ$): C(11)–C(12) 1.341(5), C(14)–C(15) 1.355(5), C(13)–O(1) 1.233(4), S(1)–C(15) 1.748(3), S(2)–C(15) 1.743(3), C(14)–C(15)–S(2) 119.9(2), C(14)–C(15)–S(1) 125.3(2), C(17)–C(16)–S(2) 109.1(3), C(16)–C(17)–S(1) 110.3(3). Ellipsoids are drawn at the 50% probability level.



Scheme 1.

inequivalence, as compared with those observed for $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{CH}=\text{C}(\text{SCH}_2\text{CH}_2\text{S})]$ (δ 3.46 and 3.37). A signal at δ 7.04 was slightly shifted to lower field than the observed in the organosulphur precursor (δ 6.77), and was assigned to the $\text{CH}=\text{C}$ proton. The remaining resonances are slightly modified as compared to those

exhibited for the ketene dithioacetal. Its ^{13}C NMR spectrum shows all resonances corresponding to the ferrocenyl, olefinic and carbonyl groups present in the cluster. The structure of compound **2** has been confirmed by X-ray studies and it is shown with an atom numbering scheme in Fig. 2.

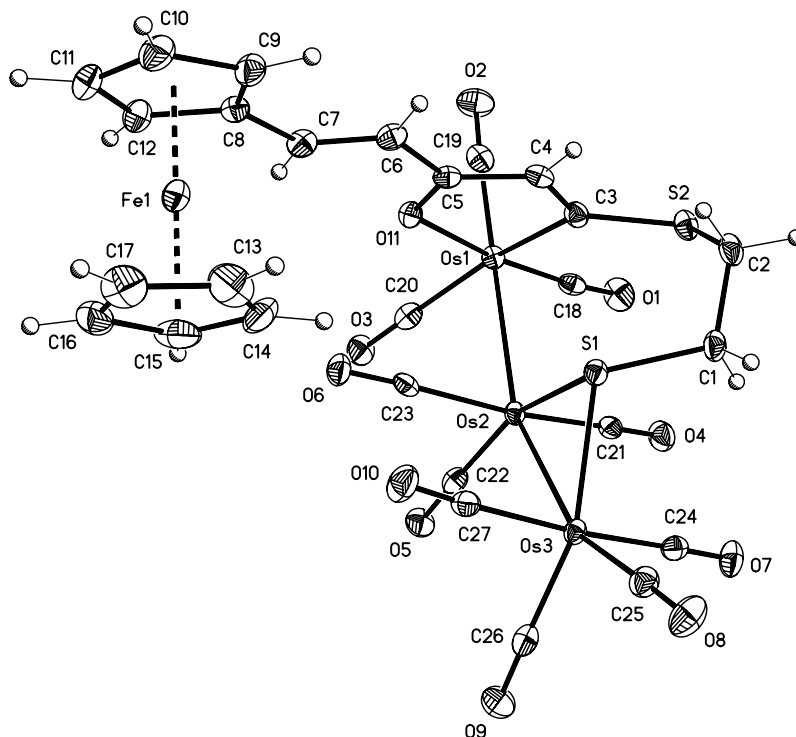


Fig. 2. Molecular structure of **2**. Selected lengths (\AA) and angles ($^\circ$): $\text{Os}(1)\text{--Os}(2)$ 2.9168(2), $\text{Os}(2)\text{--Os}(3)$ 2.8660(2), $\text{Os}(1)\text{--O}(11)$ 2.107(2), $\text{O}(11)\text{--C}(5)$ 1.297(5), $\text{C}(3)\text{--C}(4)$ 1.372(5), $\text{S}(1)\text{--Os}(2)$ 2.436(1), $\text{S}(1)\text{--Os}(3)$ 2.417(1), $\text{Os}(1)\text{--Os}(2)\text{--Os}(3)$ 156.171(7). Ellipsoids are drawn at the 50% probability level.

The crystal analysis reveals that the opening of the triangular osmium activated cluster as well as the cleavage of one S–C bond in the dithioacetal takes place in the reaction of $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{CH}=\text{C}(\text{SCH}_2\text{CH}_2\text{S})]$ with $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$. The new organic ligand oxidatively adds to the Os(1) atom towards an σ -C coordination and to the Os(2) and Os(3) atoms towards a thiolate ligand. The S(1) atom bridges the two osmium atoms almost symmetrically [Os(2)–S(1) 2.4363(9) and Os(3)–S(1) 2.4174(9) Å]. In addition, the coordination of the ketonic group by an σ -O bond to the Os(1) atom gives rise to a five-membered oxametallacycle. The value of $156.171(7)^\circ$ for Os(3)–Os(2)–Os(1) corresponds to a *quasi* linear metal core. Angles of 153.08° , $160.554(15)^\circ$ and $162.91(3)^\circ$ have been observed in the analogous compounds such as, $[\text{Os}_3(\text{CO})_{10}\{\mu\text{-(SCH}_2\text{CMe}_2\text{CH}_2)_3\}]$ [8], $[\text{Os}_3(\text{CO})_{11}(\mu_3\text{-}\eta^4\text{-Fc-C}_4\text{-C}\equiv\text{C-C=C-Fc})]$ [10a] and $[\text{Os}_3(\text{CO})_{11}(\mu_3\text{-}\eta^4\text{-(C}_4\text{H}_3\text{S})C}_2\text{C}_2\text{(C}_4\text{H}_3\text{S})]$ [10b] respectively, while angles of $70.4(1)^\circ$, $85.71(12)^\circ$ and $75.0(1)^\circ$ have been found for the angular clusters $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^1\text{-SC}\equiv\text{CSiMe}_3)$ ($\mu\text{-}\eta^2\text{-C}\equiv\text{CFc}$) [11], $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{CH}=\text{CHCH}_2\text{S})]$ [12], and $[\text{Os}_3(\text{CO})_9(\mu_3\text{-S})(\mu_3\text{-}\eta^2\text{-}\{(\text{Me}_3\text{Si})\text{CCC}\equiv\text{CFc}\})]$ [11] respectively.

The Os(1)–Os(2) and Os(2)–Os(3) bond distances are 2.9168(2) and 2.8660 Å(2) which are in the range expected for osmium–osmium bonds. 2.967(2) and 2.851(2) Å, 2.9431(4) and 2.9346(4) Å as well as 2.906(2) and 2.911(2) Å have been reported for the open triangular clusters $[\text{Os}_3(\text{CO})_{10}\{\mu\text{-(SCH}_2\text{CMe}_2\text{CH}_2)_3\}]$ [8], $[\text{Os}_3(\text{CO})_{11}(\mu_3\text{-}\eta^4\text{-Fc-C}_4\text{-C}\equiv\text{C-C=C-Fc})]$ [10a] and $[\text{Os}_3(\text{CO})_{11}(\mu_3\text{-}\eta^4\text{-(C}_4\text{H}_3\text{S})C}_2\text{C}_2\text{(C}_4\text{H}_3\text{S})]$ [10b] respectively.

The ferrocene unit is not much affected in the formation of **2** as compared with the uncoordinated ketene dithioacetal and the C–C bond distances and C–C–C-angles are in the usual range found in many other ferrocene derivatives. The open triangular cluster $[\text{Os}_3(\text{CO})_{10}\{\mu\text{-(SCH}_2\text{CMe}_2\text{CH}_2)_3\}]$ [8] in which, in addition to a thiolate group bridging two osmium atoms, there is a sulphurmetallacycle located around the third osmium instead of the oxametallacycle, is the most similar compound to cluster **2**, found in the library.

In addition to compound **2** a small amount of the new compound $[\text{Os}_3(\text{CO})_9\{\mu, \eta^3\text{-(SCH}_2\text{CH}_2\text{SC}=\text{CHC}(\text{O})\text{CH}=\text{CH}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)\})]$ (**3**) was separated as a second band by TLC. Analytical data as well as the presence in the FAB mass spectrum of the molecular peak (m/z 1179) and other peaks corresponding to the loss of nine carbonyls are in agreement with this formula. We initially thought that compound **3** could be generated from **2** by loss of one CO. However, when a dichloromethane solution of **2** was kept at the temperature reaction for 5 h, its conversion to compound **3** was not observed. This feature seems to indicate that both compounds are formed in different ways.

We were unable to grow suitable crystals for X-ray diffraction studies of compound **3**, but we speculate that it probably may show the structure indicated in Scheme 1, on the basis of spectroscopic data. The similarity observed

in the ^1H and ^{13}C NMR spectra of compounds **2** and **3** (see Section 5) seems to indicate that the same oxametallacycle has been formed in both compounds and no coordination towards the CH=C group to other osmium atom, has taken place. In addition, one remarkable feature that supports the proposed structure for **3** comes from its IR spectrum. The pattern exhibited in the carbonyl region (2087 m, 2048 s, 2013 vs, 2004 s, 2000 m, 1978 w, 1936 w) compare well with that showed by the compound $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2, \eta^4, \eta^3\text{-}[\text{Me}_3\text{SiCC}(\text{C}_2\text{Fc})\text{SC}(\text{Fc})\text{CSC}\equiv\text{CSiMe}_3])]$ [13] (2097m, 2071 s, 2036 vs, 2002 s, 1982 m) whose crystal structure, solved by X-ray diffraction confirmed that this ruthenium compound is formed by the $\text{Ru}(\text{CO})_3$ and $\text{Ru}_2(\text{CO})_6$ fragments linked by an organic ligand.

When the reaction between $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ and $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{CH}=\text{C}(\text{SCH}_2\text{CH}_2\text{S})]$ was carried out in toluene at 85°C for 5 h, the new compound $[\text{Os}_3(\text{CO})_8\{\mu_3, \eta^2\text{-}\{C=\text{CHC}(\text{O})\text{CH}=\text{CH}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)\}(\text{SCH}_2\text{CH}_2\text{S})\}]$ (**4**) was isolated as the main product together to compounds **2** and **3** and another uncharacterized green derivative. Compound **4** has been crystallographically characterized (Fig. 3).

The molecule is made up of the $\text{Os}(\text{CO})_2$ and $\text{Os}_2(\text{CO})_6$ fragments joined by vinylidene and dithiolate ligands which have been generated by cleavage of the two S–C bonds in the dithioacetal. The vinylidene group acts as $\mu_3\text{-}\eta^2$ ligand being $\sigma\text{-C}(1)$ coordinated to the Os(1) and Os(2) atoms and $\pi\text{-C}=\text{C}$ to the third Os(3) atom.

Although C=C double bond distances of 1.39(2) and 1.35(2) Å have been found in polynuclear derivatives, containing $\mu_3, \eta^2\text{-C}=\text{CH}(\text{R})$ ligands such as $[\text{Os}_3\text{H}_2\{C\text{-CH}(\text{OEt})\}]$ [14] and $[\text{Co}_2\text{Fe}(\text{CO})_9(\text{CCHFc})]$ [15], a value of 1.47(3) Å has been observed in compound **4**, which agrees with the value found [1.43(19) Å] in the tetra ruthenium compound containing a oxametallacycle $[\text{Ru}_4(\text{CO})_{10}\{\mu_3\text{-(SCH}_2\text{CH}_2\text{S})\}\{\mu_4, \eta^3\text{-(C}=\text{CHC}(\text{O})\text{CH}=\text{CHC}_5\text{H}_4\text{Fe}(\text{C}_5\text{H}_5)\})]$ [2e] [1.43(19) Å].

The five-membered oxametallacycle Os(1)O(3)–C(3)–C(2)C(1) is also present in compound **4**. The dithiolate ligand $\text{SCH}_2\text{CH}_2\text{S}$ acts as a 6-electron donor, bridging the three metals. A shift of the resonance of the vinylidene proton $\text{C}=\text{CH}(\text{R})$ group to higher field (δ 4.65), as compared to the respective values of δ 4.65, 7.04 and 7.34 for compounds **1**, **2** and **3** respectively, was observed in the ^1H NMR spectrum as a consequence of the π -coordination of this olefinic group to the Os(3) atom. The resonance corresponding to the C_α (85.1 ppm) of the vinylidene group was not observed in the ^{13}C NMR spectrum however; signals for the C_β of this group as well as that related to the other groups were seen.

We have before mentioned that compound **2** was not the precursor of compound **3**, however the compound **2** is totally converted to compound **4** by heating a sample of it in toluene at 85°C during 24 h. In all cases, the compounds obtained involve a five-membered oxametallacycle and only in compound **4** is, this metallacycle, coordinated to another osmium metal towards the olefinic group.

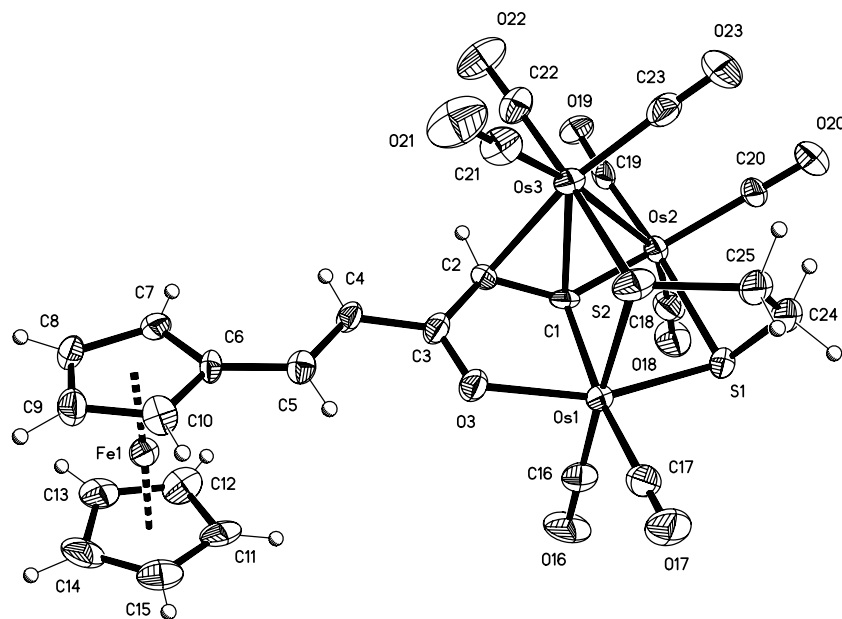


Fig. 3. Molecular structure of **4**. Selected lengths (Å): Os(2)–Os(3) 2.905(11), Os(1)–O(3) 2.119(9), O(3)–C(3) 1.255(16), C(1)–C(2) 1.429(18), Os(1)–S(1) 2.343(4), Os(2)–S(1) 2.506(4) Os(1)–S(2) 2.430(4), Os(3)–S(2) 2.443(4). Ellipsoids are drawn at the 50% probability level.

3. Electrochemical studies

The $(C_5H_5)Fe(C_5H_4)$ is an important donor electron group. Its presence at the end of an unsaturated polycarbon chain attached to three metals in the polynuclear derivatives **2** and **4** prompted us to explore the possible electronic communication between metal centres. Electrochemical studies of the precursor, compound **1**, have been also carried out.

The cyclic voltammogram of compound **1** shows one reversible redox wave, with a formal potential value of 0.57 V vs. SCE, which is clearly assigned to the oxidation of the ferrocenyl unit. This potential value is considerably more positive than the corresponding process for ferrocene (0.45 V in CH_2Cl_2). This is due to the electron-withdrawing effect of the $CH=CH-C=O$ fragment when bound directly to the cyclopentadienyl ring, making the oxidation of the ferrocene unit more difficult than of the non substituted metallocene.

For compounds **2** and **4**, two oxidation signals were observed in the voltammograms, and when the potential scan was reversed, two reduction signals were detected. The cyclic voltammogram for compound **2** is indicated in Fig. 4.

The anodic and cathode peak potential values for these signals are 0.63, 0.73, 0.68, and 0.54 V vs. SCE respectively. The dependence of signal A with A' and signal B with B' was established by modifying the switching potentials. The value of ΔE_p for process A/A' in both compounds is lower than that obtained for the ferrocene/ferricinium couple and suggests that former can be attribute to a possible adsorption [16]. In addition, upon continuous scanning over the range 0 to +1.2 V, an important increase in the first peak current is observed while at the same time the ori-

ginal second redox wave disappears. This behavior is characteristic of an adsorption with a simultaneous oxidation process followed by a diffusion-controlled oxidation (B/B').

Due to the adsorption processes observed for compounds **2** and **4**, the electronic interaction between the osmium metals and the ferrocenyl unit cannot be unambiguously proved.

Taking advantage of the adsorption processes observed for compounds **2** and **4**, electrodes modified with these ferrocenyl derivatives were obtained after a period of scanning in a rigorously deaerated compound containing solution. Electrodes thus coated were rinsed with dichloromethane to remove any adhering solution, and dried in air. The redox behavior of films of the compounds **2** and **4** electrodeposited onto electrode surfaces were examined in dichloromethane electrolyte solutions.

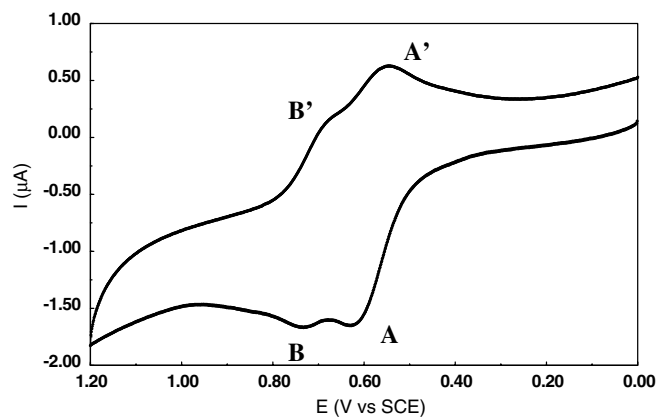


Fig. 4. Cyclic voltammogram of **2** measured in $CH_2Cl_2/0.1$ M TBAH (scan rate 100 $mV s^{-1}$).

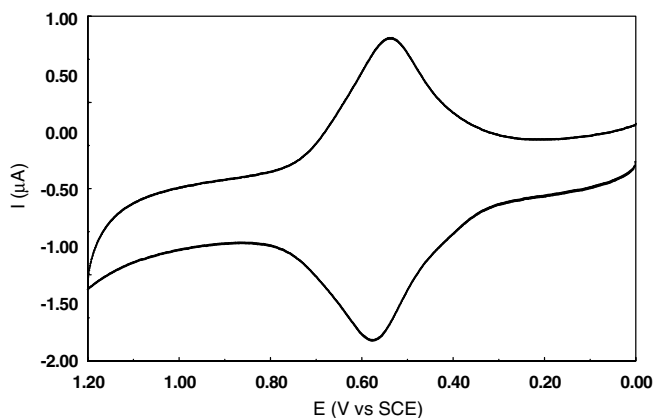


Fig. 5. Voltammetric response of a Pt disk electrode modified with a film of **2**, measured in $\text{CH}_2\text{Cl}_2/0.1 \text{ M TBAH}$. Scan rate 100 mV s^{-1} .

The voltammetric response of a film of compound **2** is shown in Fig. 5.

A well-defined redox process corresponding to the ferrocene/ferricinium system is observed at 0.56 V, which is virtually identical to the redox potential of the first redox wave of compound **2** in solution. The redox wave is symmetric and characteristic of a surface-confined redox couple, with the expected linear relationship of peak current with the potential sweep rate [17]. For films examined at scan rates lower than 100 mV s^{-1} , a peak splitting ΔE_p of 10 mV, for the redox couple was observed and the i_{pa}/i_{pc} ratio was close to unity.

Electrodeposited films of compound **4** showed similar voltammetric responses and a similar stability to the redox processes.

4. Conclusions

The results here reported together to those previously described, allow us to conclude that $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{CH}=\text{C}(\text{SCH}_2\text{CH}_2\text{S})]$ reacts with carbonyl clusters of iron triad to afford species of different nuclearity depending on the metal. In all of them, the oxametallacycle $[\text{M}(\text{CO})_3\{\text{C}(\text{R})=\text{CHC}(\text{O})\text{CH}=\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5\}]$ is present.

The cleavage of S–C bonds in the ketene dithioacetal, $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{CH}=\text{C}(\text{SCH}_2\text{CH}_2\text{S})]$ in the presence of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$, have yielded to several tris-osmium compounds, including a vinylidene derivative. As far as we know, only a few examples on homopolynuclear compounds of the iron triad metals, containing bridging vinylidene ligands have reported.

Although an electronic communication between the ferrocenyl group and the osmium atoms in compounds $[\text{Os}_3(\text{CO})_{10}\{\mu, \eta^3\text{-(SCH}_2\text{CH}_2\text{SC}=\text{CHC}(\text{O})\text{CH}=\text{CH}(\text{C}_5\text{H}_4)\text{-Fe}(\text{C}_5\text{H}_5)\}]$ (**2**) and compounds $[\text{Os}_3(\text{CO})_8\{\mu_3, \eta^2\text{-}\{\text{C}=\text{CHC}(\text{O})\text{CH}=\text{CH}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)\}(\text{SCH}_2\text{CH}_2\text{S})\}]$ (**4**) cannot be definitively confirmed because of the adsorption processes, the electrochemical studies have indicated that both compounds are able to modify the electrode surfaces.

5. Experimental

5.1. General procedures

All reactions were performed under an argon atmosphere. Reagent grade solvents by the standard procedures were dried and freshly distilled prior to use. Were recorded the infrared spectra on a Perkin–Elmer 1650 FTIR spectrophotometer. ^1H and ^{13}C NMR spectra and recorder on a Bruker AMX-300 and DRX-500 instruments, respectively. $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ [18] and $[\text{C}_5\text{H}_5\text{Fe}\{\text{C}_5\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{CH}=\text{C}(\text{SCH}_2\text{CH}_2\text{S})\}]$ [2e] were prepared according to published procedures. TLC using silica plates performed product separations.

5.2. Electrochemical measurements

All the electrochemical experiments were performed also with a BAS CV-50W potentiostat. A platinum disk working electrode (0.02 cm^2), tungsten counter electrode, and saturated calomel (SCE) reference electrode were fitted to a 5 mL, single-compartment electrochemical cell. The surface of the working electrode was polished with either $1 \mu\text{m}$ diamond paste (Buehler) or $0.05 \mu\text{m}$ alumina/water slurry and rinsed thoroughly with purified water and acetone before each cyclic voltammetric run. Were purged the solutions for the electrochemical experiments with nitrogen and kept them under an inert atmosphere throughout the measurements. Typically, a 0.5 mM solution of the electroactive compound in 0.1 M supporting electrolyte solution (tetra-*n*-butylammonium hexafluorophosphate, TBAH) was prepared for the electrochemical experiments.

5.3. Reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{CH}=\text{C}(\text{SCH}_2\text{CH}_2\text{S})]$

5.3.1. Method A

$\text{C}_5\text{H}_5\text{Fe}\{\text{C}_5\text{H}_4\text{CH}=\text{CHC}(\text{O})\text{CH}=\text{C}(\text{SCH}_2\text{CH}_2\text{S})\}$ (176 mg, 0.49 mmol) was added to a solution of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ (185 mg, 0.20 mmol) in dichloromethane (30 mL). The mixture was stirred at $45 \text{ }^\circ\text{C}$ for 5 h to give to a red-brown solution. The solvent was removed under vacuum, and the residue separated by TLC using a mixture of hexane and dichloromethane (8:7) as eluent. A dark red band of compound **2** (35 mg, 0.029 mmol, 13.24%) was recovered, followed of a second band of compound **3** (8.5 mg, 0.004 mmol, 3.23%). Single crystals of **2** were obtained from xylene at room temperature.

Spectral data for **2**: ^1H NMR (CDCl_3 , 300 MHz, $22 \text{ }^\circ\text{C}$) δ 7.48 (d, 1H, $J = 15.60 \text{ Hz}$, $\text{HC}=\text{CHCO}$), 7.04 (s, 1H, $\text{COCH}=\text{CS}$), 6.46 (d, 1H, $J = 15.60 \text{ Hz}$, $\text{HC}=\text{CHCO}$), 4.55, 4.52, 4.49 and 4.46 (m, 4H, C_5H_4), 4.09 (s, 5H, C_5H_5), 3.77, 3.17, 2.93 and 2.58 (m, 4H, $\text{SCH}_2\text{CH}_2\text{S}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 500 MHz, $22 \text{ }^\circ\text{C}$) δ 194.3 ($\text{COCH}=\text{CS}$), 192.3 ($\text{COCH}=\text{CS}$), 187.5, 185.5, 184.1 and 179.1 (CO's), 145.2 ($\text{COCH}=\text{CS}$), 132.1 ($\text{HC}=\text{CHCO}$), 119.6 ($\text{CH}=\text{CHCO}$), 79.6, 71.5 and 67.4

(C₅H₄), 70.1 (C₅H₅), 42.5 and 39.6 (SCH₂CH₂S). IR (hexane) cm⁻¹ ν_{CO}: 2109 m, 2071 vs, 2030 sh, 2028 s, 2005 s, 1985 m, 1975 w, 1962 w. MS(FAB⁺) *m/z*: 1208 [M⁺+H], 1179–956 [M⁺+H–*n*CO, *n* = 1–9]. Anal. Calc. for C₂₇H₁₆FeO₁₁Os₃S₂ · 0.5 hexane: C, 28.79; H, 1.76; S, 5.12. Found: C, 28.78; H, 1.86; S, 5.50%.

Spectral data for **3**: ¹H NMR (CDCl₃, 300 MHz, 22 °C) δ 7.50 (d, 1H, *J* = 15.68 Hz, HC=CHCO), 7.34 (s, 1H, COCH=CS), 6.53 (d, 1H, *J* = 15.68 Hz, HC=CHCO), 4.55 and 4.52 (m, 4H, C₅H₄), 4.16 (s, 5H, C₅H₅), 3.48, 3.32, 3.12 and 2.97 (m, 4H, SCH₂CH₂S). ¹³C{¹H} NMR (CDCl₃, 500 MHz, 22 °C) δ 218.0 COCH=CS, 202.7 COCH=CS, 190.6, 182.5, 178.9, 177.8, 177.0, 170.5 (CO's), 146.4 (HC=CHCO), 127.9 (COCH=CS), 120.8 (HC=CHCO), 79.2, 71.9, 68.7 (C₅H₄), 70.1 (C₅H₅), 48.9, 42.9 (SCH₂CH₂S). IR (hexane) cm⁻¹ ν_{CO}: 2087 m, 2048 s, 2013 vs, 2004 s, 2000 m, 1978 w, 1936 w. MS(FAB⁺) *m/z*: 1180 [M⁺+H], 1152–928 [M⁺+H–*n*CO, *n* = 1–9], 872 [M⁺+H–9CO–C₂S]. Anal. Calc. for C₂₆H₁₆FeO₁₀–Os₃S₂ · 2/3 hexane: C, 29.14; H, 2.05; S, 5.18. Found: C, 29.06; H, 2.28; S, 4.68%.

5.3.2. Method B

A mixture of Os₃(CO)₁₀(NCMe)₂ (185 mg, 0.20 mmol) and [C₅H₅Fe{C₅H₄CH=CHC(O)CH=C(SCH₂CH₂S)}]

(176 mg, 0.49 mmol) in toluene (50 mL) was stirred at 85 °C for 5 h to give a red-brown solution. The solvent was removed under vacuum and the residue purified by TLC using a mixture of *n*-hexane/dichloromethane (2:1) as eluent. A dark red band followed by a purple band were recovered and purified again by using TLC. The former, using a mixture of *n*-hexane/dimethyl ether/dichloromethane (70:25:5) as eluent, yielded compound **4** (6 mg, 0.005 mmol, 2.5%) and another unidentified compound. Single red crystal of compound **4** was obtained by slow diffusion of xylene/hexane system at room temperature. The later band, using *n*-hexane/tetrahydrofurane/dichloromethane (90:15:5) gave compounds **2** (60 mg, 0.05 mmol, 25%) and **3** (traces).

Spectral data for **4**: ¹H NMR (CDCl₃, 300 MHz, 22 °C) δ 8.04 (d, 1H, *J* = 15.6 Hz, CH=CHCO), 6.84 (d, 1H, *J* = 15.6 Hz, HC=CHCO), 4.71 and 4.67 (m, 4H, C₅H₄), 4.65 (s, 1H, COCH=C), 4.26 (s, 5H, C₅H₅), 3.19, 3.03, 2.72 and 2.24 (m, 4H, SCH₂CH₂S). ¹³C{¹H} NMR (CDCl₃, 500 MHz, 22 °C) δ 207.2 (COCH=C), 187.7 (HC=CHCO), 179.1, 177.7, 176.3, 173.4, 173.0 (CO's), 152.4 (HC=CHCO), 116.0 (HC=CHCO), 85.1 (COCH=C), 78.3, 73.0 and 69.9 (C₅H₄), 70.4 (C₅H₅), 38.3 and 35.6 (SCH₂CH₂S). IR (hexane) cm⁻¹ ν_{CO}: 2080 m, 2050 s, 2010 vs, 1999 s, 1982 w, 1948 m. MS(FAB⁺)

Table 1
Data collection and structure refinement details for compounds **1**, **2** and **4**

	1	2	4
Chemical formula	C ₁₇ H ₁₆ FeOS ₂	C ₃₅ H ₂₆ FeO ₁₁ Os ₃ S ₂	C ₂₅ H ₁₆ FeO ₉ Os ₃ S ₂
Fw	356.27	1313.13	1150.95
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Pn</i>	<i>P2₁/n</i>	<i>C2/c</i>
<i>T</i> (K)	100(2)	100(2)	298(2)
<i>λ</i> (Å)	1.54178	1.54178	0.71073
<i>a</i> (Å)	5.7722(1)	17.4286(2)	28.398(9)
<i>b</i> (Å)	11.8678(2)	10.3846(1)	7.391(2)
<i>c</i> (Å)	11.0166(2)	21.4078(2)	27.735(9)
<i>α</i> (°)	90	90	
<i>β</i> (°)	92.344(1)	111.088(1)	103.113(7)
<i>γ</i> (°)	90	90	
<i>U</i> Å ³	754.04(2)	3615.09(7)	5669(3)
<i>Z</i>	2	4	8
<i>D</i> _{calc.} (g cm ⁻³)	1.569	2.413	2.697
<i>μ</i> (mm ⁻¹)	10.552	24.171	14.103
<i>F</i> (000)	368	2440	4192
Crystal size (mm)	0.25 × 0.12 × 0.06	0.15 × 0.10 × 0.04	0.15 × 0.05 × 0.03
<i>θ</i> Range for data collection (°)	3.72–70.60	2.82–70.70	1.85–25.10
Index ranges	–6 ≤ <i>h</i> ≤ 6, –13 ≤ <i>k</i> ≤ 14, –13 ≤ <i>l</i> ≤ 12	–19 ≤ <i>h</i> ≤ 21, –12 ≤ <i>k</i> ≤ 12, –26 ≤ <i>l</i> ≤ 26	–33 ≤ <i>h</i> ≤ 33, –8 ≤ <i>k</i> ≤ 8, –32 ≤ <i>l</i> ≤ 32
Number of reflections collected	7224	31809	22279
Number of independent reflections (<i>R</i> _{int})	2349 (0.0353)	6729 (0.0472)	5009 (0.1116)
Data/restraints/parameters	2349/2/191	6729/0/471	5009/272/426
GoF on <i>F</i> ²	1.026	1.050	1.050
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b (<i>I</i> > 2σ(<i>I</i>))	0.0300, 0.0696	0.0228, 0.0563	0.0547, 0.1059
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b (all data)	0.0310, 0.0704	0.0244, 0.0572	0.0785, 0.1147
Flack's parameter	0.073(6)	–	–
Largest difference in peak/hole, (e Å ⁻³)	0.741/–0.380	0.985/–0.685	1.715/–1.016

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

m/z : 1151 [M^+], 1123–927 [$M^+ - nCO$, $n = 1-8$], 897 [$M^+ - 7CO - HC_2S$], 869 [$M^+ - 8CO - HC_2S$]. Anal. Calc. for $C_{25}H_{16}FeO_9Os_3S_2 \cdot xylene$: C, 31.51; H, 2.10; S, 5.10. Found: C, 31.79; H, 2.35; S, 4.74%.

5.4. X-ray diffraction analyses

X-ray crystals of **1**, **2** and **4** were grown by slow diffusion using CH_2Cl_2 /hexane at $-20^\circ C$, slow evaporation of xylene at room temperature and xylene/hexane at room temperature respectively. Data were collected on a Bruker SMART APEX diffractometer, using ω and ϕ scan types.

Absorption corrections: multiscan. The structures were solved by direct methods and refined on F^2 using the program SHELXL-97 [19]. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. Further details on the data collection and refinement methods can be found in Table 1. Compound **1** proved to be racemic twinned with 0.93:0.07 ratio. In Compound **4**, the unsubstituted ferrocene ring and dithiolate moieties show orientational disorder and was modelled as two contributors (0.63:0.37 and 0.55:0.45) respectively.

6. Supplementary material

CCDC 644498, 644499 and 644500 contain the supplementary crystallographic data for **1**, **2** and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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