

Reactivity of the electron deficient compound $[(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}]$ with thiols¹

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Abstract

The reactions of the electron deficient cluster $[(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}]$ **5** with $\text{C}_2\text{H}_5\text{SH}$, $\text{C}_6\text{H}_5\text{SH}$ and H_2S are reported. The reaction of **5** with RSH at 25°C affords the dihydrido clusters $[\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SR})]$ ($\text{R} = \text{C}_2\text{H}_5$ **6**, $\text{R} = \text{C}_6\text{H}_5$ **7**) in which the hydrides exhibit dynamic behaviour on the NMR timescale while reaction with H_2S yields the known S-capped dihydrido cluster $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})]$ **8**. The cluster **6** is thermally decarbonylated to give $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_8\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SC}_2\text{H}_5)]$ **9**, $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-SC}_2\text{H}_5)]$ **10** and **8**. Compounds **6** and **7** react with CCl_4 at 77°C to give $[\text{Os}_3(\text{CO})_8\text{Cl}_2\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SR})]$ ($\text{R} = \text{C}_2\text{H}_5$ **11**, $\text{R} = \text{C}_6\text{H}_5$ **12**). All the compounds have been characterized by ^1H NMR, infrared spectroscopy and elemental analysis. Compound **6** has also been characterized by X-ray crystallography. © 1997 Elsevier Science S.A.

Keywords: Osmium; Cluster; Hydride; Electron deficient; Crystal structure; Decarbonylation; Reactivity

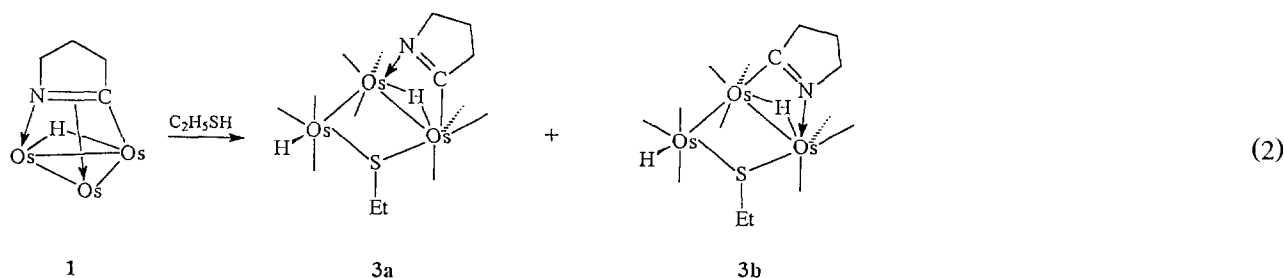
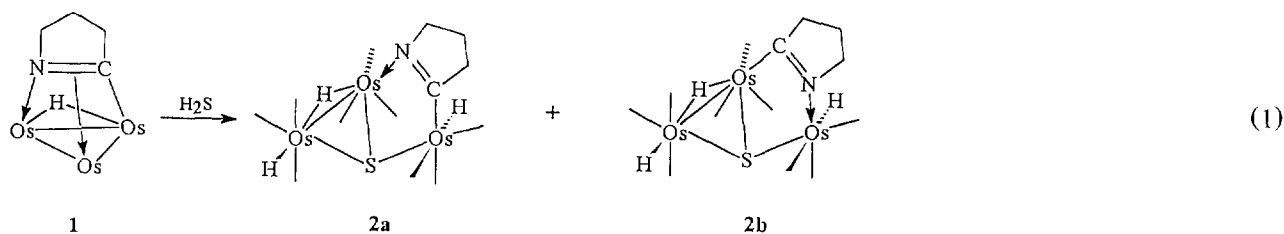
1. Introduction

There are numerous examples in the literature of the reactivity of the valence saturated triosmium clusters with thiols [1–8]. For example, $[\text{Os}_3(\text{CO})_{12}]$ reacts with H_2S to give the S-capped triosmium cluster $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})]$ [1,2], while reactions with the labile clusters $[\text{Os}_3(\text{CO})_{10}(\text{C}_6\text{H}_8)]$ and $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ give the simple oxidative addition product $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-SH})]$ [3,4]. The analogous reactions of $[\text{Os}_3(\text{CO})_{12}]$, $[\text{Os}_3(\text{CO})_{10}(\text{C}_6\text{H}_8)]$ or

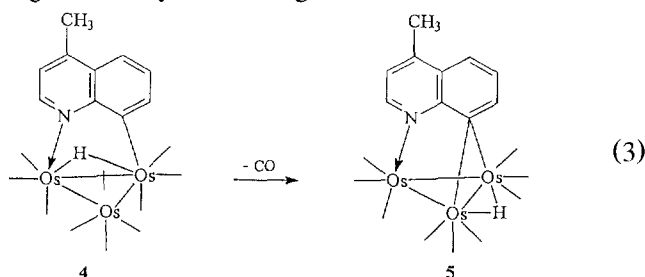
$[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with RSH ($\text{R} = \text{Et}$, Pr or Ph) also give the simple oxidative addition product $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-SR})]$ [3–6]. The prevalence of sulfur-capped and sulfur-bridged trimetallic clusters demonstrates the unique properties of sulfur in the reactions of many transition metal clusters [8,9]. Previously we reported that the reactions of the valence saturated μ_3 -imidoyl cluster $[(\mu\text{-H})(\text{Os}_3\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\overline{\text{C}}=\text{NCH}_2\text{CH}_2\overline{\text{C}}\text{H}_2)]\text{CH}_2$ **1** with H_2S yields two isomeric trihydride clusters $[\text{H}_2(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^2\text{-}\overline{\text{C}}=\text{NCH}_2\text{CH}_2\overline{\text{C}}\text{H}_2)(\mu_3\text{-S})]$ (Eq. (1), **2a** and **2b**) containing two terminal and one bridging hydride ligand, while reaction with $\text{C}_2\text{H}_5\text{SH}$ yields the isomeric dihydride clusters $[\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^2\text{-}\overline{\text{C}}=\text{NCH}_2\text{CH}_2\overline{\text{C}}\text{H}_2)\text{C}=\text{NCH}_2\text{CH}_2\overline{\text{C}}\text{H}_2](\mu\text{-S})]$ (Eq. (2), **3a** and **3b**) containing one terminal and one bridging hydride ligand [8].

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¹ Dedicated to the memory of Professor Yuri T. Struchkov in recognition of both his outstanding contributions to structural organometallic chemistry and the friendship he bestowed to many of us.



We have recently reported the 46-electron triosmium cluster $[(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}]$ **5**, which is obtained in good yields from decarbonylation of $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}]$ (Eq. (3), **4**), which is in turn synthesized by the room temperature reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with 4-methyl quinoline [10]. We found that this complex exhibits unusually high reactivity towards ligand addition reactions [10].

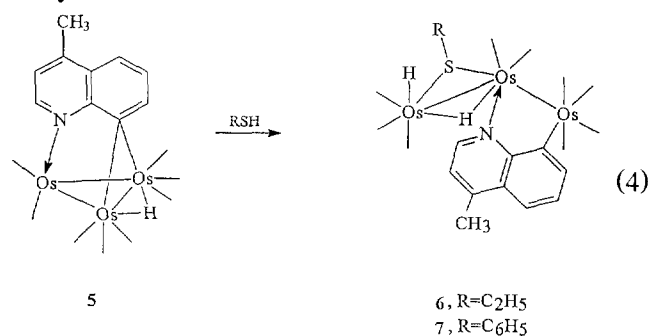


In the present paper we report the results of our studies on the reactions of **5** with a range of thiols and the isolation of triosmium complexes containing one terminal and one bridging hydride ligand in which one of the three metal–metal bonds is cleaved. We also report the X-ray crystal structure as well as the decarbonylation and hydride exchange reactions of **6**.

2. Results and discussion

Compound **5** represents an unusual example of a $46e^-$ triosmium cluster which is highly reactive towards hydride donors and hydrogenation [10]. Since the μ_3 -imidoyl cluster **1** undergoes facile reaction with ethanethiol and H_2S to give structurally unusual clusters with cleavage of metal–metal bonds [8], we thought it would be interesting to explore the reactivity of **5** with thiols to see if it would exhibit the same type of

reactivity. The reaction of **5** with ethanethiol at room temperature over a period of 24 h leads to the quantitative conversion (by analytical TLC) to a compound whose formula $[\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SC}_2\text{H}_5)]$ (Eq. (4), **6**, isolated yield 85%) is based on ^1H NMR, infrared and elemental analysis.



The ^1H NMR spectrum of **6** showed the presence of a relatively complex mixture of isomers, each having a terminal and a bridging hydride ligand. We therefore undertook an X-ray crystallographic investigation of **6** to elucidate the exact stoichiometry, bonding mode of the organic ligand and disposition of the hydrides to the cluster. The molecular structure of **6** is shown in Fig. 1, and selected bond distances and angles are presented in Table 1. The structure depicted in Fig. 1 represents the 'average' of three structural isomers **6a**, **6b** and **6d** in Scheme 1, which are present in 66, 24 and 10% yields respectively (details in Section 3) and differ only in the relative orientation of the terminal hydride on Os(3). The basic structure consists of three osmium atoms with two metal–metal bonds [$\text{Os}(1)\text{-Os}(2) = 2.8250(6)$ and $\text{Os}(1)\text{-Os}(3) = 3.0188(6)$ Å]. The $\text{Os}(2) \cdots \text{Os}(3)$ distance of $4.8413(6)$ Å indicates that there is no bonding interaction between these atoms. The $\text{Os}(1)\text{-Os}(3)$ bond

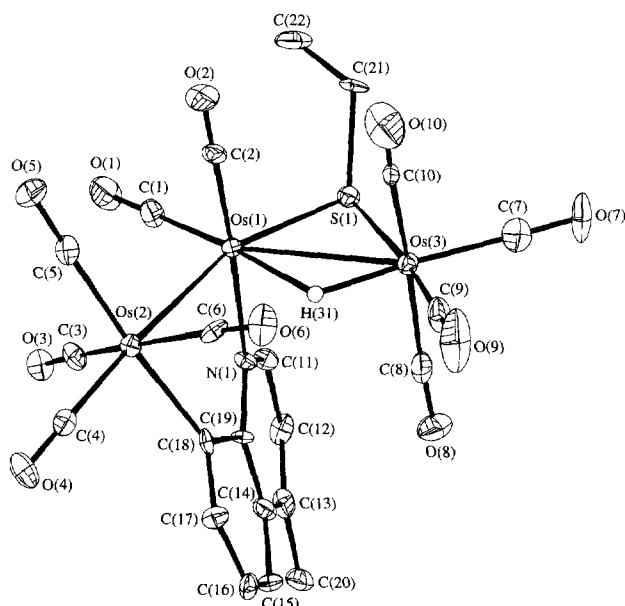


Fig. 1. Solid state structure of $[\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_9\text{H}_5\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3\text{N})(\mu\text{-SCH}_2\text{CH}_3)\}]$ **6** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. The ring hydrogen atoms have been omitted for clarity. [The figure depicts the average of three structural isomers with positions of the terminal hydride along Os(3)–C(10) **6a** (66%), Os(3)–C(8) **6b** (24%) or Os(3)–C(9) **6d** (10%).]

[3.0188(6) Å] spanned by the two bridging ligands is significantly longer than the Os(1)–Os(2) bond [2.8250(6) Å], which is shorter than the average Os–Os distance of 2.877(3) Å in $[\text{Os}_3(\text{CO})_{12}]$ [11]. The heterocyclic ligand bridges the Os(1)–Os(2) edge and donates three electrons to the cluster via a two-electron donor σ -bond between N(1) and Os(1) and a one-electron σ -bond from C(18) to Os(2). The Os(1)–N(1) and Os(2)–C(18) distances, 2.167(8) and 2.154(11) Å respectively, are similar to those observed in related trimetallic clusters containing N-heterocyclic ligands [12].

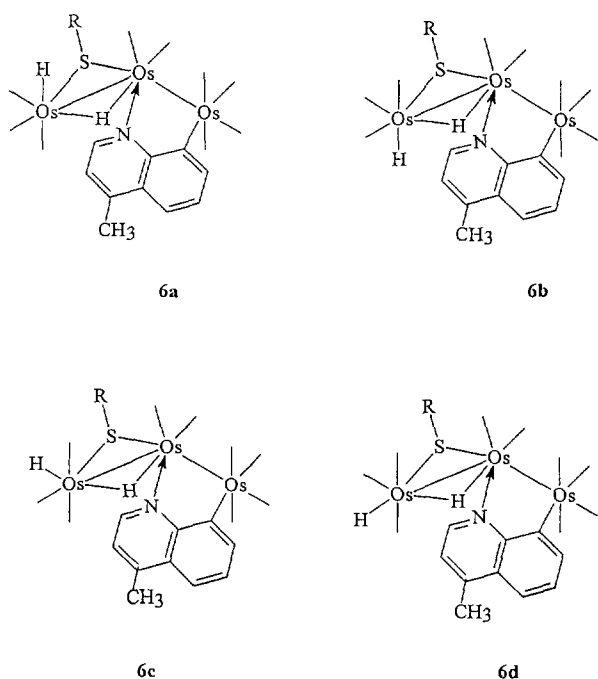
The sulfur atom of the thiolate ligand symmetrically bridges Os(1) and Os(2) [Os(1)–S(1) = 2.388(3) and Os(3)–S(1) = 2.398(3) Å] and donates three electrons to the metal. The bridging hydride was located along the Os(1)–Os(3) edge. Although the terminal hydride was not located clearly from the difference electron density map, the distribution of CO and other ligands indicates that it is coordinated to Os(3). It is interesting to note that the Os(3)–Os(1)–Os(2) angle [111.84(2)°] is severely compressed from a linear arrangement of the metal chains because of the distortions caused by the bridging ligands. Similar distortions in the Os–Os–Os angles from linearity have been reported for other triosmium clusters containing two metal–metal bonds, one of which is bridged by an organic ligand. Examples of such compounds are $[\text{HOs}_3(\text{CO})_{10}(\text{PET}_3)(\text{CF}_3\text{C}=\text{CHCF}_3)]$ [162.3(1)°] [13], $[\text{HOs}_3(\mu\text{-CH}=\text{CHNC}_5\text{H}_4)(\text{CO})_{10}]$ [160.0(1)°] and $[\text{HOs}_3(\mu\text{-CH}=\text{CHNC}_5\text{H}_4)(\text{CO})_9(\text{PMe}_2\text{Ph})]$ [160.4(1)°] [14]. In case of **6** the distortion is more pronounced because of the presence of three bridging ligands in the trinuclear cluster. The structure of **6** is unique, to our knowledge, in that it contains two metal–metal bonds with three bridging ligands. The coordination around each osmium is distorted octahedral.

The geometry parameters related to the CO groups

Table 1
Selected bond lengths (Å) and angles (°) for **6**

Os(1)–Os(2)	2.8250(6)	Os(1)–Os(3)	3.0188(6)
Os(1)–N(1)	2.167(8)	Os(1)–S(1)	2.388(3)
Os(2)–C(18)	2.154(11)	Os(3)–S(1)	2.398(3)
Os(1)–H(31)	1.99	Os(3)–H(31)	1.68
S(1)–C(21)	1.823(10)	N(1)–C(11)	1.312(13)
N(1)–C(19)	1.393(13)	C(11)–C(12)	1.40(2)
C(12)–C(13)	1.32(2)	C(13)–C(14)	1.46(2)
C(13)–C(20)	1.49(2)	C(14)–C(15)	1.40(2)
C(14)–C(19)	1.40(2)	C(15)–C(16)	1.366(14)
C(16)–C(17)	1.40(2)	C(17)–C(18)	1.38(2)
C(18)–C(19)	1.484(14)	C(21)–C(22)	1.51(2)
Os–C(CO)	1.92(2) *	C–O	1.14(2) *
C(1)–Os(1)–C(2)	91.4(5)	C(1)–Os(1)–N(1)	89.3(4)
C(2)–Os(1)–N(1)	175.4(4)	C(1)–Os(1)–S(1)	98.9(3)
C(2)–Os(1)–S(1)	96.5(3)	N(1)–Os(1)–S(1)	87.9(2)
C(1)–Os(1)–Os(2)	97.5(3)	C(2)–Os(1)–Os(2)	92.0(3)
N(1)–Os(1)–Os(2)	83.4(2)	S(1)–Os(1)–Os(2)	161.26(7)
C(1)–Os(1)–H(31)	175	C(2)–Os(1)–H(31)	93
N(1)–Os(1)–H(31)	86	S(1)–Os(1)–H(31)	82
Os(2)–Os(1)–H(31)	81	C(4)–Os(2)–C(3)	96.0(4)
C(4)–Os(2)–C(5)	95.0(5)	C(3)–Os(2)–C(5)	93.5(5)
C(4)–Os(2)–C(6)	97.3(5)	C(3)–Os(2)–C(6)	163.5(4)
C(5)–Os(2)–C(6)	95.0(5)	C(4)–Os(2)–C(18)	91.5(4)
C(3)–Os(2)–C(18)	83.7(4)	C(5)–Os(2)–C(18)	173.2(4)
C(6)–Os(2)–C(18)	86.2(4)	C(4)–Os(2)–Os(1)	172.6(3)
C(3)–Os(2)–Os(1)	80.0(3)	C(5)–Os(2)–Os(1)	91.5(3)
C(6)–Os(2)–Os(1)	85.8(3)	C(18)–Os(2)–Os(1)	81.9(3)
C(7)–Os(3)–C(9)	93.7(5)	C(7)–Os(3)–C(10)	96.3(9)
C(9)–Os(3)–C(10)	78.3(10)	C(7)–Os(3)–C(8)	88.9(6)
C(9)–Os(3)–C(8)	91.1(7)	C(10)–Os(3)–C(8)	168.4(10)
C(7)–Os(3)–S(1)	94.6(4)	C(9)–Os(3)–S(1)	170.9(4)
C(10)–Os(3)–S(1)	97.0(10)	C(8)–Os(3)–S(1)	92.9(5)
C(7)–Os(3)–H(31)	176	C(9)–Os(3)–H(31)	83
C(10)–Os(3)–H(31)	85	C(8)–Os(3)–H(31)	89
S(1)–Os(3)–H(31)	89	Os(1)–H(31)–Os(3)	111
OS–C–O	177.3 *		
C(21)–S(1)–Os(1)	109.3(4)	C(21)–S(1)–Os(3)	109.9(4)
Os(1)–S(1)–Os(3)	78.21(8)	C(11)–N(1)–C(19)	117.1(9)
C(11)–N(1)–Os(1)	120.9(7)	C(19)–N(1)–Os(1)	121.6(6)
N(1)–C(11)–C(12)	124.3(10)	C(13)–C(12)–C(11)	121.0(10)
C(12)–C(13)–C(14)	117.7(10)	C(12)–C(13)–C(20)	123.1(10)
C(14)–C(13)–C(20)	119.2(11)	C(15)–C(14)–C(19)	119.2(10)
C(15)–C(14)–C(13)	122.4(11)	C(19)–C(14)–C(13)	118.3(10)
C(16)–C(15)–C(14)	120.6(10)	C(15)–C(16)–C(17)	119.9(11)
C(18)–C(17)–C(16)	123.8(10)	C(17)–C(18)–C(19)	114.4(10)
C(17)–C(18)–Os(2)	123.1(8)	C(19)–C(18)–Os(2)	121.7(8)
N(1)–C(19)–C(14)	121.4(8)	N(1)–C(19)–C(18)	118.0(9)
C(14)–C(19)–C(18)	120.3(9)	C(22)–C(21)–S(1)	112.7(8)

* Average values.

Scheme 1. R = C₂H₅.

and the organic ligands are as expected. The average Os–C(CO) and C–O distances and Os–C–O angle are 1.92(2), 1.14(2) Å and 1773(10)° respectively. It is also noted that the C₉H₅(CH₃)N ring system is somewhat twisted and some of the ring angles show significant deviations [up to 5.6(10)°] from 120°; these distortions may be attributed both to the severe strain imposed by the bridge formation and also to interligand steric interactions. The minimum intermolecular short contact between non-hydrogen atoms is 3.369 Å [C(16)···O(6) at 1 – x, – y, 1 – z], which suggests that the cluster molecules pack fairly closely in the crystal.

The ¹H NMR data are consistent with the solid state structure described above. The ¹H NMR spectrum of **6** (Fig. 2) at –40 °C contains four sets of hydride doublets [–8.66 (*J* = 4.5 Hz), –8.72 (*J* = 4.4 Hz), –10.71 (*J* = 4.1 Hz) and –10.77 (*J* = 3.5 Hz) ppm] for the terminal hydride as well as four sets of hydride doublets [–13.78 (*J* = 4.1 Hz), –13.83 (*J* = 4.5 Hz), –13.69 (*J* = 4.5 Hz) and –13.73 (*J* = 3.5 Hz) ppm] for the bridging hydride with relative intensities 4:1:3.5:1.2 indicating the presence of four isomers in solution. There are some additional resonances which are extremely low in intensity and remained rigid throughout the temperature range examined. These may be due to minor impurities and will not be considered further. The presence of four isomers can be accounted for if the terminal hydride occupies each of the four non-equivalent terminal sites at one osmium atom (**6a–6d**, Scheme 1). In the solid state the presence of the major isomer **6a** (66%) and two minor isomers **6b** (24%) and **6d** (10%) is clearly proved by the present crystallographic studies.

The existence of isomer **6c** (two hydrides in *trans* positions) is not impossible, but this must be the least favorable one from steric considerations. As the temperature is increased to –10 °C, the doublet resonances due to the minor isomers average with the broadened singlets of the major isomer. At +20 °C, the bridging hydride resonances average to a broad singlet at –13.40 ppm, while the terminal hydride resonances average to two broadened resonances at –8.60 and –10.65 ppm. If the temperature is further increased to +50 °C, all the hydride resonances are broadened nearly into the baseline. Above this temperature, the hydride resonances all begin to coalesce, but the onset of decomposition of **6** precludes achieving the high temperature limit. This behavior is consistent with the interconversion of terminal and bridging hydride ligands and similar to that reported for [H(μ-H)Os₃(CO)₁₀(L)] (L = 2e[–] donor), which contains a terminal and a bridging hydride that undergo site exchange on the NMR timescale [15].

In order to ascertain whether the steric bulk of the substituent group on the thiol played any role on its reactivity with **5**, as we observed with the reactivity of the μ₃-imidoyl cluster **1** [8], we reacted **5** with C₆H₅SH.

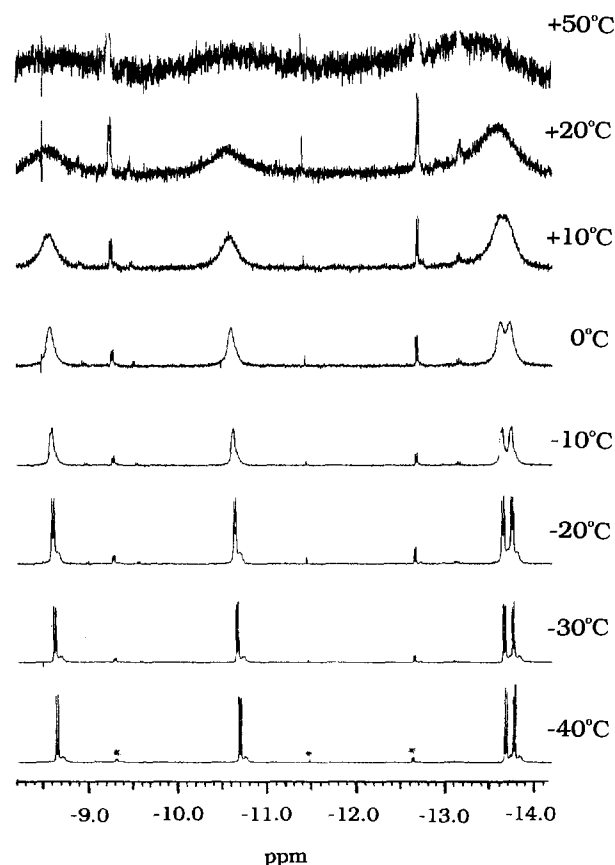


Fig. 2. Variable temperature ¹H NMR spectra of **6** in CD₂Cl₂ in the hydride region (asterisks denote trace amounts of impurities present in the sample).

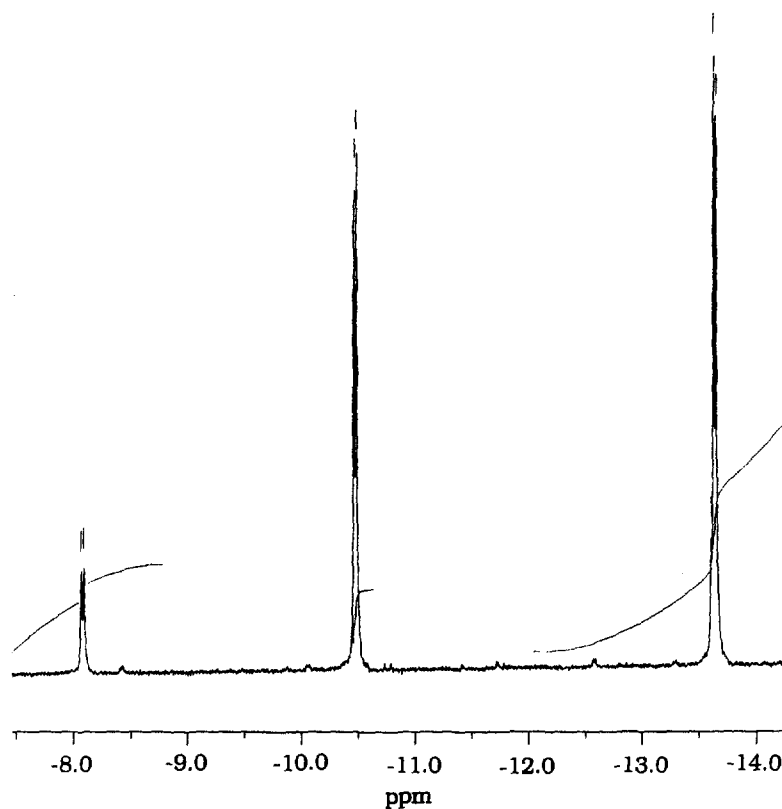


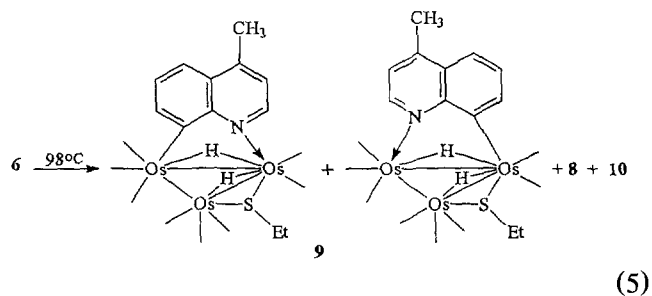
Fig. 3. ^1H NMR spectra of **7** in CD_2Cl_2 in the hydride region at -40°C .

The reaction of **5** with $\text{C}_6\text{H}_5\text{SH}$ leads to the formation of the dihydrido cluster $[\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SC}_6\text{H}_5)]$ **7** in 82% yield, whose ^1H NMR, infrared and elemental analyses are consistent with the proposed structure. The ^1H NMR spectrum of **7** (Fig. 3), in the hydride region, at -40°C showed the compound to exist as two isomers (intensity ratio 4:1). We believe that these two isomers are most likely due to a very low population of the other two isomers in **7**, where the terminal hydride occupies the equatorial sites. The variable temperature ^1H NMR spectrum of **7** is very similar to that of **6**.

In the light of the fact that $\text{C}_2\text{H}_5\text{SH}$ and $\text{C}_6\text{H}_5\text{SH}$ react with **5** to give compounds **6** and **7** respectively, containing one terminal and one bridging hydride, it would be of interest to see the structural consequences of H_2S addition to **5**, since the presence of an additional hydrogen could lead to further rearrangement of the cluster. We found that, in sharp contrast to the above results, H_2S reacts with **5** at room temperature to displace the heterocyclic ligand and produce the known cluster $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})]$ **8** in 45% yield.

Thermolysis of **6** in heptane at 98°C leads to the formation of one new compound $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_8\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SC}_2\text{H}_5)]$ with two possible structural isomers (Eq. (5), **9**) and two known compounds $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})]$ **8** and $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-SC}_2\text{H}_5)]$ **10**, in addition to non-specific decomposition.

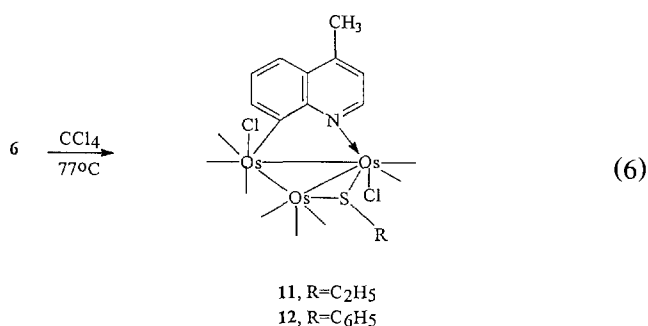
Compound **9** has been characterized by ^1H NMR, infrared and elemental analyses. Compounds **8** and **10** have been reported previously from the reactions of $[\text{Os}_3(\text{CO})_{12}]$ with H_2S [3] and $\text{C}_2\text{H}_5\text{SH}$ [5] respectively.



We were unable to obtain suitable single crystals of **9** for X-ray analysis and therefore could not determine its structure without any ambiguity. It is presumed, however, that the presence of two bridging hydrides, the thiolate and heterocyclic ligands, and the loss of one CO have required the three osmium atoms to reform the osmium triangle with three metal–metal bonds. The ^1H NMR spectrum of **9** shows four sets of hydride doublets at -13.03 , -13.10 , -13.58 and -13.55 ppm with relative intensities 9:1:9:1, indicating the presence of two isomers (9:1 ratio) in solution which differ in the disposition of the organic ligand. The signals of the ring and thiolate protons of the minor isomer are overlapped

with the signals of the major isomer. ^1H NMR results did not provide any evidence of interconversion of these isomers up to $+50^\circ\text{C}$.

There are examples in the literature of exchange of terminal hydrides with halides when treated with CCl_4 or CBr_4 , whereas the bridging hydrides are more resistant to attack [16,17]. For example, the cluster $[\text{H}_2\text{Os}_3(\text{CO})_{12}]$ reacts with CCl_4 or CBr_4 to give the corresponding dihalides $[\text{Os}_3\text{X}_2(\text{CO})_{12}]$ [16], but $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}]$ is stable in CCl_4 over a period of several days [17]. Thus, in order to probe the presence of terminal hydride in **6** and **7**, we examined their reactivity with CCl_4 . It was found that both these compounds react with CCl_4 at 77°C to give $[\text{Os}_3(\text{CO})_8\text{Cl}_2\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SR})]$ ($\text{R} = \text{C}_2\text{H}_5$ **11**, $\text{R} = \text{C}_6\text{H}_5$ **12**) in 76 and 69% yields respectively.



The structures of **11** and **12** are tentative and based on elemental analyses and ^1H NMR and infrared spectral data. Attempts to grow X-ray quality single crystals of these compounds were unsuccessful. It is, however, interesting to note that both the terminal and bridging hydrides in **6** and **7** have been exchanged with chlorides. This is probably due to the dynamic behaviour of the hydrides in these compounds, which undergo slow bridge–terminal exchange under the conditions of the experiment.

3. Experimental

All the reactions were performed under an atmosphere of prepurified nitrogen, unless stated otherwise. Methylene chloride was distilled from calcium hydride and hexane and toluene from sodium benzophenone ketyl prior to use. Infrared spectra were recorded on a Bruker IFS 25 spectrophotometer and ^1H NMR spectra on a Bruker AC-200 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, Institut für Anorganische und Analytische Chemie, Universität Freiburg, Germany. The cluster $[(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}]$ **5** was prepared as described previously [10].

3.1. Reaction of $[(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}]$ **5** with $\text{C}_2\text{H}_5\text{SH}$

Ethanethiol (14 μl , 0.183 mmol) was added to a dichloromethane solution (20 ml) of **5** (0.118 g, 0.122 mmol) and the reaction mixture was stirred at room temperature for 24 h, during which time the color changed from green to pale yellow. Analytical TLC showed complete consumption of **5** with the formation of a single product. The solvent and excess ethanethiol were removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (5:1, v/v) gave a single band which, on removal of solvent followed by recrystallization from hexane/ CH_2Cl_2 at -20°C , gave $[\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SC}_2\text{H}_5)]$ **6** as pale yellow crystals (0.107 g, 85%). Anal. Found: C, 24.66; H, 1.51; N, 1.37. $\text{C}_{21}\text{H}_{15}\text{NO}_9\text{Os}_3\text{S}$ (1028.0) Calc.: C, 24.54; H, 1.47; N, 1.36%. IR (hexane, νCO): 2104m, 2089s, 2033s, 2020s, 2002vs, 1995sh, 1941m cm^{-1} . ^1H NMR (CD_2Cl_2 , -40°C , low temperature limit): major isomers 8.68 (d, $J = 5.3$ Hz, 1H), 8.56 (d, $J = 5.22$ Hz, 1H), 8.34 (dd, $J = 5.3$ and 1.3 Hz, 1H), 8.30 (dd, $J = 5.2$ and 1.3 Hz, 1H), 7.47 (t, $J = 1.4$ Hz, 1H), 7.44 (t, $J = 1.4$ Hz, 1H), 7.23 (m, 2H), 6.96 (d, $J = 5.3$ Hz, 2H), 3.11 (m, 2H), 2.82 (m, 2H), 2.55 (s, 3H), 2.59 (s, 3H), 1.50 (s, 3H), -8.66 (d, $J = 4.5$ Hz, 1H), -10.71 (d, $J = 4.1$ Hz, 1H), -13.69 (d, $J = 4.5$ Hz, 1H), -13.78 (d, $J = 4.1$ Hz, 1H) ppm.

3.2. Reaction of **5** with $\text{C}_6\text{H}_5\text{SH}$

A reaction, similar to that above, of **5** (0.107 g, 0.111 mmol) with $\text{C}_6\text{H}_5\text{SH}$ (17 μl , 0.166 mmol) followed by similar chromatographic separation gave $[\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SC}_6\text{H}_5)]$ **7** as pale yellow crystals (0.098 g, 82%) from hexane/ CH_2Cl_2 at -20°C . Anal. Found: C, 27.84; H, 1.42; N, 1.27. $\text{C}_{25}\text{H}_{15}\text{NO}_9\text{Os}_3\text{S}$ (1076.1) Calc.: C, 27.90; H, 1.41; N, 1.30%. IR (hexane, νCO): 2106m, 2093m, 2041s, 2033s, 2023s, 2004vs, 1996sh, 1943s cm^{-1} . ^1H NMR (CD_2Cl_2 , -40°C , low temperature limit): 8.74 (d, $J = 6.1$ Hz, 1H), 8.34 (d, $J = 5.91$ Hz, 1H), 7.66 (d, $J = 5.9$ Hz, 1H), 7.49 (d, $J = 6.1$ Hz, 1H), 7.26 (m, 5H), 6.98 (d, $J = 1.9$ Hz, 1H), 2.61 (s, 3H), -8.08 (d, $J = 4.6$ Hz, 1H), -10.48 (d, $J = 4.0$ Hz, 1H), -13.63 (d, $J = 4.6$ Hz, 1H), -13.65 (d, $J = 4.0$ Hz, 1H) ppm.

3.3. Thermolysis of **6**

A heptane solution (30 ml) of **6** (0.060 g, 0.058 mmol) was heated to reflux for 3 h. After cooling, the solvent was removed by rotary evaporation and the residue chromatographed by TLC on silica gel. Elution with

hexane gave three major and several very minor bands. The major bands gave the two previously reported products $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})]$ **8** (0.005 g, 10%) [3] and $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-SC}_2\text{H}_5)]$ **10** (0.005 g, 9%) [5], as confirmed by analytical and spectral data, and also a new compound $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_8\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SC}_2\text{H}_5)]$ **9** (0.012 g, 21%) as yellow crystals from hexane/ CH_2Cl_2 at -20°C . Data for compound **9**. Anal. Found: C, 24.15; H, 1.58; N, 1.41. $\text{C}_{20}\text{H}_{15}\text{NO}_8\text{Os}_3\text{S}$ (1000.0) Calc.: C, 24.02; H, 1.51; N, 1.40%. IR (hexane, νCO): 2084s, 2049vs, 2010vs, 1995m, 1990sh, 1978s, 1964s cm^{-1} . ^1H NMR (CD_2Cl_2): 7.93 (d, $J = 4.6$ Hz, 1H), 7.87 (d, $J = 4.5$ Hz, 1H), 7.83 (d, $J = 4.6$ Hz, 1H), 7.52 (d, $J = 4.5$ Hz, 1H), 7.40 (d, $J = 4.5$ Hz, 1H), 2.82 (q, $J = 7.4$ Hz, 2H), 0.95 (t, $J = 7.4$ Hz, 3H), -13.03 (d, $J = 0.9$ Hz, 1H), -13.10 (d, $J = 0.8$ Hz, 1H), -13.58 (d, $J = 0.8$ Hz, 1H), -13.55 (d, $J = 0.8$ Hz, 1H) ppm.

3.4. Reaction of **6** with CCl_4

In a Schlenk flask **6** (0.075 g, 0.73 mmol) and CCl_4 (20 ml) were mixed. The reaction mixture was heated to reflux for 2 h, during which time IR analysis indicated complete consumption of the starting material. The solvent was removed by rotary evaporation and the residue was chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (10:3, v/v) gave a single band which afforded $[\text{Os}_3(\text{CO})_8\text{Cl}_2\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SC}_2\text{H}_5)]$ **11** as pale yellow crystals (0.060 g, 76%) from hexane/ CH_2Cl_2 at -20°C . Anal. Found: C, 22.75; H, 1.42; N, 1.35. $\text{C}_{20}\text{H}_{13}\text{Cl}_2\text{NO}_8\text{Os}_3\text{S}$ (1068.9) Calc.: C, 22.47; H, 1.23; N, 1.31%. IR (hexane, νCO): 2073s, 2034vs, 1994vs, 1974s, 1960s cm^{-1} . ^1H NMR (CD_2Cl_2): 9.29 (d, $J = 5.5$ Hz, 1H), 8.45 (dd, $J = 5.5$ and 1.4 Hz, 1H), 7.59 (dd, $J = 4.5$ and 1.4 Hz, 1H), 7.25 (dd, $J = 5.8$ and 1.5 Hz, 1H), 6.99 (d, $J = 5.5$ Hz, 1H), 2.88 (q, 2H), 2.70 (s, 3H), 1.41 (t, $J = 7.4$ Hz, 3H) ppm.

3.5. Reaction of **7** with CCl_4

A similar reaction of **7** (0.050 g, 0.046 mmol) with CCl_4 (20 ml) for 2 h followed by similar chromatographic separation gave $[\text{Os}_3(\text{CO})_8\text{Cl}_2\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SC}_6\text{H}_5)]$ **12** as pale yellow crystals (0.036 g, 69%) from hexane/ CH_2Cl_2 at -20°C . Anal. Found: C, 25.95; H, 1.35; N, 1.32. $\text{C}_{24}\text{H}_{13}\text{Cl}_2\text{NO}_8\text{Os}_3\text{S}$ (1116.9) Calc.: C, 25.81; H, 1.18; N, 1.25%. IR (hexane, νCO): 2071s, 2042vs, 2001vs, 1975s, 1962s cm^{-1} . ^1H NMR (CD_2Cl_2): 9.88 (d, $J = 5.5$ Hz, 1H), 8.57 (dd, $J = 6.9$ and 1.5 Hz, 1H), 7.50 (dd, $J = 6.5$ and 1.4 Hz, 1H), 7.02–7.41 (m, 5H), 6.55 (d, $J = 5.5$ Hz, 1H), 6.45 (d, $J = 5.5$ Hz, 1H), 2.69 (s, 3H) ppm.

3.6. Reaction of **5** with H_2S

Hydrogen sulfide gas was bubbled through a toluene solution (15 ml) of **5** (0.025 g, 0.026 mmol) for 2 min and then the reaction mixture was stirred for an additional 1 h. The solvent was removed by rotary evaporation and the residue chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (5:1, v/v) gave one major and three very minor bands. The major band yielded $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})]$ **8** as yellow crystals (0.10 g, 45%). Each of the minor bands gave a small quantity (around 0.002 g) of an uncharacterized compound.

3.7. X-ray crystallography for $[\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_9\{\mu\text{-}\eta^2\text{-C}_9\text{H}_5(\text{CH}_3)\text{N}\}(\mu\text{-SC}_2\text{H}_5)]$ **6**

Light yellow crystals of compound **6** suitable for X-ray work were grown from hexane/ CH_2Cl_2 at 20°C . The unit cell dimensions and intensity data were measured at 150 K using a Delft Instruments FAST TV area detector diffractometer positioned at the window of a

Table 2
Crystal data and details of data collection and structure refinement for **6**

Empirical formula	$\text{C}_{21}\text{H}_{15}\text{NO}_9\text{Os}_3\text{S}$
Formula weight	1028.00
Temperature (K)	150(2)
Wavelength (\AA)	0.71069
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 8.5504(6) \text{\AA}$ $b = 18.703(2) \text{\AA}$ $c = 15.7779(14) \text{\AA}$ $\beta = 94.073(8)^\circ$
Volume (\AA^3)	2516.9(4)
Z	4
Density (calc.) (Mg m^{-3})	2.713
Absorption coefficient (mm^{-1})	15.240
$F(000)$	1856
Crystal size (mm^3)	$0.24 \times 0.20 \times 0.10$
Theta range for data collection	2.18 to 25.05°
Index ranges	$-10 \leq h \leq 5$, $-20 \leq k \leq 20$, $-15 \leq l \leq 17$
Reflections collected	9237
Absorption correction factors	0.873 to 1.116
Independent reflections	3768 [$R_i = 0.0755$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3768/60/336
Goodness-of-fit on F^2	1.022
Final R indices (all 3768 data)	$R_1 = 0.0497$, $wR_2 = 0.0967$
R indices	$R_1 = 0.0417$, $wR_2 = 0.0951$
[3208 data with $I > 2\sigma(I)$]	
Largest difference peak and hole ($e \text{\AA}^{-3}$)	2.509 and -1.702

$$R_1 = \sum(\Delta F) / \sum(F_o); \quad wR_2 = [\sum\{(w\Delta F^2)^2\} / \sum\{w(F_o^2)^2\}]^{1/2}; \quad w = 1 / [\sigma^2(F_o^2) + (0.0479P)^2], \quad \text{where } P = [\max(F_o^2) + 2F_c^2] / 3.$$

rotating anode generator using Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$) by following procedures described elsewhere [18]. The data were corrected for Lorentz and polarization factors and also for absorption effects [19]. The structure was solved by Patterson methods (SHELXS-86) [20] and difference synthesis and refined on F^2 by full-matrix least-squares (SHELXL-93) [21]. Initial results suggested a model in which one osmium atom [Os(3)] contained four terminally bonded carbonyl groups, but large displacement coefficients for three of these groups suggested that they might be partially occupied. It was also realised that this particular osmium atom contained the terminal hydride, which would be disordered along the positions of the three partially occupied carbonyl groups. The refinement suggested one of the CO groups

[C(7)–O(7)] was fully occupied, whereas the other two were disordered between three positions exchanging sites with the terminal hydride. In the final model (Fig. 1), the C(8)–O(8), C(9)–O(9) and C(10)–O(10) groups were refined with occupancies of 0.76, 0.90 and 0.34 respectively. Refinement based on this model resulted in acceptable displacement coefficients for all non-hydrogen atoms. The terminal (disordered) hydride was ignored. The bridging hydride was located from a difference map, but this was not refined. Other hydrogens in the structure were included in calculated positions (riding model) with U_{iso} being tied to the U_{eq} of the parent atoms. Final R and wR values were 0.0497 and 0.0967 respectively for all 3768 data and 336 parameters. The corresponding R values for 3208 data with $I > 2\sigma(I)$ were 0.0417 and 0.0951 respectively. The adopted model is in accord with the spectral data which clearly reveal the presence of both a bridging and a terminal hydride in the structure. All non-hydrogen atoms were anisotropic with the restraint parameters 'ISOR 0.01' and 'ISOR 0.015' being included for C(9), C(10), C(12), C(15), C(16), C(18), C(19) and O(8), O(9), O(10) respectively. The crystal data, details of data collection and structure refinement parameters and fractional atom coordinates are given in Tables 2 and 3 respectively. Anisotropic displacement coefficients, hydrogen atom parameters, tables of full bond lengths and angles, and lists of observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Centre. The calculations were performed on a Pentium P5-90 personal computer. Sources of scattering factors as in Ref. [21].

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6**

Atom	x	y	z	U_{eq}
Os(1)	1215.3(5)	478.0(2)	2063.2(3)	13(1)
Os(2)	936.3(5)	-371.7(2)	3525.1(3)	16(1)
Os(3)	4009.2(5)	1466.0(2)	2261.2(3)	17(1)
S(1)	2312(3)	1215(2)	1021(2)	18(1)
O(1)	-1299(12)	-225(5)	921(6)	47(3)
O(2)	-1065(10)	1570(4)	2656(5)	34(2)
O(3)	-138(10)	-1467(4)	2138(5)	27(2)
O(4)	929(11)	-1443(5)	5004(5)	37(2)
O(5)	-2389(10)	209(5)	3738(6)	35(2)
O(6)	2623(11)	856(5)	4516(5)	38(2)
O(7)	5987(11)	2539(6)	1353(6)	46(3)
O(8) ^{*a}	6420(14)	316(7)	1855(8)	42(3)
O(9) ^{*b}	5657(16)	1727(8)	4001(7)	70(4)
O(10) ^{*c}	1969(41)	2581(17)	3095(18)	58(9)
N(1)	2811(11)	-359(4)	1727(5)	14(2)
C(1)	-376(15)	42(6)	1371(7)	26(3)
C(2)	-194(14)	1165(6)	2436(7)	21(3)
C(3)	249(14)	-1048(6)	2653(7)	21(3)
C(4)	928(14)	-1035(6)	4456(7)	21(3)
C(5)	-1162(15)	-18(6)	3654(7)	21(3)
C(6)	1988(13)	412(6)	4148(7)	20(3)
C(7)	5256(16)	2141(7)	1706(8)	30(3)
C(8) ^{*a}	5495(20)	719(9)	1995(10)	31(4)
C(9) ^{*b}	5091(17)	1617(8)	3350(9)	32(3)
C(10) ^{*c}	2671(37)	2158(17)	2760(20)	16(7)
C(11)	3095(14)	-473(6)	932(7)	20(3)
C(12)	4194(14)	-965(6)	670(7)	21(3)
C(13)	5134(14)	-1313(6)	1230(7)	24(3)
C(14)	4923(14)	-1195(6)	2127(7)	21(3)
C(15)	5921(13)	-1495(6)	2773(7)	20(3)
C(16)	5647(13)	-1393(6)	3607(7)	20(3)
C(17)	4298(13)	-1026(6)	3820(7)	22(3)
C(18)	3243(13)	-712(5)	3231(6)	15(2)
C(19)	3714(12)	-738(5)	2344(6)	10(2)
C(20)	6319(14)	-1846(6)	984(8)	26(3)
C(21)	1019(14)	1975(6)	781(7)	20(3)
C(22)	-428(16)	1773(7)	231(8)	37(3)

* Atoms belonging to the disordered CO groups refined with partial occupancies ^a 0.76, ^b 0.90, ^c 0.34.

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

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