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# Reactions of benzothiazolide triosmium clusters with tetramethylthiourea

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**Abstract**

The valence saturated benzothiazolide triosmium cluster $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_7H_4NS)(\mu\text{-}H)]$ (**1**) reacts with tetramethylthiourea in refluxing toluene to give $[Os_3(CO)_8(\mu\text{-}\eta^2\text{-}C_7H_4NS)(\eta^2\text{-}SCNMe_2NMeCH_2)(\mu\text{-}H)_2]$ (**5**), which exists as a mixture of two isomers in solution, whereas the electron-deficient cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_4NS)(\mu\text{-}H)]$ (**2**) reacts with tetramethylthiourea in refluxing cyclohexane to give two new compounds $[Os_3(CO)_8(\mu\text{-}\eta^2\text{-}C_7H_4NS)(\eta^2\text{-}SCNMe_2NMeCH_2)(\mu\text{-}H)_2]$ (**6**) and $[Os_3(CO)_9(\mu\text{-}\eta^2\text{-}C_7H_4NS)(\eta^1\text{-}SC(NMe_2)_2)(\mu\text{-}H)]$ (**7**). In contrast, the reaction of $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)NS)(\mu\text{-}H)]$(**3**) with tetramethylthiourea in refluxing cyclohexane at 81 °C, gives only $[Os_3(CO)_9(\mu\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)NS)(\eta^1\text{-}SC(NMe_2)_2)(\mu\text{-}H)]$ (**8**) in 15% yield. Compound **7** converts into **6** in refluxing toluene whereas a similar thermolysis of **8** results non-specific decomposition. All the compounds have been characterized by elemental analysis, IR, $^1H$ NMR and mass spectroscopic data together with single crystal X-ray diffraction analysis for **5** and **7**. Both compounds **5** and **6** contain a cyclometallated tetramethylthiourea ligand which is chelating at the rear osmium atom and are structurally very similar. In **5**, the benzothiazolide ligand is coordinated to $Os_3$ triangle *via* the nitrogen lone pair and C(2) carbon atom of the heterocyclic ring whereas in **6** the ligand is coordinated to the $Os_3$ triangle *via* the nitrogen lone pair and the C(7) carbon atom of carbocyclic ring. In **7** and **8**, the tetramethylthiourea ligand is coordinated at an equatorial site of the osmium atom which is also bound to the nitrogen atom of the benzothiazolide ligand.

*Keywords:* Trisomium clusters; Benzothiazilide; Cyclometallated tetramethylthiourea; Crystal structure

## 1. Introduction

Electron-deficient or coordinatively unsaturated transition metal cluster compounds have received considerable attention for many years because they are generally much more reactive relative to their electron precise counterparts [1–3]. This feature may play a key role in the future development of these compounds as catalysts [4–6]. We have recently reported synthetic procedures for a novel class of electron-deficient clusters $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-benzoheterocycle})(\mu\text{-}H)]$, which result from the reaction of $[Os_3(CO)_{10}(CH_3CN)_2]$ with a wide range of benzoheterocycles followed by thermolysis or photolysis of the initially formed decacarbonyls [7–15]. The electron deficiency in these complexes arises from the presence of a three centre two electron bond β to the coordinated pyridinyl nitrogen. The reactions of these complexes with neutral nucleophiles such as phosphines and amines result in ligand addition at the metal core [7,8] while with anionic nucleophiles such as hydride or

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carbanions, nucleophilic addition is at the carbocyclic ring [9,11]. We have demonstrated that despite their structural similarities, the reactivity of these complexes along with their product distributions and structures are sensitive to the nature of the heterocyclic ring. For example, the 2-methylbenzothiazole cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)NS)(\mu\text{-}H)]$ (**3**) reacts with diazomethane to give $[Os_3(CO)_9(CH_2)(CH_3)(\mu_3\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)NS)(\mu\text{-}H)]$, containing an edge bridging methylene group and a σ-bound methyl group whereas the benzothiazole cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_4NS)(\mu\text{-}H)]$ (**2**) and the quinoline cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)]$ (**4**) react with diazomethane under the same conditions to give $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CHC_7H_4NS)(\mu\text{-}H)_2]$ and $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CHC_9H_6N)(\mu\text{-}H)_2]$, respectively [16]. We have also observed that **4** reacts with $PPh_3$ at room temperature to give a single addition product $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)(PPh_3)(\mu\text{-}H)]$ whereas **3** gives two separable isomers of $[Os_3(CO)_9(\mu\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)NS)(PPh_3)(\mu\text{-}H)]$ in 51% and 40% yields which differ in the location of the $PPh_3$ ligand [17].

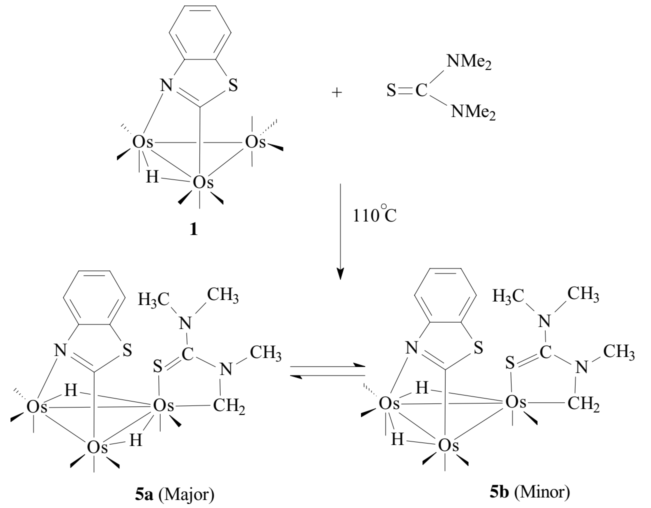
The reactions of thiourea and a number of its derivatives with dodecacarbonyl triruthenium have attracted increasing attention because these reactions are usually associated with the cleavage of C–S, C–N, N–H and/or C–H bonds of the alkyl substituted thiourea ligands were found to give, depending upon the substituents, and the reaction conditions, a large variety of ruthenium clusters containing not only thioureato, hydrido and sulfido ligands but also carbene, dicarbene and carbyne ligands derived from the thiourea employed [18–25]. Related chemistry of N,N-diethyl-N′-*p*-tolylthiourea with polynuclear rhenium carbonyl complexes has been reported by Adams et al. [26]. In comparison with the extensive ruthenium carbonyl cluster chemistry of thiourea ligands only a very limited number of thiourea derived osmium carbonyl cluster compounds have been described in the literature. We [27] and others [28] have reported triosmium clusters containing edge and triply bridging thioureato as well as S-coordinated tetramethyl thiourea ligands from the reactions of the lightly stabilized cluster $[Os_3(CO)_{10}(MeCN)_2]$ or $[Os_3(CO)_{12}]$ with thiourea and tetramethylthiourea. Recently, we have reported the triosmium cluster $[Os_3(CO)_8(\mu\text{-dppm})(\mu_3\text{-}S)_2]$ containing bridging dppm and capping sulfido ligand from the reaction of $[Os_3(CO)_{10}(\mu\text{-dppm})]$ with tetramethylthiourea [29]. In connection with our ongoing investigations of the synthesis and reaction chemistry of electron-deficient benzoheterocycle triosmium clusters, we have investigated the reactions of **2** and **3** with tetramethylthiourea. We have also investigated the reaction of the saturated cluster **1** with tetramethylthiourea in order to better understand how the bonding mode of the benzoheterocycle impacts its coordination chemistry.

## 2. Results and discussion

The reaction of the saturated benzothiazolide triosmium cluster **1** with two equivalents of tetramethylthiourea in refluxing toluene at 110 °C gives $[Os_3(CO)_8(\mu\text{-}\eta^2\text{-}C_7H_4NS)(\eta^2\text{-}SCNMe_2NMeCH_2)(\mu\text{-}H)_2]$ (**5**) as pale yellow crystals from hexane/$CH_2Cl_2$ in 15% yield (Scheme 1). The compound **5** has been characterized by IR, $^1H$ NMR and mass spectroscopic data together with single crystal X-ray diffraction analysis.

The solid-state structure of **5** is depicted in Fig. 1, crystal data are given in Table 1 and selected bond distances and angles are collected in Table 2. The molecule consists of a triangular cluster of osmium atoms, eight terminal carbonyl ligands, an edge bridging benzothiazolide ligand on the Os(1)–Os(2) edge and a chelating $\eta^2$-$SCNNMe_2NMeCH_2$ ligand on Os(3). The $Os_3$ triangle is significantly distorted and has two long bonds, Os(2)–Os(3) = 3.1337(4) and Os(1)–Os(3) = 3.0851(5) Å and one short bond, Os(1)–Os(2) = 2.811(4) Å. The latter is even significantly shorter than the average metal–metal bond length in $[Os_3(CO)_{12}]$ (2.877 (3) Å) [30]. Eight terminal carbonyl ligands are arranged such that three are bonded to each of Os(1) and Os(2) and two to Os(3). The hydride ligands were located crystallographically and refined. The hydrides bridge the Os(2)–Os(3) and the Os(1)–Os(3) edges and lie almost in the plane of the metal triangle. In general, when the Os–Os bonds are 3 Å this indicates an in plane metal hydride bridge [31].

An intriguing structural feature of **5** is that a metallated tetramethylthiourea ligand $SCNNMe_2NMeCH_2$, formed by the activation of one of the methyl groups of the tetramethylthiourea ligand, is bonded to Os(3) and produces the five member chelate ring, Os(3)–S(2)–C(108)–N(2)–C(109) and is coordinated to Os(3) at the site of the C–H cleavage as well by the sulfur



Scheme 1.

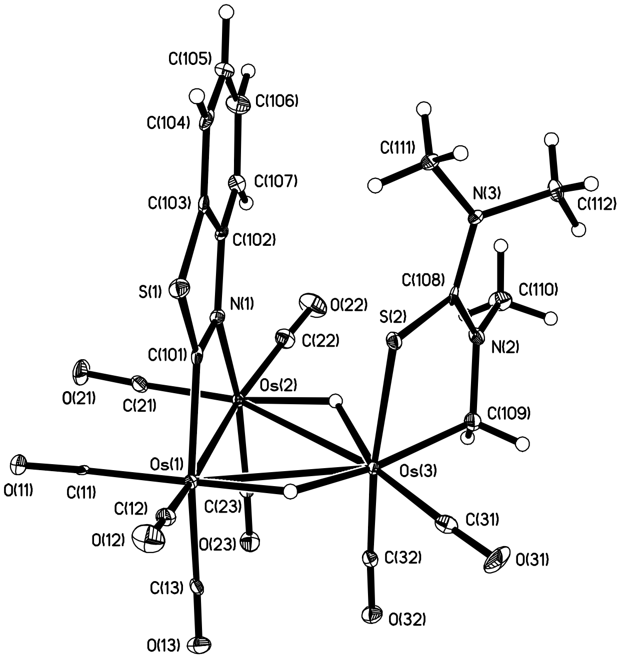


Fig. 1. Solid state structure of $[Os_3(CO)_8(\mu\text{-}\eta^2\text{-}C_7H_4NS)(\eta^2\text{-}SCNMe_2NMeCH_2)(\mu\text{-}H)_2]$ (**5**).

atom. The metallated carbon atom (C(109)) occupies an equatorial coordination site in the plane of the $Os_3$ triangle.

The benzothiazolide ligand is coordinated to Os(2) *via* the nitrogen lone pair and to Os(2) through the C(101) carbon atom. The Os(2)–N(1) bond distance of 2.121(5) Å and the Os(1)–C(101) bond distance of 2.093(6) are comparable to the corresponding distances in the quinoline complex $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)]$ [32]. All other features of the molecular geometry are within the expected range. The C–C distances within the carbocyclic ring are in the range 1.356(10)–1.406(9) Å. Individual Os–CO distances range from 1.870(7) to 1.937(6) Å, C–O bond lengths range from 1.129(8) to 1.161(8) Å and Os–C–O angles are in the range 175.1(6)–178.8(6) Å. The cluster is electron precise with 48 electrons as expected for a closed triangular cluster. Both the benzothiazolide and the chelating thiourato rings are essentially perpendicular to the plane of the metal triangle.

The infrared spectrum of **5** in the carbonyl stretching region shows *v*CO bands characteristic of terminal carbonyl ligands. The mass spectrum exhibits the molecular ion peak at *m*/*z* 1061 corresponding to the molecular ion of **5** and fragmentation peaks due to the sequential loss of eight CO ligands. The $^1H$ NMR spectrum of **5** in the aromatic region shows two sets of eight signals indicating that the compound exists as two isomers in solution in a ratio of 1:3. The signals at $\delta$ 7.73 (d, $J = 7.6$ Hz), 7.42 (d, $J = 7.6$ Hz), 7.36 (t, $J = 7.6$ Hz) and 7.20 (t, $J = 7.6$ Hz) are due to the major isomer while at $\delta$ 7.68 (d, $J = 8.0$ Hz), 7.60 (d, $J = 8.0$ Hz), 7.49 (t, $J = 8.0$ Hz), 7.24 (t, $J = 8.0$ Hz) are due to the minor isomer. The aliphatic region of the spectrum also contains two sets of methyl resonances for the two isomers in the same ratio. The signals at $\delta$ 3.19 and 2.20 are due to the major isomer while those at $\delta$ 3.21 and 2.66 are due to the minor isomer. The hydride region of the spectrum contains four signals at $\delta$ −13.56, −14.00, −15.56 and −15.76 consistent with the presence of two isomers in solution. We believe that the isomers differ in the location of the bridging hydride ligand as proposed in Scheme 1 and assuming that the elongated metal–metal bonds reflect the disposition of the hydrides in the major isomer. One might expect the interchange between the two isomers to be accessible on the NMR time scale at elevated temperatures. However the compound proved to be insoluble in all common organic solvents except for methylene chloride which boils at 42 °C. On the basis of the evidence presented here we cannot exclude the possibility that the two isomers differ by the relative disposition of the coordinated rings (i.e. on the same or opposite faces of the metal triangle).

No reaction was observed between the electron-deficient cluster **2** and tetramethylthiourea at room temperature. However, heating the reaction mixture at 80 °C in cyclohexane leads to the formation of two new compounds $[Os_3(CO)_8(\mu\text{-}\eta^2\text{-}C_7H_4NS)(\eta^2\text{-}SCNMe_2NMeCH_2)(\mu\text{-}H)_2]$ (**6**) and $[Os_3(CO)_9(\mu\text{-}\eta^2\text{-}C_7H_4NS)(\eta^1\text{-}SC(NMe_2)_2)(\mu\text{-}H)]$ (**7**) (Scheme 2) in 12% and 9% yields, respectively. Compound **6** has been characterized by elemental analysis, infrared, $^1H$ NMR and mass spectroscopic data. The pattern of the IR spectrum of **6** is similar to that of **5** indicating that they have similar distributions of the carbonyl ligands. The aromatic region of the $^1H$ NMR spectrum of **6** shows four equal intensity signals, two doublets at $\delta$ 7.89 ($J = 8.2$ Hz) and 7.36 ($J = 8.2$ Hz), a triplet at 7.01 ($J = 8.2$ Hz) and a singlet at $\delta$ 9.13. The doublets at $\delta$ 7.49 and 7.36 are assigned to the protons on C(4) and C(6) interchangeably. The triplet at $\delta$ 7.01 is assigned to the proton on C(5) while the singlet at $\delta$ 9.13 is assigned to the C(2) proton. The aliphatic region of the $^1H$ NMR spectrum contains two singlets at $\delta$ 3.08 and 2.35 and two doublets at $\delta$ 4.69 and 4.59 ($J = 9.8$ Hz) with a relative intensity of 6:3:1.1. The doublets at 4.69 and 4.59 are due to the two nonequivalent $CH_2$ protons which indicate that one of methyl groups of the tetramethylthiourea ligand has been activated. The hydride region of the spectrum contains two equal intensity singlets at $\delta$ −13.17 and −15.45, indicating the presence of two bridging hydride ligands. The formula of **6** can also be established by a mass spectral analysis which shows a parent ion at *m*/*z* 1061 plus ions corresponding to the loss of each of eight CO ligands. Compound **6** is obviously closely related to **5**, but in **5** the benzothiazolide ligand is coordinated through the C(2) carbon and the nitrogen atom in an

Table 1
Crystal data and structure refinement for **5** and **7**

| | **5** | **7** |
|---|---|---|
| Chemical formula | $C_{20}H_{17}N_3O_8Os_3S_2$ | $C_{21}H_{17}N_3O_9Os_3S_2$ |
| Formula weight | 1062.09 | 1090.10 |
| Temperature (K) | 150 (2) | 293(2) |
| Radiation, wavelength (Å) | Mo Kα, 0.71073 | 0.71073 |
| Crystal system, space group | Triclinic, $P\bar{1}$ | Monoclinic, $P2_1/n$ |
| Unit cell parameters | | |
| $a$ (Å) | 9.3523(12) | 11.5035(7) |
| $b$ (Å) | 10.3028(13) | 14.8115(9) |
| $c$ (Å) | 14.5517(19) | 16.7945(10) |
| $\alpha$ (°) | 97.274 (2) | 90 |
| $\beta$ (°) | 106.681(2) | 101.1950(10) |
| $\gamma$ (°) | 101.465 | 90 |
| $V$ (Å$^3$) | 1290.9 (3) | 2807.1(3) |
| $Z$ | 2 | 4 |
| Calculated density (g/cm$^3$) | 2.732 | 2.579 |
| Absorption-coefficient $\mu$ (mm$^{-1}$) | 14.939 | 13.746 |
| $F(000)$ | 964 | 1984 |
| Data collection method | Bruker SMART APEX diffractometer<br>ω rotation with narrow frames | Bruker SMART APEX diffractometer<br>ω rotation with narrow frames |
| Crystal size (mm$^3$) | 0.30×0.25×0.14 | 0.40×0.24×0. 04 |
| $\theta$ Range for data collection (°) | 2.06–28.30 | 1.85–28.26 |
| Index ranges | $-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-18 \leqslant l \leqslant 18$ | $-15 \leqslant h \leqslant 14$, $-19 \leqslant k \leqslant 19$, $-22 \leqslant l \leqslant 22$ |
| Completeness to $\theta$ | 92.6% ($\theta = 28.30$) | 99.7% ($\theta = 26.00$) |
| Reflections collected | 11348 | 24366 |
| Independent reflections | 5958 ($R_{\text{int}} = 0.0317$) | 6690 ($R_{\text{int}} = 0.0483$) |
| Reflections with $F^2 > 2\sigma$ | 5616 | 5522 |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Minimum and maximum transmission | 0.0941 and 0.2289 | 0.0727 and 0.5830 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Weighing parameters $a$, $b$ | 0.0459, 1.7572 | 0.03260, 2.9915 |
| Data/restraints/parameters | 5958/0/332 | 6692/0/350 |
| Final $R$ indices [$F^2 > 2\sigma$] | $R_1 = 0.0343$, $wR_2 = 0.0860$ | $R_1 = 0.0373$, $wR_2 = 0.0763$ |
| $R$ indices (all data) | $R_1 = 0.0366$, $wR_2 = 0.0877$ | $R_1 = 0.0484$, $wR_2 = 0.0808$ |
| Goodness-of-fit on $F^2$ | 1.094 | 1.023 |
| Largest and mean shift/su | 0.001 and 0.000 | 0.001 and 0.000 |
| Largest differential peak and hole (eÅ$^{-3}$) | 3.497 and −3.706 | 1.260 and −1.890 |

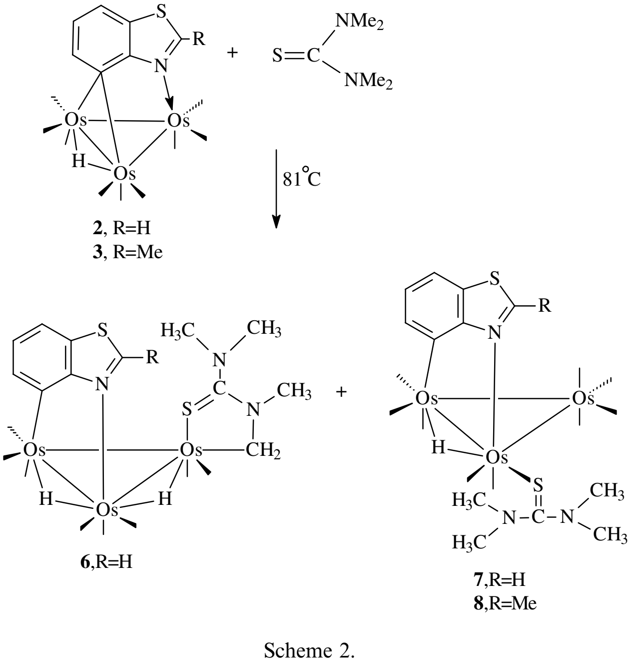
μ-η$^2$-bonding mode, whereas in **6** the benzothiazolide ligand is coordinated through the C(7) carbon and the nitrogen in the μ-η$^2$-bonding mode. There are examples of the activation of methyl group of tetramethylthiourea ligand on a triruthenium center but to our knowledge compounds **5** and **6** provide first examples of activation of a tetramethylthiourea ligand on a single osmium atom of a triosmium center. Interestingly, only one isomer is observed for **6** and if we assume that its structure is the same as that observed in the solid state for **5** this suggests that the N-C(2) bonding mode creates a less crowded environment allowing population of a second isomer. This idea supports the suggestion that the isomers differ by the disposition of the hydride ligands because one would expect a shortening of one osmium-osmium bond if one of the hydrides is moved to the edge of the cluster bridged by the heterocycle.

The solid-state structure of **7** is shown in Fig. 2, crystallographic data are given in Table 1 and selected bond distances and angles are collected in Table 3. The molecule contains a triangular cluster of osmium atoms (Os(1)–Os(3) = 2.8581(3), Os(1)–Os(2) = 2.9659 (3) and Os(2)–Os(3) = 2.8948 (4) Å). One of these distances is slightly shorter and one is slightly longer than average Os–Os bond distance of 2.877(3) Å found in $Os_3(CO)_{12}$ while the other one is substantially longer [30]. Nine linear carbonyl ligands are arranged such that each osmium atom has three. The hydride ligand was located crystallographically and refined and the benzothiazolide ligand and hydride ligand simultaneously span the Os(1)–Os(2) edge. The heterocyclic ligand is nearly perpendicular to plane of the $Os_3$ triangle and Os(2)–C(3) bond distance of 2.161(7) Å and Os(1)–N(1) bond distance of 2.135(5) Å are comparable to the corresponding distances in the related quinoline complex [(μ-H)$Os_3(CO)_{10}$(μ-η$^2$-$C_9H_6N$)] [32].

The tetramethylthiourea ligand is coordinated at an equatorial site to osmium which is also bound to nitrogen atom of the heterocyclic ligand. The Os(1)–S(2) bond distance of 2.4604(16) Å is comparable to the Os–S bond distance of the η$^1$-coordinated tetramethylthiourea ligand in [$Os_3(CO)_{11}$(η$^1$-SC(NMe$_2$)$_2$)] [27].

Table 2
Selected bond distances (Å) and bond angles (°) for **5**

| *Bond distances* (Å) | |
|---|---|
| Os(1)–Os(3) | 3.0851(5) |
| Os(2)–Os(3) | 3.1337(4) |
| Os(1)–Os(2) | 2.8111(4) |
| Os(1)–C(101) | 2.093(6) |
| Os(2)–N(1) | 2.121(5) |
| Os(3)–C(109) | 2.145(7) |
| S(1)–C(101) | 1.739(6) |
| Os(3)–S(2) | 2.4277(15) |
| S(1)–C(103) | 1.743(7) |
| N(2)–C(108) | 1.321(8) |
| N(2)–C(109) | 1.468(8) |
| N(3)–C(112) | 1.448(8) |
| C(102)–C(107) | 1.356(10) |
| C(103)–C(104) | 1.380(9) |
| C(105)–C(106) | 1.373(12) |
| S(2)–C(108) | 1.719(6) |
| N(1)–C(101) | 1.299(8) |
| N(2)–C(110) | 1.463(8) |
| N(3)–C(108) | 1.356(8) |
| N(3)–C(111) | 1.470(8) |
| N(1)–C(102) | 1.414(8) |
| | |
| *Bond angles* (°) | |
| Os(1)–Os(3)–Os(2) | 53.740(8) |
| Os(1)–Os(2)–Os(3) | 62.247(11) |
| Os(2)–Os(1)–Os(3) | 64.013(9) |
| C(101)–Os(1)–Os(2) | 67.91(16) |
| C(101)–Os(1)–Os(3) | 84.54(16) |
| N(1)–Os(2)–Os(1) | 69.96(14) |
| N(1)–Os(2)–Os(3) | 85.73(14) |
| C(31)–Os(3)–C(109) | 88.7(3) |
| C(109)–Os(3)–S(2) | 80.21(18) |
| S(2)–Os(3)–Os(2) | 93.50(4) |



Scheme 2.

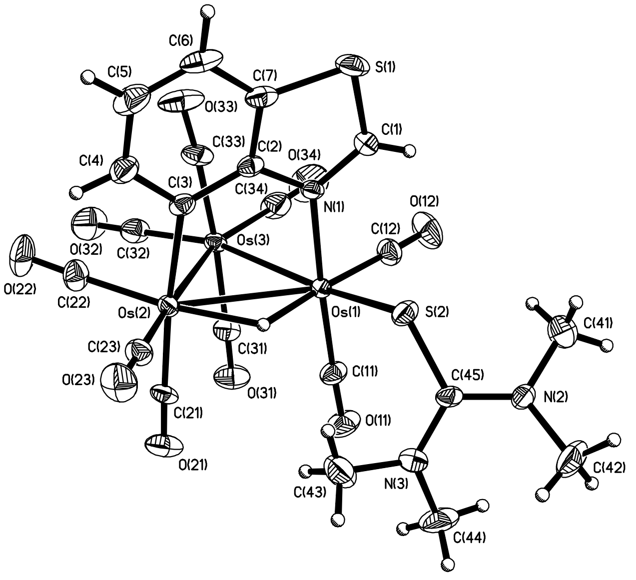


Fig. 2. Solid state structure of $[Os_3(CO)_9(\mu\text{-}\eta^2\text{-}C_7H_4NS)(\eta^1\text{-}SC(NMe_2)_2)(\mu\text{-}H)]$ (**7**).

Table 3
Selected bond distances (Å) and bond angles (°) for **7**

| *Bond distances* (Å) | |
|---|---|
| Os(1)–Os(3) | 2.8581(3) |
| Os(2)–Os(3) | 2.8948(4) |
| Os(1)–Os(2) | 2.9659(3) |
| Os(1)–S(2) | 2.4604(16) |
| Os(2)–C(3) | 2.161(7) |
| S(1)–C(1) | 1.710(7) |
| S(1)–C(7) | 1.725(8) |
| N(1)–C(1) | 1.303(8) |
| N(2)–C(45) | 1.337(8) |
| N(2)–C(42) | 1.469(9) |
| N(3)–C(43) | 1.437(9) |
| C(2)–C(7) | 1.396(8) |
| C(3)–C(4) | 1.391(8) |
| C(5)–C(6) | 1.360(12) |
| S(2)–C(45) | 1.721(6) |
| N(1)–C(2) | 1.403(7) |
| N(2)–C(41) | 1.433(9) |
| N(3)–C(45) | 1.328(8) |
| N(3)–C(44) | 1.476(9) |
| C(2)–C(3) | 1.409(9) |
| C(4)–C(5) | 1.386(10) |
| C(6)–C(7) | 1.400(10) |
| | |
| *Bond angles* (°) | |
| Os(1)–Os(3)–Os(2) | 62.064(8) |
| Os(3)–Os(1)–Os(2) | 59.575(9) |
| Os(3)–Os(2)–Os(1) | 58.361(8) |
| N(1)–Os(1)–Os(3) | 89.52(12) |
| N(1)–Os(1)–Os(2) | 83.06(13) |
| C(3)–Os(2)–Os(3) | 92.28(17) |
| C(3)–Os(2)–Os(1) | 83.82(15) |
| C(45)–S(2)–Os(1) | 111.8(2) |
| S(2)–Os(1)–Os(3) | 165.58(4) |
| S(2)–Os(1)–Os(2) | 110.86(5) |

The spectroscopic data obtained for **7** indicate that the molecular structure found in the solid-state is maintained in solution. The infrared spectrum of **7** in the carbonyl stretching region shows absorption bands characteristic of terminal carbonyl groups. The $^1$H NMR spectrum of **7** shows peaks at $\delta$ 9.15 (s), 8.02 (d, $J=7.6$ Hz), 7.40 (d, $J=7.6$ Hz), 7.01 (t, $J=7.6$ Hz), 3.05 (s) and −12.53 (s) with a relative intensity 1:1:1:1:12:1. The doublets at $\delta$ 8.02 and 7.40 are assigned to the C(4) and C(6) protons interchangeably. The triplet at $\delta$ 7.01 is assigned to the C(5) proton and the singlet at $\delta$ 9.15 can be assigned to the proton on C(2). The singlet at $\delta$ 3.05 has been assigned to the methyl protons of tetramethylthiourea ligand while the singlet at $\delta$ −12.53 is due to the bridging hydride ligand. The mass spectrum shows the molecular ion peak at *m*/*z* 1089 corresponding to the formulation of **7** and ions due to the successive loss of nine carbonyl groups plus the tetramethylthiourea ligand are observed.

Compound **7** converts to **6** in 42% yield when heated at 110 °C in refluxing toluene showing that **7** is the direct precursor to **6**. This transformation is complex, but most likely involves CO dissociation from the $Os(CO)_4$ moiety of **7** followed by migration of the nitrogen of the benzothiazole ring to the open coordination site and then by CH oxidative addition to the now open coordination site on the sulfur bound osmium atom. This type of edge to edge migration of the heterocyclic ring has been previously reported in the thermal rearrangements and coordination chemistry of related compounds [8,12].

In contrast to the reaction of **2** with tetramethylthiourea, the reaction of **3** with tetramethylthiourea in refluxing cyclohexane at 81 °C gives only $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)NS)(\eta^1\text{-}SC(NMe_2)_2)(\mu\text{-}H)]$ (**8**) in 15% yield. The compound has been characterized by elemental analysis, infrared, $^1$H NMR and mass spectroscopic data. The infrared spectrum in the carbonyl stretching region is very similar to that of **7**. From the similarities of their IR spectra it can be concluded that **8** is structurally analogous to **7**. The $^1$H NMR spectrum of **8** in $CD_2Cl_2$ shows signals at $\delta$ 7.97 ($J=6.8$ Hz), 7.25 (d, $J=6.8$ Hz), 6.98 (t, $J=6.8$ Hz), 3.10 (s) and −12.03 (s) with a relative intensity of 1:1:1:12:1. The doublets at $\delta$ 7.97 and 7.25 are assigned to the C(4) and C(6) protons, the triplet at $\delta$ 6.98 is assigned to the C(5) proton and the singlet at $\delta$ 3.10 is assigned to the methyl protons of the heterocyclic ligand while the singlet at $\delta$ −12.37 is assigned to the cluster bound bridging hydride ligand. The mass spectrum of **8** exhibits the molecular ion peak at *m*/*z* 1103 and fragmentation peaks due to the sequential loss of tetramethylthiourea and nine carbonyl ligands. There are many examples of mononuclear complexes containing $\eta^1$-coordinated tetramethylthiourea ligand, but to our knowledge compounds **7** and **8** provide the second and third examples of a cluster compound containing intact tetramethylthiourea ligand, the first being the $\eta^1$-S coordination of tetramethyl to an $Os_3(CO)_{11}$ cluster [27]. Apparently, the presence of the methyl group on the C(2) carbon provides sufficient steric interference to prevent the conversion of **8** to the analogue of **6**. This underlines the extreme sensitivity to steric effects of this family of clusters as previously reported for the reaction **2** and **3** with diazomethane [16].

## 3. Experimental

All solvents were dried (using appropriate desiccants), distilled before use, and store under a nitrogen atmosphere. Reactions were carried out under an atmosphere of pre-purified nitrogen by using standard Schlenk techniques. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on a Bruker DPX 400 spectrometer. Elemental analyses were carried out by the Microanalytical Laboratory at the University College London. The clusters 1, 2, and 3 were prepared according to the literature procedures [10,17].

### *3.1. Reaction of **1** with tetramethylthiourea*

A toluene solution (40 ml) of **1** (0.105 g, 0.107 mmol) and tetramethylthiourea (0.028 g, 0.212 mmol) was heated to reflux under nitrogen for 6 h The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/$CH_2Cl_2$ (3:1, v/v) developed two major and several minor bands. The faster moving major band afforded $[Os_3(CO)_8(\mu\text{-}\eta^2\text{-}C_7H_4NS)(\eta^2\text{-}SCNMe_2NMeCH_2)(\mu\text{-}H)_2]$ (**5**) (0.017 g, 15%) as pale yellow crystals after recrystallization from hexane/$CH_2Cl_2$ at 4 °C (Anal. Calc. for $C_{20}H_{17}N_3O_8Os_3S_2$: C, 22.62; H, 1.62; N, 3.96. Found: C, 22.75; H, 1.78; N, 4.05%). IR ($\nu$CO, $CH_2Cl_2$): 2083 s, 2046 s, 2021 vs, 2000 m, 1988 w, 1967 w, 1942 m, cm$^{-1}$; $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.73 (d, 1H, $J=7.6$ Hz), 7.68 (d, 1H, $J=8.0$ Hz), 7.60 (d, 1H, $J=8.0$ Hz), 7.49 (t, 1H, $J=8.0$ Hz), 7.42 (d, 1H, $J=7.6$ Hz), 7.36 (d, 1H, $J=7.6$ Hz), 3.21 (s, 3H), 3.19 (s, 3H), 2.66 (s, 3H), 2.20 (s, 6 H), −13.56 (s, 1H), −14.00 (s, 1H), −15.56 (s, 1H), −15.76 (s, 1H) mass spectrum: *m*/*z* 985 ($M^+$). The slower moving major band gave unreacted **2** (0.010 g). The minor bands were too small for characterization.

### *3.2. Reaction of **2** with tetramethylthiourea*

A cyclohexane suspension (40 ml) of **2** (0.095 g, 0.099 mmol) and tetramethylthiourea (0.026 g, 0.197 mmol) was heated to reflux under nitrogen for 6 h during which time the colour changed from green to yellow. The solvent was rotary evaporated and the residue was chromatographed by TLC on silica gel. Elution with hexane/$CH_2Cl_2$ (3:1, v/v) gave two major and three very minor bands. The faster moving major band gave [$Os_3(CO)_8(\mu$-$\eta^2$-$C_7H_4NS)(\eta^2$-$SCNMe_2NMeCH_2)(\mu$-$H)_2$] (**6**) (0.013 g, 12%) as pale yellow crystals after recrystallization from hexane/$CH_2Cl_2$ at 4 °C (Anal. Calc. for $C_{20}H_{17}N_3O_8Os_3S_2$: C, 22.62; H, 1.62; N, 3.96. Found: C, 22.79; H, 1.75; N, 4.05%). IR ($\nu$CO, $CH_2Cl_2$): 2077 s, 2039 vs, 2017 vs, 1992 w, 1979 w, 1959 w, $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$): $\delta$ 9.13 (s, 1H), 7.89 (d, 1H, $J=8.2$ Hz), 7.36 (d, 1H, $J=8.2$ Hz), 7.01 (t, 1H, $J=8.2$ Hz), 4.69 (d, 1H, $J=9.8$ Hz), 4.59 (d, 1H, $J=9.8$ Hz), 3.08 (s, 6H), 2.35 (s, 3H), −13.17 (s, 1H), −15.45 (s, 1H); mass spectrum: $m/z$ 1061 ($M^+$). The slower moving major band afforded [$Os_3(CO)_9(\mu$-$\eta^2$-$C_7H_4NS)(\eta^1$-$SC(NMe_2)_2)(\mu$-$H)$] (**7**) (0.010 g, 9%) as orange crystals after recrystallization from hexane/$CH_2Cl_2$ at 4 °C (Anal. Calc. for $C_{21}H_{17}N_3O_9Os_3S_2$: C, 23.14; H, 1.58; N, 3.86%). IR ($\nu$CO, $CH_2Cl_2$): 2083 s, 2039 vs, 2002 vs, 1985 vw, 1954 w, 1919 w, $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$): $\delta$ 9.15 (s, 1H), 8.02 (d, 1H, $J=7.6$ Hz), 7.40 (d, 1H, $J=7.6$ Hz), 7.01 (t, 1H, $J=7.6$ Hz), 3.05 (s, 12 H), −12.53 (s, 1H); mass spectrum: $m/z$ 1089 ($M^+$). The minor bands were too small for complete characterization.

### 3.3. Reaction of **3** with tetramethylthiourea

Tetramethylthiourea (0.034 g, 0.257 mmol), the unsaturated cluster [$Os_3(CO)_9(\mu_3$-$\eta^2$-$C_7H_3(2$-$CH_3)NS)(\mu$-$H)$] (0.125 g, 0.129 mmol) and cyclohexane (50 ml) were combined in a two necked 100 ml round bottom flask and the reaction mixture was heated to reflux under nitrogen for 7 h. The colour changed from green to yellow. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/$CH_2Cl_2$ gave one major band which gave [$Os_3(CO)_9(\mu_3$-$\eta^2$-$C_7H_3(2$-$CH_3)NS)$-$(\eta^1$-$SC(NMe_2)_2)(\mu$-$H)$] (**8**) (0.021 g, 15%) as orange crystals after recrystallization from hexane/$CH_2Cl_2$ at 4 °C (Anal. Calc. for $C_{22}H_{19}N_3O_9Os_3S_2$: C, 23.93; H, 1.74; N, 3.81. Found: C, 24.15; H, 1.89; N, 3.89%). IR ($\nu$CO, $CH_2Cl_2$): 2083 s, 2039 vs, 2002 vs, 1985 vw, 1954 w, 1919 w, $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$): $\delta$ 9.15 (s, 1H), 8.02 (d, 1H, $J=7.6$ Hz), 7.40 (d, 1H, $J=7.6$ Hz), 7.01 (t, 1H, $J=7.6$ Hz), 3.05 (s, 12 H), 2.68 (s, 3H), −12.53 (s, 1H); mass spectrum: $m/z$ 1103 ($M^+$).

### 3.4. Conversion of 7 to **6**

A toluene solution of **7** (0.012 g, 0.11 mmol) was heated to reflux for 2 h. The solvent was removed under reduced pressure and the residue was chromatographed as above to give **6** (0.005 g, 42%).

### 3.5. X-ray structure determination of **5** and 7

Single crystals of compounds **5** and **7** were mounted on glass fibers and all geometric intensity data were obtained from these samples on a Bruker SMART APEX CCD diffractometer using graphite-monochromatic Mo K$\alpha$ radiation ($\lambda=0.71073$ Å) at 150 ± 2 K for **5** and at 293 ± 2 K for **7**. Data reduction and integration was carried out with SAINT+ and absorption corrections applied using the program SADABS [33]. Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except those bonded to osmium, were placed in calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model). Hydrogen atoms bridging the osmium atoms were located and their positions refined using fixed isotropic thermal parameters. The SHELXTL PLUS V6.10 program packaged was used for the structure solution and refinement [33].

## 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 236392 for **5** and 236393 for compound **7**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.ac.uk).

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