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Thermal and photochemical transformations of 2-methylthiothiophene in triosmium clusters: photoinduced migrations of MeS from carbon to metal and back again

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Abstract

2-Methylthiothiophene (2-$MeSC_4H_3S$) oxidatively adds to [$Os_3(CO)_{10}(MeCN)_2$] with cleavage of the C–H bond at the 3-position to give [$Os_3(\mu\text{-}H)(\mu\text{-}MeSC_4H_2S)(CO)_{10}$] **1**, the X-ray structure of which shows that the MeS group is coordinated to osmium through the S atom while the thiophene ring is coordinated to osmium through the 3-carbon atom. Only one invertomer at sulfur is observed in solution and in the crystal the Me group is *exo*. Thermal treatment of **1** *in the dark* gives only one product, [$Os_3(\mu\text{-}H)(\mu_3\text{-}MeSC_4H_2S)(CO)_9$] **2** (X-ray structure), derived by loss of a CO from the $Os(CO)_4$ unit of **1** with concomitant η^2-coordination of the thiophene ring of bridging $MeSC_4H_2S$ at the third metal atom. Whereas thermal reaction in the dark leads only to C–H cleavage products, visible irradiation at room temperature leads to various products derived by migration of the MeS group. Thus thermal treatment of **1** in daylight for 2 h gave **2**, together with an isomer **3**. Cluster **2** converts at room temperature to **3** *in daylight* while thermal treatment of **2** *in the dark* (125°C) gave no reaction. Isomer **3** of [$Os_3(\mu\text{-}H)(\mu_3\text{-}MeSC_4H_2S)(CO)_9$] (X-ray structure) is closely related to **2** except that the MeS group and the Os–C σ-bond have interchanged sites at the thiophene ring between the 2- and the 3-positions. Visible irradiation of **1** at room temperature for 3 days in daylight gave further chemical change leading to two bridging thienyl clusters, [$Os_3(\mu\text{-}MeS)(\mu\text{-}2\text{-}C_4H_2S)(CO)_{10}$] **4** and [$Os_3(\mu\text{-}MeS)(\mu_3\text{-}2\text{-}C_4H_2S)(CO)_9$] **5**. Cluster **5** is the ultimate product of daylight irradiation of any of the clusters **1** to **4**. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Osmium; Clusters; Thiophene; Carbon–hydrogen and carbon–sulfur bond activation

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1. Introduction

The MeS-substituted thiophene, 2-$MeSC_4H_3S$, could potentially coordinate through either or both of the sulfur atoms, through the π-system of the ring or, if C–H cleavage occurs, through a metal–carbon σ-bond. This paper on this 2-substituted thiophene reports on an extension of our work on 2-Ph_2P-substituted thiophene with [$Ru_3(CO)_{12}$] [1] and [$Os_3(CO)_{12}$] [2]. Previously thienylphosphines were only known to coordinate through the phosphorus atom [3], but C–H activation at the thiophene ring dominates the chemistry in these clusters [1,2]. Our approach with both ligand systems was to allow preliminary coordination through the exocyclic heteroatom. Subsequent reaction would bring the thiophene ring into play. For example, orthometallation would lead to stable μ_2 or μ_3 ligands, while cleavage of

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the bond to the exocyclic group would give cluster-stabilizing μ_2 ligands such as MeS or Ph_2P and thienyl (C_4H_3S) ligands. This entry into thienyl cluster chemistry complements other direct routes from thiophene (or benzo- or dibenzo-thiophene) which lead to C–H cleavage or thiophene ring-opening [4], from halo-compounds [5] or from other 2-substituted thiophenes [6]. The use of RS-substituted cyclic compounds to induce metallation in organic rings has been employed in several cases [7] so it was anticipated that C–H cleavage in the ring *ortho* to the MeS group would occur.

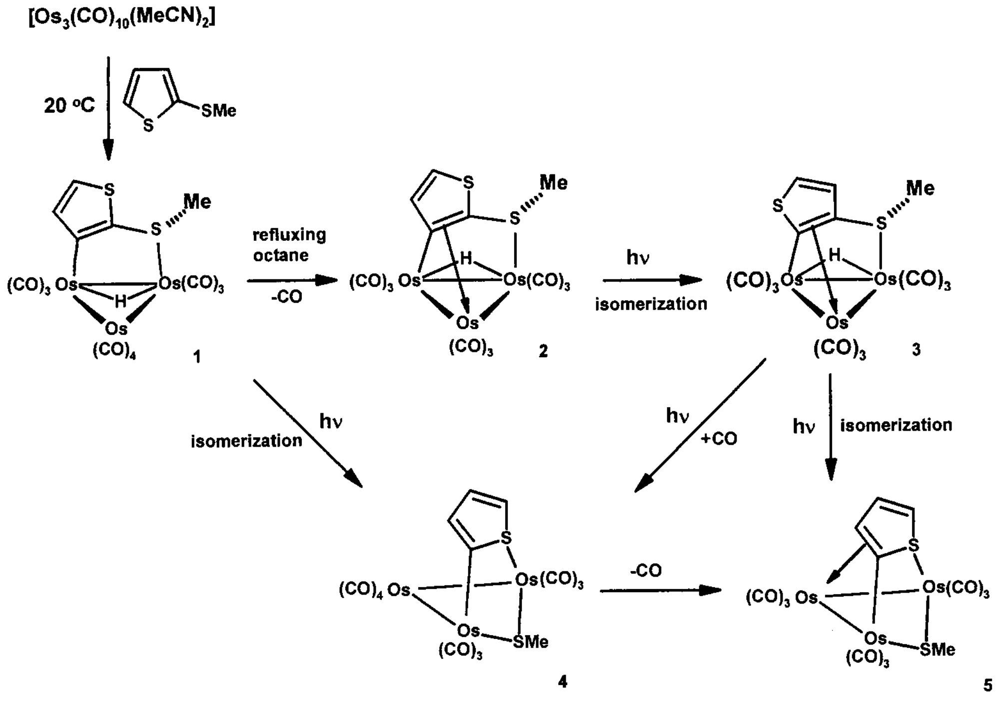
In our studies of 2-methylthiothiophene with triosmium clusters, five different ligand sets derived from this substituted thiophene were found within various triosmium products derived from both C–H and C–S bond cleavages. These products involve Os–C and Os–S σ-bonds and η^2-interactions from the 5-membered ring. Importantly, the introduction of 2-$MeSC_4H_3S$ into the cluster by thermal methods leads to C–H bond cleavage, whereas under photochemical conditions (daylight) C–S bond cleavage occurs at the exocyclic substituent leading to MeS cleavage from the thiophene ring and/or MeS migration around the thiophene ring. In spite of the considerable extent of chemical modification of the 2-methylthiothiophene that occurs in these reactions, there was no evidence for C–S bond cleavage within the thiophene ring, i.e. ring-opening.

2. Results and discussion

2.1. Thermal reaction of 2-methylthiothiophene with $[Os_3(CO)_{10}(MeCN)_2]$

Reaction of the substituted thiophene with $[Os_3(CO)_{10}(MeCN)_2]$ in dichloromethane at room temperature leads to a moderate yield (68%) of the cluster $[Os_3(\mu\text{-H})(\mu\text{-MeSC}_4H_2S)(CO)_{10}]$ **1**, which was isolated as a yellow solid. There was no evidence for unmetallated 2-methylthiothiophene as a ligand in any intermediate in the formation of cluster **1**, although such an intermediate was expected. Four ^{1}H-NMR signals were observed for a CD_2Cl_2 solution of **1**: a hydride signal at δ −14.79, a SMe singlet at δ 3.17 and two doublets for the remaining ring hydrogen atoms at δ 7.47 and 7.07 ($J_{HH} = 5.0$ Hz). The J_{HH} value indicates that the hydrogen atoms on the ring are *ortho* to each other so that metallation has occurred at the 3- or 5-positions.

Compound **1** crystallizes as very thin plates for which X-ray structure determination was rather difficult. However, the structure confirms that metallation has occurred at the 3-position as shown in Scheme 1 and Fig. 1. Selected bond lengths and angles are given in Table 1. Note that metallation of thiophene with $[Os_3(CO)_{10}(MeCN)_2]$ leads to C–H cleavage at the 2-position to give the 2-thienyl cluster $[Os_3(\mu\text{-H})(\mu\text{-C}_4H_3S)(CO)_{10}]$ as an intercoverting mixture of *exo* and *endo* isomers [4c]. In the case of the



Scheme 1. Formation of clusters **1** to **5** from 2-methylthiothiophene.

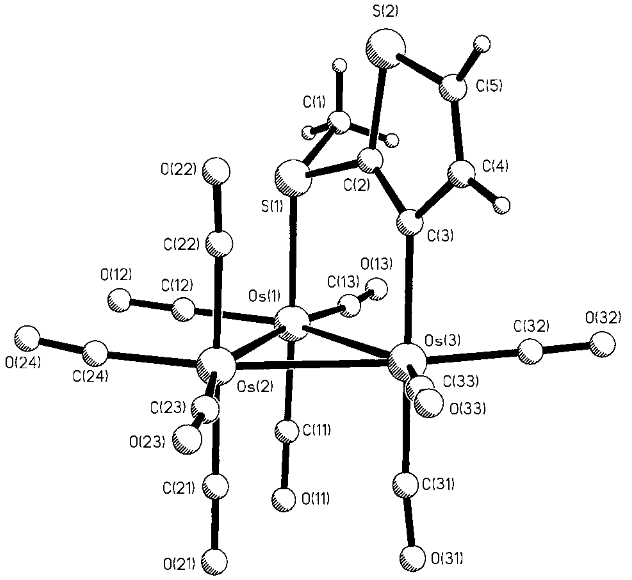


Fig. 1. Molecular structure of the cluster $[Os_3(\mu\text{-}H)(\mu\text{-}MeSC_4H_2S)(CO)_{10}]$ **1**.

MeS-substituted compound the greater coordinating ability of the MeS group compared with the thiophene ring has directed the metallation to the site *ortho* to the MeS substituent. The reaction is faster for 2-methylthiothiophene than for thiophene which supports the preliminary co-ordination and directing influence of the MeS group. The metallated ligand in **1** forms a three-atom bridge across a pair of Os atoms to give a structure closely related to that of the carboxylate derivatives $[Os_3(\mu\text{-}H)(\mu\text{-}RCO_2)(CO)_{10}]$ [8]. The exocyclic S-atom in **1** is pyramidal. The sum of the bond angles at S(1) is 318.3° and C(1) lies 1.404 Å out of the best S(1)S(2)C(2)C(3)C(4)C(5) plane, directed away from Os(2). The *endo* invertomer would have the Me group in quite close contact with the axial C(22)O(22) ligand and we presume this is the reason why only the *exo* isomer is observed both in the crystal and in solution. The ^{1}H-NMR spectra in solution gave no indication of any other isomer even in low abundance.

Table 1
Selected bond distances (Å) and angles (°) for the clusters **1** to **3**

	1	**2**	**3**
Os(1)–Os(2)	2.952(2)	2.837(1)	2.859(1)
Os(2)–Os(3)	2.922(1)	2.772(1)	2.811(1)
Os(1)–Os(3)	3.004(2)	2.999(1)	3.056(1)
Os(1)–S(1)	2.449(8)	2.387(4)	2.425(6)
Os(3)–C(3)	2.18(2)	2.10(2)	2.11(2)
Os(2)–C(2)		2.30(2)	2.38(2)
Os(2)–C(3)		2.30(2)	2.32(2)
C(1)–S(1)	1.91(5)	1.81(2)	1.84(2)
C(2)–S(1)	1.74(3)	1.78(2)	1.73(2)
C(2)–S(2)	1.78(2)	1.73(2)	
C(3)–S(2)			1.79(2)
C(5)–S(2)	1.79(4)	1.68(3)	
C(4)–S(2)		1.74(3)	
C(2)–C(3)	1.46(3)	1.39(3)	1.44(3)
C(3)–C(4)	1.45(3)	1.66(2)	
C(4)–C(5)	1.35(3)	1.45(3)	1.39(4)
C(2)–C(5)			1.54(3)
Os(3)–Os(1)–S(1)	88.8(2)	87.7(1)	87.3(1)
Os(1)–S(1)–C(1)	110(2)	111.6(7)	113(1)
Os(1)–S(1)–C(2)	107.5(7)	99.0(6)	99.1(6)
C(1)–S(1)–C(2)	101(2)	104(1)	102(1)
S(1)–C(2)–C(3)	129(2)	123(1)	123(2)
S(1)–C(2)–S(3)	117(1)	112(1)	
S(1)–C(2)–C(5)			121(2)
C(2)–C(3)–Os(3)	124(2)	127(1)	129(2)
C(3)–Os(3)–Os(1)	87.9(7)	83.0(5)	81.6(6)
S(1)–Os(1)–Os(2)	88.7(2)	74.8(1)	75.6(1)
C(3)–Os(3)–Os(2)	90.2(6)	54.2(5)	53.9(6)
C(3)–Os(2)–Os(3)		47.9(4)	47.4(5)
C(2)–Os(2)–Os(1)		76.0(5)	74.4(5)

2.2. Thermal and photochemical reactions of $[Os_3(\mu\text{-}H)(\mu\text{-}MeSC_4H_2S)(CO)_{10}]$ 1

Cluster **1** is very slow to lose CO in the solid state or in solutions kept in the dark and good rates of decarbonylation only occur in refluxing octane. A decarbonylation product $[Os_3(\mu\text{-}H)(\mu_3\text{-}MeSC_4H_2S)(CO)_9]$ was obtained from refluxing octane under normal laboratory conditions of light which appeared to be a mixture of two isomers since two sets of ^{1}H-NMR signals were observed. One isomer gave ^{1}H-NMR signals in CD_2Cl_2 at δ 7.32, 7.26, 1.94 and −16.63 (cluster **2**) while the other isomer had a closely similar set of signals at δ 7.38, 6.92, 1.90 and −16.66 (cluster **3**). We believed initially that these might be related simply by inversion at the co-ordinated MeS group. However, extended treatment of **1** in refluxing octane (125°C) *in the dark* gave only isomer **2** with no indication for the formation of isomer **3**. However, if cluster **2** in dichloromethane is irradiated in daylight at room temperature, then its isomer **3** is obtained. Therefore we believe that **2** is the thermal decarbonylation product from **1** and that **3** is formed by subsequent photoisomerization of **2**. Treatment of **1** with daylight at room temperature initially gives **3**, although other products are obtained after extended photolysis (see below). We have not yet established the frequency or intensity dependence of the photochemistry, except to show that the conversion of **2** to **3** does not occur in the dark but does so if a solution is placed at 20°C near the window of a London laboratory in summer.

The IR spectra around 2000 cm^{-1} for **2** and **3** are indistinguishable in terms of the number of peak maxima and their wavenumbers and therefore they must be very similar structurally. Also their ^{1}H-NMR spectra are closely similar (see above), especially the hydride signals (δ −16.63 for **2** and −16.66 for **3**). However, it was unlikely that these are related by inversion at S since there was no thermal interconversion at 125°C.

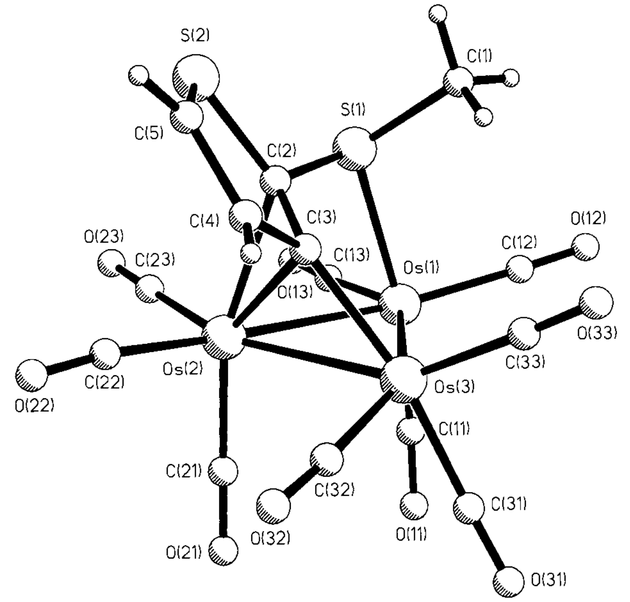


Fig. 2. Molecular structure of the cluster $[Os_3(\mu\text{-H})(\mu\text{-}MeSC_4H_2S)(CO)_9]$ **2**.

Single crystal XRD structures have been determined for both isomers but we had some problems since they only gave very thin plates and this crystal shape limited the quality of the structural data we could obtain. Molecular structures are shown in Figs. 2 and 3 for clusters **2** and **3**, respectively; selected bond lengths and angles are in Table 1. Their superficial resemblance is obvious. They have the same configuration at sulfur (*exo* methyl groups). The modes of attachment of the μ_3-ligands are essentially the same and the hydride ligand is positioned along the Os(1)–Os(3) edge in each cluster. This is the longest Os–Os bond in both compounds [2.999(1) in **2** and 3.056(1) Å in **3**] compared with the other Os–Os distances [2.837(1) and 2.772(1) Å in **2** and 2.859(1) and 2.811(1) Å in **3**]. The hydrides are expected to lie close to the intersection of the C(13)Os(1) and C(32)Os(3) directions, slightly above the Os_3 plane on the side of the μ_3-ligand. The CO positions support this proposal for the hydride positions in **2** and **3**.

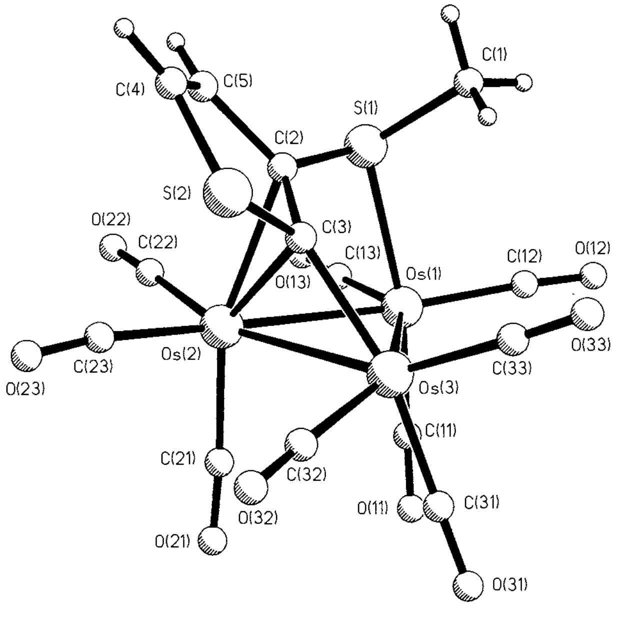


Fig. 3. Molecular structure of the cluster $[Os_3(\mu\text{-H})(\mu\text{-}MeSC_4H_2S)(CO)_9]$ **3**.

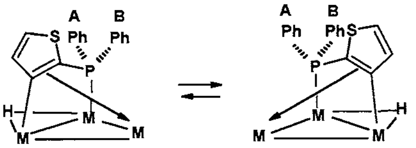


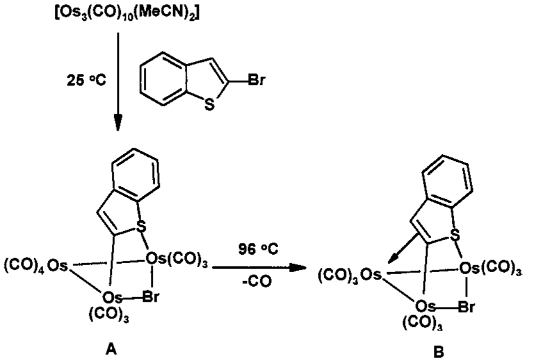
Fig. 4. Mechanism established for $[Ru_3(\mu\text{-H})(\mu\text{-}Ph_2PC_4H_2S)(CO)_9]$ that leads to the exchange of phenyl groups A and B. If applied to clusters **2** or **3**, this would lead to sulfur inversion.

The overall structures of **2** and **3** are closely related to those of other compounds of the type $[M_3(\mu\text{-H})(\mu_3\text{-}L)(CO)_9]$ where M=Ru or Os and $L = Ph_2PC_4H_2S$ [1], $PhSC_4HMeBu^t$ [7] or $MePhPC_6H_4$ [9], which are derived generally by metallation at the β position with respect to the donor heteroatom of the ligand. The μ_3-ligands in **2** and **3** are both co-ordinated through a pyramidal MeS group to Os(1), through a σ Os(3)–C(3) bond and through an η^2-interaction of C(2)–C(3) to Os(2). Whereas the thiophene ring in cluster **1** is approximately perpendicular to the Os_3 ring (92.7°), the rings are tilted in **2** and **3** with dihedral angles between the C_4S and Os_3 rings of 127.3 and 131.7°, respectively. This tilt is to accommodate the η^2-interaction. There is evidence in the solid state and in solution for only one configuration at sulfur with the Me group *exo*. There are two potential mechanism for inversion at sulfur: direct inversion via an intermediate with a planar S atom or a migration of C(3) between Os(2) and Os(3) with corresponding switching of the η^2-interaction between these metal atoms and a hydride transfer. This is a fast exchange (enantiomerization) process in the related cluster $[Ru_3(\mu\text{-H})(\mu_3\text{-}Ph_2PC_4H_2S)(CO)_9]$ [1] and a rather slower one in the osmium analogue [2]. This degenerate process in the PPh_2-derivative (Fig. 4) if applied to **2** or **3** would result in an effective inversion at sulfur. We believe therefore that there is nothing to prevent facile inversion in the MeS-derivatives and that the *exo* isomers **2** and **3** are sufficiently lower in energy to make the *endo* isomers unobservable.

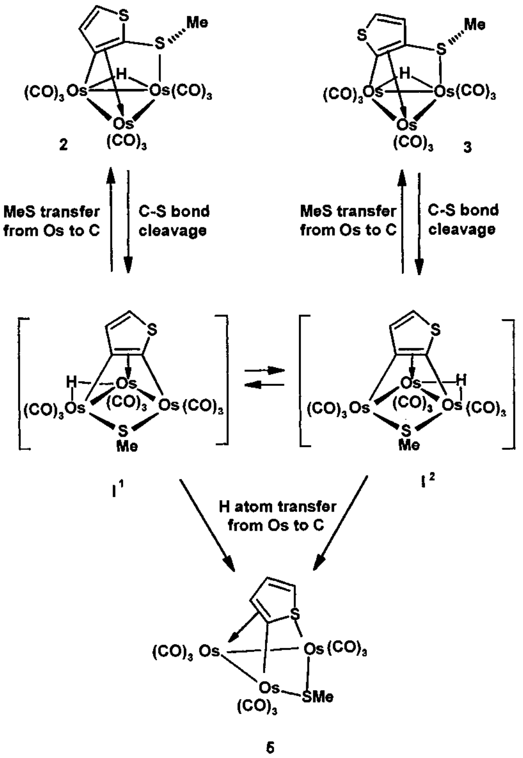
Clearly the major difference between **2** and **3** is the position of S(2) in the thiophene ring with respect to the MeS group. Cluster **2** retains the original ligand structure but there has been a remarkable photoinduced transformation to give **3**, which is formally derived from 3-methylthiothiophene. There have been migrations of both MeS and a H-atom at the thiophene ring.

2.3. Extended photolysis of cluster **1**

Photolysis of cluster **1** in dichloromethane in available sunlight for 3 days in a closed vessel gives different products from **2** and **3**. Note that 2 h irradiation by London summer daylight is sufficient to get significant conversion from **1** to **2** and **3**. However, clusters **2** and **3** were not detected after 3 days irradiation, but instead two new products were obtained: $[Os_3(\mu\text{-MeS})(\mu\text{-}C_4H_3S)(CO)_{10}]$ **4** (an isomer of **1**) and $[Os_3(\mu\text{-MeS})(\mu_3\text{-}C_4H_3S)(CO)_9]$ **5** (an isomer of **2** and **3**). These were isolated in yields of 19 and 71%, respectively. Both **4** and **5** contain the thienyl ligands (C_4H_3S) as shown by the three mutually coupled ^{1}H-NMR signals observed for these ligands. Therefore the initial thermal C–H cleavage in cluster **1** leading to **2**, and its photoproduct **3**, has been reversed on extended visible photolysis and C–S cleavage has occurred instead. The new products **4** and **5** were characterised by IR, ^{1}H-NMR, mass spectrometry and elemental analysis but not by single-crystal XRD. However, there are close similarities between the spectra of **4** and **5** (especially IR) and those of $[Os_3(\mu\text{-Br})(\mu\text{-}C_8H_5S)(CO)_{10}]$ and of $[Os_3(\mu\text{-Br})(\mu_3\text{-}C_8H_5S)(CO)_9]$ formed by oxidative addition of 2-bromobenzothiophene at $[Os_3(CO)_{10}(MeCN)_2]$ (Scheme 2) [5]. These bromo-clusters have been structurally characterized, supporting the structures formulated for **4** and **5** in Scheme 1. The IR ν(CO) spectra of **4** and **5** are similar to those of the corresponding compounds **A** and **B**, respectively, in Scheme 2 except that **4** and **5** are more 'electron-rich' and as a result cluster **4** has lower ν(CO) wavenumbers than for **A** (by 3–8 cm^{-1}) and cluster **5** lower than for **B** (by 5–9 cm^{-1}). Cluster **4** decarbonylates in daylight irradiation to give **5** and is only a minor product from the photolysis of cluster **1**. It seems that irradiation in a closed vessel (to prevent solvent evaporation) has prevented the removal of CO which partially reverses the conversion of **4** to **5**. It was separately observed that daylight irradiation of solutions of cluster **3** gives **5** and that cluster **3** is an intermediate in the photoinduced formation of **4** and **5** from **1**. Hence in our work we have synthesised two isomers with the formula '$Os_3(CO)_{10}L$' and three with the formula '$Os_3(CO)_9L$' where L = $C_5H_6S_2$. This multiplicity of isomers is a consequence of the variety of co-ordination modes possible and the fine detail of C–H versus C–S bond cleavage.



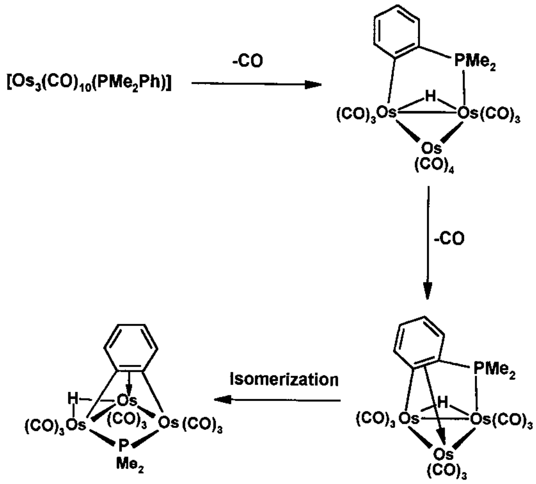
Scheme 2. Formation of μ and μ_3 benzothienyl clusters from 2-bromobenzothiophene.



Scheme 3. Proposed route for photoinduced formation of isomers **3** and **5** from isomer **2**.

2.4. Isomerization mechanisms

The isomerization of **2** to **3** requires the migration of a MeS group. We propose that there is a photochemical C–S cleavage as in Scheme 3 in which **2** converts to the thiophyne intermediates **I**^{1} and **I**^{2}. This is a not unexpected process because it occurs in analogous systems to give isolable products related to the proposed intermediates. Thus the cluster $[Os_3(CO)_{11}(PMe_2Ph)]$ thermally loses CO to form $[Os_3(\mu\text{-H})(\mu\text{-}Me_2P)(\mu_3\text{-}C_6H_4)(CO)_9]$ [9]. This process seems to involve an initial orthometallation to give the clusters $[Os_3(\mu\text{-H})(\mu\text{-}Me_2PC_6H_4)(CO)_x]$ ($x = 9$ or 10) and the final product $[Os_3(\mu\text{-H})(\mu\text{-}Me_2P)(\mu_3\text{-}C_6H_4)(CO)_9]$ is formed by P–C cleavage (Scheme 4). Also the direct thermal reaction of thiophene with $[Os_3(CO)_{12}]$ gives the thiophyne cluster $[Os_3(\mu\text{-H})_2(\mu_3\text{-}C_4H_2S)(CO)_9]$ which contains the same μ_3-ligand as in **I**^{1} and **I**^{2}. In view of these observations, it was surprising to us that the intermediates **I**^{1} and **I**^{2} corresponding to the stable product in Scheme 4 were



Scheme 4. Proposed route for the formation of a benzyne cluster.

not detected in this present system. Rather a C–S bond is reformed at either of the osmium-bound carbon atoms, which provides a pathway for the isomerisation of **2** to **3**. The same intermediates I^1 and I^2 can be invoked in the formation of the final product from photolysis, cluster **5**. Thus if a hydrogen atom instead of a MeS group transfers from metal sites to the thiophyne ligand in I^1 or I^2 then cluster **5** is generated. This is the major product (71%) on extended irradiation of cluster **1**.

3. Conclusions

Thiophene (C_4H_4S) is a remarkably versatile ligand. Even though it is relatively weakly co-ordinated to metals, it can coordinate in a number of ways, through carbon or sulfur as a 2-electron through to a 6-electron donor. The derivatives, thienyl (C_4H_3S) and thiophyne (C_4H_2S) bind to metal atoms in clusters strongly and may be the favoured products. There are now several known ways in which thienyl may coordinate as shown in Fig. 5. Terminal thienyl is well known [10]. Thienyl bridges of the type **C** and **E** are described in this paper, type **B** is found in $[Os_3(\mu\text{-}H)(\mu\text{-}C_4H_3S)(CO)_{10}]$ [4c] and we will report shortly our results on dimanganese and dirhenium compounds in which thienyl bridges of type **C** and **D** are found [11].

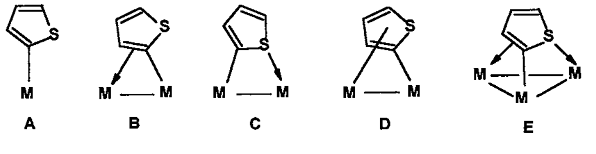


Fig. 5. Modes of thienyl co-ordination.

4. Experimental

The cluster $[Os_3(CO)_{10}(MeCN)_2]$ was prepared according to literature methods [12] and 2-methylthiothiophene was used as obtained from Aldrich.

4.1. Synthesis of $[Os_3(\mu\text{-}H)(\mu\text{-}MeSC_4H_2S)\ (CO)_{10}]$ **1**

A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.200 g, 0.021 mmol) and 2-methylthiothiophene (0.024 cm^3) in dichloromethane (60 cm^3) was stirred at room temperature for 1 h, after which time the IR spectrum showed the starting material had been consumed. The yellow residue after the removal of solvent was chromatographed on a column (Kieselgel) eluting with hexane and then with a dichloromethane:hexane mixture with increasing dichloromethane. When the volume ratio of CH_2Cl_2:hexane was 3:2, a yellow band was eluted from which product **1** (0.132 g, 68%) was obtained. (Found: C, 18.36; H, 0.51. Calc. for $C_{15}H_6O_{10}Os_3S_2$: C, 18.35; H, 0.61%). IR (cyclohexane): 2107w, 2065vs, 2057vs, 2026s, 2014s, 2007w, 1995s, 1985w, 1979w cm^{-1}. FAB-MS: *m*/*z* 981 (parent molecular ion), main fragments observed (M–*x*CO) and (M–*x*CO–Me). ^{1}H-NMR (CD_2Cl_2): δ 7.47 (d, 1H, *J* 5.0 Hz, $\mu\text{-}C_4H_2S$), 7.07 (d, 1H, *J* 5.0 Hz, $\mu\text{-}C_4H_2S$), 3.17 (s, 3H, SMe), -14.79 (s, 1H, μ-*H*).

4.2. Synthesis of $[Os_3(\mu\text{-}H)(\mu\text{-}MeSC_4H_2S)(CO)_9]$ isomer **2** and $[Os_3(\mu\text{-}H)(\mu\text{-}MeSC_4H_2S)(CO)_9]$ isomer **3**

A solution of $[Os_3(\mu\text{-}H)(\mu\text{-}MeSC_4H_2S)(CO)_{10}]$ **1** (0.070 g) in octane was refluxed for 1 h in normal laboratory daylight. The IR spectrum of a sample in CH_2Cl_2 showed no presence of the starting material after this time. After removal of solvent under reduced pressure, the resulting yellow residue was chromatographed on TLC plates (SiO_2; eluant 1:4 CH_2Cl_2:hexane) to give a yellow band characterised as a mixture of **2** and **3** in mol ratio 2:1 as a yellow powder (0.025 g, 36%). (Found: C, 17.63; H, 0.51. Calc. for $C_{14}H_6O_9Os_3S_2$: C, 17.63; H, 0.63%). ν(CO) cm^{-1} (cyclohexane): 2093s, 2065vs, 2039vs, 2018s, 2003m, 1999s, 1988w, 1978w, 1972w. FAB-MS: *m*/*z* 954 (parent molecular ion), main fragments observed (M–*x*CO) and (M–*x*CO–Me). ^{1}H-NMR (CD_2Cl_2): cluster **2**: δ 7.32 (d, 1H, *J* 5.5 Hz, $\mu\text{-}C_4H_2S$), 7.26 (d, 1H, *J* 5.5 Hz, $\mu\text{-}C_4H_2S$), 1.94 (s, 3H, SMe), -16.63 (s, 1H, μ-H); cluster **3**: δ 7.38 (d, 1H, *J* 5.5 Hz, $\mu\text{-}C_4H_2S$), 6.92 (d, 1H, *J* 5.6 Hz, $\mu\text{-}C_4H_2S$), 1.90 (s, 3 H, SMe), -16.66 (s, 1H, μ-H). Compound **2** was formed exclusively from **1** under the same conditions (1 h in refluxing octane) but in the dark. Compound **2** was converted to **3** by stirring a CH_2Cl_2 solution of the mixture in sunlight for 2 h.

Table 2
Crystallographic data for clusters **1** to **3**[a]

	1	**2**	**3**
Formula	$C_{15}H_6O_{10}Os_3S_2$	$C_{14}H_6O_9Os_3S_2$	$C_{14}H_6O_9Os_3S_2$
M	980.92	952.91	952.91
Description	Yellow plate	Yellow plate	Yellow plate
Crystal size (mm)	0.50 × 0.40 × 0.06	0.35 × 0.14 × 0.08	0.48 × 0.30 × 0.08
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	8.154(2)	9.835(4)	9.578(2)
b (Å)	9.287(2)	10.257(3)	14.561(3)
c (Å)	16.435(3)	10.702(3)	15.098(3)
α (°)	95.64(3)	79.85(2)	90
β (°)	97.38(3)	77.97(2)	97.36(30)
γ (°)	115.51(3)	76.15(3)	90
U (Å^3)	1097.4(4)	1016.0(5)	2088.3(7)
Z	2	2	4
D_c (g cm^{-3})	2.969	3.115	3.031
μ(Mo–K$_\alpha$) (mm^{-1})	17.56	18.96	18.45
Scan mode	ω-2θ	ω-2θ	ω-2θ
2θ range (°)	5–50	5–50	5–50
Total data	4115	3778	3885
Unique data	3826	3558	3658
Data, restraints, parameters	3825, 0, 271	3556, 0, 253	3655, 0, 248
$R1$, $wR2$ ($I>2\sigma(I)$)	0.087, 0.266	0.0517, 0.127	0.081, 0.226
$R1$, $wR2$ (all data)	0.097, 0.299	0.0627, 0.135	0.096, 0.267
Goodness-of-fit on F^2	1.066	1.110	1.074
Max, min residual electron density (eÅ^{-3})	7.1, −8.2	2.1, −2.6	6.25, −6.68

[a] All structures: Direct methods structure solution, graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å), three standard reflections every 97, no decay, data corrected for absorption empirically by Ψ-scan method, full-matrix least-squares refinement on F^2.

*4.3. Extended irradiation of [$Os_3(\mu\text{-}H)(\mu\text{-}MeSC_4H_2S)(CO)_{10}$] **1** to give the clusters [$Os_3(\mu\text{-}SMe)(\mu\text{-}C_4H_3)(CO)_{10}$] **4** and [$Os_3(\mu\text{-}SMe)(\mu\text{-}C_4H_3)(CO)_9$] **5***

A solution of cluster [$Os_3(\mu\text{-}H)(\mu\text{-}MeSC_4H_2S)(CO)_{10}$] **1** (0.062 g) in a mixture of hexane (250 cm^3) and dichloromethane (10 cm^3) was stirred in available sunlight for 3 days. The solvents were removed and the reaction mixture was chromatographed on TLC plates (silica, CH_2Cl_2:hexane, 5:45 by volume) to give two bands. The first orange band was characterised as **4** (0.012 g, 19%) and the second yellow band as **5** (0.043 g, 71%) (Found for **5**: C, 17.98; H, 0.43. Calc. for $C_{14}H_6O_9Os_3S_2$: C, 17.63; H, 0.63%). ν(CO) cm^{-1} (cyclohexane): cluster **4**: 2104m, 2068vs, 2054m, 2021vs, 2013s, 2005m, 1990m, 1978m; cluster **5**: 2087w, 2064vs, 2030s, 2011s, 2002m, 1994m, 1982s, 1970w, 1964w. ^{1}H-NMR (CD_2Cl_2): cluster **4**: δ 7.61 (d, 1H, J 5.2 Hz, μ-C_4H_3S), 7.28 (d, 1H, J 3.3 Hz, μ-C_4H_3S), 7.16 (dd, 1H, J 5.2, 3.3 Hz, μ-C_4H_3S), 1.98 (s, 3 H, SMe); cluster **5**: δ 7.29 (dd, 1H, J 5.5, 2.8 Hz, μ-C_4H_3S), 6.95 (d, 1H, J 5.5 Hz, μ-C_4H_3S), 4.81 (d, 1H, J 2.9 Hz, μ-C_4H_3S), 2.56 (s, 3 H, SMe). FAB-MS: cluster **4**: m/z 980 (parent molecular ion), cluster 5: m/z 954 (parent molecular ion), main fragments observed for both **4** and **5**, (M−xCO) and (M−xCO−Me).

*4.4. Conversion of cluster **4** to cluster **5***

A sample of compound **4** in $CDCl_3$ in an NMR tube was exposed to available sunlight for 3 days. After this time, the ^{1}H-NMR spectrum of the solution showed a partial conversion of **4** to compound **5**. Final mol ratio (**5**:**4**) of 2.6:1.

*4.5. Conversion of cluster **3** to cluster **5***

A sample of compound **3** in hexane solution was exposed to available sunlight for 7 days. The resultant solution was pumped to dryness and the residue dissolved in CD_2Cl_2. A ^{1}H-NMR spectrum of the residue showed partial conversion to **5** with final mol ratio (**5**:**3**) of 5.0. No cluster **4** was observed.

*4.6. Evidence for cluster **3** in the extended irradiation of compound **1** to give **4** and **5***

A sealed NMR tube containing **1** in CD_2Cl_2 solution was placed in available sunlight, and chemical changes monitored by ^{1}H-NMR spectra over several days. After 24 h clusters **1**, **4** and **3** were observed to be present, but not **5**. The concentration of cluster **3** reached a maximum after 3 days but then progressively decreased with the appearance of cluster **5**. Finally, after 12 days, no **3** was observed, and the final mol ratio (**5**:**4**) was 1.5:1.

*4.7. Crystal structure determinations for compounds **1**, **2** and **3***

In each case suitable crystals were obtained by slow evaporation of a dichloromethane solution of the pure product. In each case the formation of thin plates of no more than 0.08 mm thickness limited the quality of the absorption corrections and of the structure determinations. Table 2 lists the crystal data for each compound, together with details of the intensity data collections and the structure solutions and refinements. Data for each crystal were collected at 20°C using a Nicolet R3V/m diffractometer using graphite-monochromated $Mo-K_\alpha$ radiation. Data were corrected for Lorentz and polarisation effects and for absorption based on Ψ-scans. Instrument and crystal stabilities were checked by measuring three standard reflections periodically; only minor variations of intensities were observed and corrections were made for these.

Structures were determined by direct methods in the space groups given in Table 2. For each structure, all non-H atoms were refined anisotropically and H-atoms on the $MeSC_4H_2S$ were included in the model in idealised positions riding on the carbon atoms with C–H distances fixed at 0.96 Å and thermal parameters at 0.08 $Å^3$. Hydride ligands were not included in any of the models.

All calculations were carried out using SHELXTL PLUS [13] or SHELXL93 [14]. Fractional atomic coordinates for **1**, **2** and **3** together with additional material comprising thermal parameters and full tables of bond lengths and angles are available from the Cambridge Crystallographic Data Centre.

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