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Decarbonylation Reaction of [$Os_3(CO)_{10}(\mu$-H)(μ-$SN_2C_4H_5$)]: X-ray Structures of the Two Isomers of [$Os_3(CO)_9(\mu$-H)(μ_3-η^2-$SN_2C_4H_5$)]

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Decarbonylation Reaction of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SN_2C_4H_5)]$: X-ray Structures of the Two Isomers of $[Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_5)]$

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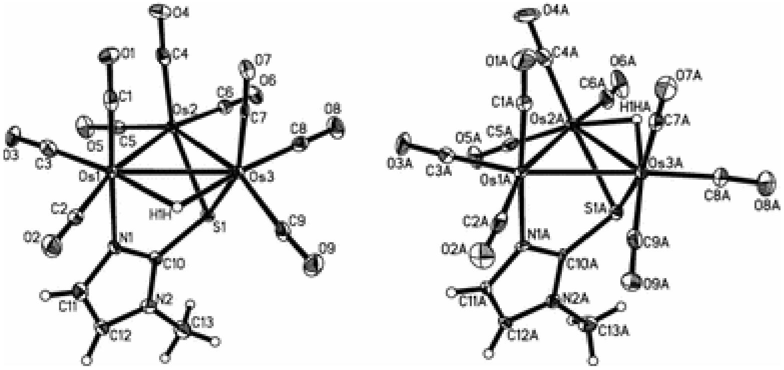
Abstract

The thermal reaction of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-}SN_2C_4H_5)]$ (**1**) at 110 °C afforded the new compound $[Os_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_5)]$ (**2**) in 84% yield. Compound **2** exists as two isomers, which differ in the disposition of the bridging hydride ligand. Both of the isomers of **2** have been characterized by a combination of elemental analysis, infrared and ^{1}H NMR spectroscopic data together with single crystal X-ray crystallography. The isomers crystallize together in the triclinic space group *P*-1
with $a = 10.4775(2)$, $b = 13.3056(3)$, $c = 15.0325(3)$ Å, $\alpha = 110.8890(10)$, $\beta = 99.3880(10)$, $\gamma = 96.1620(10)°$, $Z = 2$ and $V = 1900.31(7)$ Å^3.

Index Abstract

The synthesis and the molecular structures of the two isomers of $[Os_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_5)]$ are described. The isomers differ in the disposition of the hydride ligand.



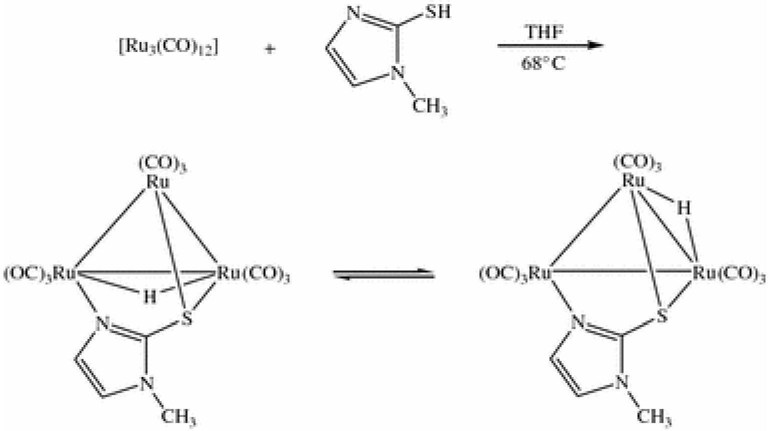
Keywords

Decarbonylation, Triosmium cluster. 2-Mercapto-1-methylimidazole, X-ray structure

Introduction

In recent years, the reactions of transition metal carbonyl clusters with heterocyclic ligands containing more than one hetero-atoms have been widely investigated.[1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18] These reactions are markedly influenced by the structure of the heterocyclic ring, starting clusters and also by the reaction conditions employed. Trinuclear osmium clusters have proved to be useful system for modeling heterogeneous catalytic processes such as hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) which are associated with the cleavage of C–X bonds (X = S, N).[1,2,3,4,5,6,7,8,10,12,13,19,20,21,22,23] The presence of heteroatom's such as sulfur[24,25,26] and nitrogen[27,28,29] not only stabilizes the metal cluster framework with respect to degradational fragmentation in drastic conditions but also provide new types of reactivities and increase the coordination potential towards multi-metal centers. Many of the resultant complexes are biologically important as they can be used as models for metal-centers in metalloproteins[30,31,32,33,34] and also possess different industrial applications such as anticorrosion and as accelerators in the rubber vulcanization process.[35]

The reactions of trimetallic clusters with nitrogen and sulfur containing heterocycles such as 4-methylthiazole,[12] 2,4,5-trimethylthiazole,[9] thiazole,[13,16] thiomorpholine,[14] thiazolidine,[14] 2-methyl-2-thiazoline,[10] benzothiazole,[15] pyrimidine-2-thiol[15] and pyridine-2-thiol[11] have been demonstrated by us. The neutral ligand 2-mercapto-1-methylimidazole can in principle coordinates both in the 'thione' and in the tautomeric 'thiol' form ($-NH-C{=}S \rightleftharpoons -N{=}C-SH-NH-C{=}S \rightleftharpoons -N{=}C-SH$) which gives rise to a wide range of coordination compounds with considerable structural diversity.[35,36,37,38,39] Recently, we reported the reactions of 2-mercapto-1-methylimidazole with a series of trimetallic clusters, $[Os_3(CO)_{10}(MeCN)_2]$, $[Ru_3(CO)_{12}]$, $[Os_3(CO)_8(\mu\text{-}H)\{Ph_2PCH_2P(Ph)C_6H_4\}]$, $[Os_3(CO)_{10}(\mu\text{-dppm})]$ and $[Ru_3(CO)_{10}(\mu\text{-dppm})]$.[40] The reaction of $[Ru_3(CO)_{12}]$ with 2-mercapto-1-methylimidazole at 68 °C afforded $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_5)]$; whereas, the lightly stabilized cluster $[Os_3(CO)_{10}(MeCN)_2]$ gave $[Os_3(CO)_{10}(\mu\text{-}H)(\mu_3\text{-}SN_2C_4H_5)]$ (**1**) at 25 °C (Scheme 1).



Scheme 1

As a continuation of our previous work, we investigated the thermal reaction $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SN_2C_4H_5)]$ at 110 °C in an attempt to synthesize the osmium analog of $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_5)]$ and the results of this study are reported herein.

Experimental

All the reactions were performed under a dry oxygen-free nitrogen atmosphere using standard Schlenk techniques. Reagent grade solvents were freshly distilled from appropriate drying agents prior to use. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on a Bruker DPX 400 instrument. Elemental analysis was performed by BCSIR Laboratories, Dhaka. [$Os_3(CO)_{12}$] was purchased from Strem Chemicals Inc. and used without further purification. 2-Mercapto-1-methylimidazole was purchased from Sigma–Aldrich Chemical Company and used as received. [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-}SN_2C_4H_5)$][40] (**1**) was prepared according to the published method. Preparative thin layer chromatography was carried out on 1 mm plates prepared from silica gel GF254 (type 60, E. Merck) at Jahangirnagar University.

Decarbonylation of [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-}SN_2C_4H_5)$] (1)

A toluene solution (10 mL) of [$Os_3(CO)_{10}(\mu\text{-H})(\mu_3\text{-}SN_2C_4H_5)$] (**1**) (50 mg, 0.052 mmol) was heated to reflux for 5 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (7:3, v/v) developed a single band which afforded [$Os_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_5)$] (**2**) (41 mg, 84%) as orange crystals after recrystallization from hexane/CH_2Cl_2 at −4 °C. Anal. Calcd. for $C_{13}H_6N_2O_9Os_3S$: C, 16.66; H, 0.65. Found: C, 16.81; H, 0.83%. IR(ν_{CO}, CH_2Cl_2): 2086 m, 2054 s, 2026 vs, 1997s, 1985s, 1951 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.99 (*d*, *J* = 1.5 Hz, 1H), 6.87 (*d*, *J* = 1.5 Hz, 1H), 6.53 (*d*, *J* = 1.4 Hz, 1H), 6.44 (*d*, *J* = 1.4 Hz, 1H), 3.62 (s, 3H), 3.60 (s, 3H), −12.47 (s, 1H), −14.70 (s, 1H); mass spectrum: m/z 938 (M^+), 910 (M^+-CO), 882 (M^+-2CO), 854 (M^+-3CO), 826 (M^+-4CO), 798 (M^+-5CO), 770 (M^+-6CO), 742 (M^+-7CO), 714 (M^+-8CO), 686 (M^+-9CO).

X-ray Crystallography

Crystals of **2** suitable for X-ray diffraction were obtained by recrystallization from hexane/CH_2Cl_2 at 4 °C and mounted on a nylon fiber with a mineral oil. Diffraction data were collected at 100(2) K on a Bruker AXS SMART diffractometer equipped with an APEX CCD detector using graphite-monochromated Cu Kα radiation (λ = 1.54178 Å). Integration of intensities and data reduction was performed using SAINT program.[41] Multi-scan absorption correction was applied using SADABS procedure.[42]

The structures were solved by direct methods[43] and refined by full-matrix least squares on F^2.[44] All non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms were calculated geometrically and were included into refinement with U(iso) = 1.2 U(iso/eq) of an adjacent carbon atom using a riding model. All pertinent crystal data and other experimental conditions and refinement details are summarized in Table 1.

Table 1

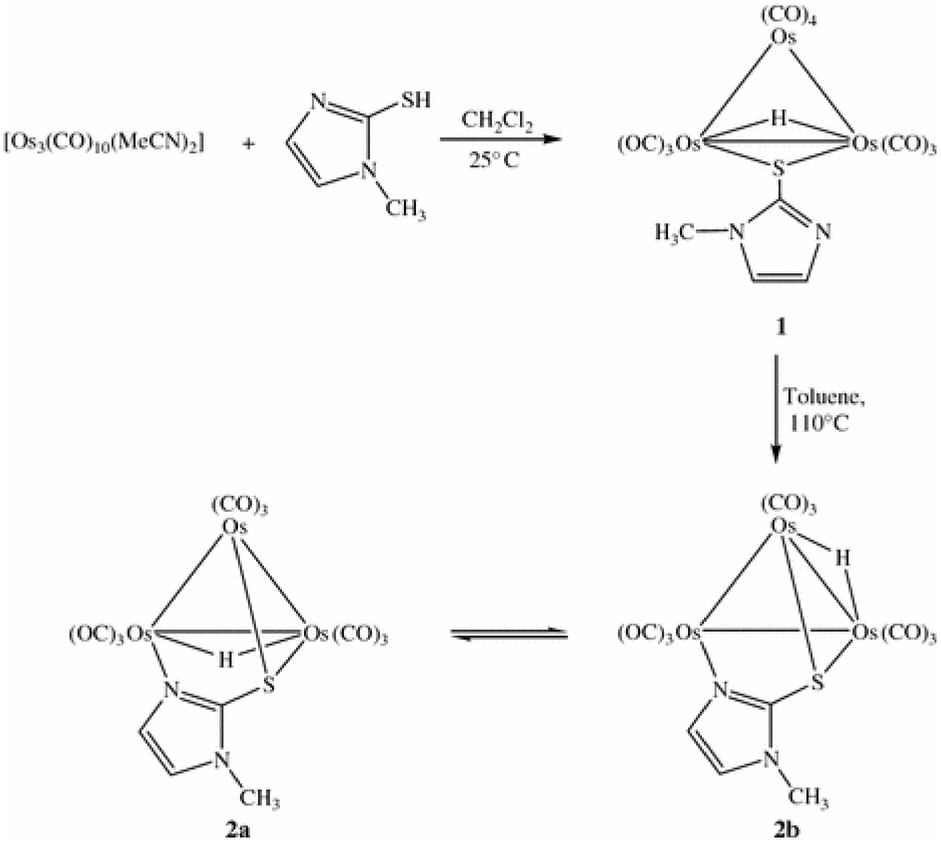
Crystal and structural refinement data for [$Os_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_5)$] (**2**)

Empirical formula	$C_{26}H_{12}N_4O_{18}Os_6S_2$
CCDC deposit no.	669,776
Formula weight	1,873.72
Temperature (K)	100(2)
Wavelength (Å)	1.54178
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	
a (Å)	10.4775(2)
b (Å)	13.3056(3)
c (Å)	15.0325(3)
α (°)	110.8890(10)
β (°)	99.3880(10)
γ (°)	96.1620(10)
Volume ($Å^3$)	1,900.31(7)
Z	2
Density (calculated) (Mg/m^3)	3.275
Absorption coefficient (mm^{-1})	38.567
F(000)	1,656
Crystal size (mm^3)	0.46 × 0.30 × 0.12
ϑ range for data collection (°)	3.22–67.10
Index ranges	$-12 \leq h \geq 12$
	$-15 \leq k \geq 14$
	$0 \leq l \geq 17$
Reflections collected	15,782
Independent reflections	6,267 [*R*(int) = 0.0368]

Completeness to $\vartheta = 67.10°$	92.2%
Max. and min. transmission	0.0904 and 0.0202
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6267/0/516
Goodness-of-fit on F^2	1.142
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0262$, $wR_2 = 0.0642$
R indices (all data)	$R_1 = 0.0278$, $wR_2 = 0.0651$
Largest diff. peak and hole (e Å^{-3})	1.189 and −1.726

Results and Discussion

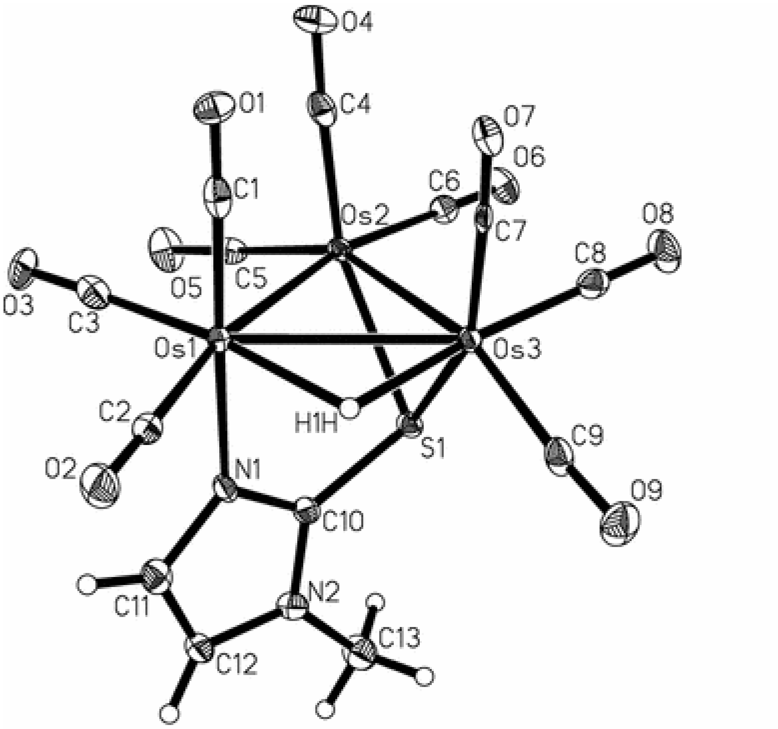
It was previously reported by us that the cluster $[Os_3(CO)_{10}(MeCN)_2]$ reacts with 2-mercapto-1-methylimidazole to give $[Os_3(CO)_{10}(\mu\text{-H})(\mu_3\text{-SN}_2C_4H_5)]$ (**1**) at 25 °C whereas $[Ru_3(CO)_{12}]$ gives $[Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-SN}_2C_4H_5)]$ at 68 °C.[40] With this in mind, we investigated the thermal reaction of **1** in toluene. The thermolysis of **1** in refluxing toluene for 5 h affords $[Os_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-SN}_2C_4H_5)]$ (**2**), as orange crystals in 84% yield (Scheme 2).



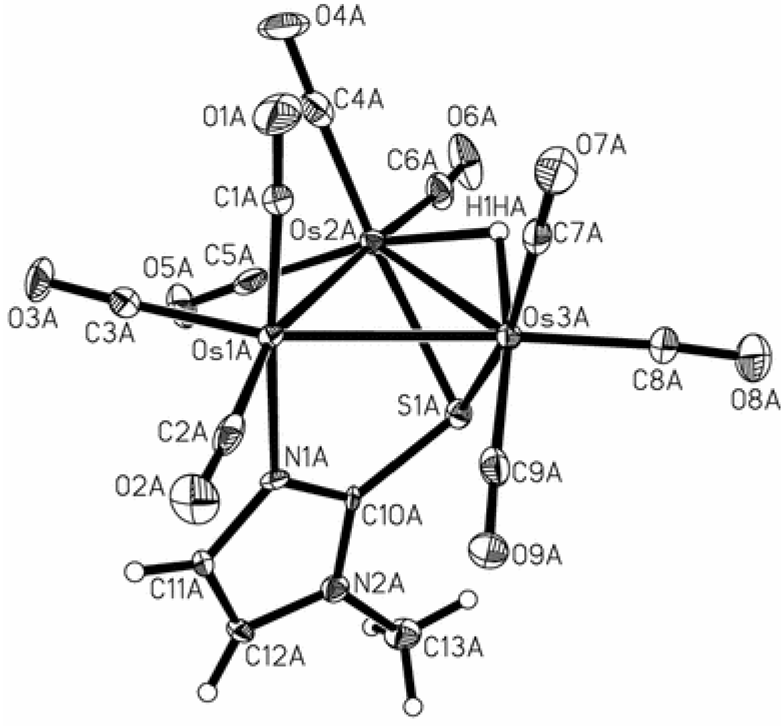
Scheme 2

Several compounds of this type, $[Os_3(CO)_9(\mu\text{-H})L]$, were previously reported[2,3,4] but they were characterized by spectroscopic methods only. However, we have successfully grown X-ray quality crystals of **2** and have undertaken a solid-state structural investigation to establish the ligand arrangement in **2**.

Compound **2** exists as two independent isomers in the asymmetric unit. The solid-state structures of the two molecules of **2** are shown in Fig. 1, crystallographic data are collected in Table 1, and selected bond lengths and angles are listed in Table 2. The crystallographic atom numbers given for the two molecules are the same, with those in molecule 2 being designated by an additional A. The structure of each molecule consists of an irregular triangle of osmium atoms, each of which is coordinated by three carbonyl ligands. A triply bridging 2-mercapto-1-methylimidazole ligand and a bridging hydrido ligand complete the coordination sphere of the cluster. The molecules differ in the relative disposition of the hydrido ligand within the cluster. In molecule 1, it is located across the Os(1)–Os(3) edge and this is consistent with the observation that this edge is significantly elongated {Os(1)–Os(3) = 2.9973(4) Å} compared with the other two metal–metal bonds {Os(1)–Os(2) = 2.8526(4) Å and Os(2)–Os(3) = 2.7316(4) Å}. Every metal center, Os(1), Os(2) and Os(3), is bounded to three terminal carbonyl ligands. The positions of the carbonyl ligands once again confirm the position of the hydride ligand. The CO groups are opened out away from the Os(1)–Os(3) bond as expected by the presence of the hydride {Os(3)–Os(1)–C(2) = 116.4(2)° and Os(1)–Os(3)–C(9) = 117.4(2)°}. However, in molecule 2 the hydride ligand bridges the Os(2A)–Os(3A) edge which is also consistent with the observation as this edge is slightly elongated {Os(2A)–Os(3A) = 2.8550(4) Å} compared with the other two metal–metal distances {Os(1A)–Os(2A) = 2.8213(4) Å and Os(1A)–Os(3A) = 2.8373(4) Å} but all the three Os–Os distances are shorter than those reported for $[Os_3(CO)_{12}]$ {2.877(3) Å}. As expected the location of the hydride ligand across the Os(2A)–Os(3A) edge is also consistent with the opening out of the CO groups along this edge, {Os(3A)–Os(2A)–C(6A) = 118.5(2)° and Os(2A)–Os(3A)–C(8A) = 115.7(2)°}. Molecule 2 contains a noncrystallographic mirror plane of symmetry passing through the plane of the heterocyclic ring of the ligand and also containing Os(1A), H(1HA), C(1A) and O(1A) atoms. Another important difference between the two molecules is that in molecule 1 the three metal–metal bond distances are significantly different; whereas, in molecule 2 the three osmium atoms define an approximate isosceles triangle. However, in both molecules the $\mu_3\text{-}SN_2C_4H_5$ ligand, which acts as a five-electron donor, is coordinated through the nitrogen atom in axial position to Os(1) and to Os(2) and Os(3) through the bridging exocyclic sulfur atom. This type of ligand arrangement has also been observed in $[Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_5)]$,[40] $[Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_3)]$[15] and $[Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}SN_2C_7H_5)]$.[15] In molecule 1, the sulfur atom asymmetrically bridges the Os(2)–Os(3) edge {Os(2)–S(1) = 2.4133(15) Å and Os(3)–S(1) = 2.4442(16) Å} whereas it bridges the Os(2A)–Os(3A) edge almost symmetrically {Os(2A)–S(1A) = 2.4467(16) and Os(3A)–S(1A) = 2.4365(16) Å} in molecule 2 and the Os–S bond distances in both the molecules are comparable to those observed in **1** and the other μ-SR triosmium clusters.[2,3,4,40] The Os–N bond distances in both molecules are comparable {Os(1)–N(1) = 2.144(6) Å in molecule 1 and Os(1A)–N(1A) = 2.139(5) Å in molecule 2} and are quite similar with those found in other triosmium clusters.[11]



Molecule 1



Molecule 2

Fig. 1

X-ray structure of $[Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_5)]$ (**2**) showing the atom labeling scheme used. Thermal ellipsoid are drawn at 50% probability level

Table 2

Selected bond distances (Å) and angles (°) for $[Os_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_5)]$ (**2**)

Molecule 1		**Molecule 2**	
Bond distances (*Å*)			
Os(1)–Os(2)	2.8526(4)	Os(1A)–Os(2A)	2.8213(4)
Os(1)–Os(3)	2.9973(4)	Os(1A)–Os(3A)	2.8373(4)
Os(2)–Os(3)	2.7316(4)	Os(2A)–Os(3A)	2.8550(4)
Os(2)–S(1)	2.4133(15)	Os(2A)–S(1A)	2.4467(16)
Os(3)–S(1)	2.4442(16)	Os(3A)–S(1A)	2.4365(16)
Os(1)–N(1)	2.144(6)	Os(1A)–N(1A)	2.139(5)
C(10)–S(1)	1.742(7)	C(10A)–S(1A)	1.750(7)
C(10)–N(1)	1.326(9)	C(10A)–N(1A)	1.315(9)
C(11)–N(1)	1.377(9)	C(11A)–N(1A)	1.366(9)
C(10)–N(2)	1.355(9)	C(10A)–N(2A)	1.358(8)
C(12)–N(2)	1.372(9)	C(12A)–N(2A)	1.386(9)
C(13)–N(2)	1.462(9)	C(13A)–N(2A)	1.465(9)
C(11)–C(12)	1.340(11)	C(11A)–C(12A)	1.359(10)
Os(1)–H(1H)	1.94(8)	Os(2A)–H(1HA)	1.83(8)
Os(3)–H(1H)	1.99(8)	Os(3A)–H(1HA)	1.66(8)
C–O[a]	1.913(9)	C–O[a]	1.915(5)
Bond angles (°)			
C(1)–Os(1)–Os(2)	92.6(2)	N(1A)–Os(1A)–Os(2A)	84.71(16)
C(3)–Os(1)–Os(2)	85.2(2)	C(1A)–Os(1A)–Os(3A)	88.9(2)
C(2)–Os(1)–Os(2)	170.1(2)	C(3A)–Os(1A)–Os(3A)	155.4(2)
N(1)–Os(1)–Os(2)	86.85(15)	C(2A)–Os(1A)–Os(3A)	106.0(2)

Molecule 1		**Molecule 2**	
C(1)–Os(1)–Os(3)	91.6(2)	N(1A)–Os(1A)–Os(3A)	87.43(16)
C(3)–Os(1)–Os(3)	140.8(2)	Os(2A)–Os(1A)–Os(3A)	60.601(10)
C(2)–Os(1)–Os(3)	116.4(2)	C(4A)–Os(2A)–Os(1A)	86.0(2)
N(1)–Os(1)–Os(3)	86.76(15)	C(5A)–Os(2A)–Os(1A)	84.8(2)
Os(2)–Os(1)–Os(3)	55.606(9)	C(6A)–Os(2A)–Os(1A)	177.3(2)
S(1)–Os(2)–Os(3)	56.32(4)	S(1A)–Os(2A)–Os(1A)	81.70(4)
C(4)–Os(2)–Os(1)	89.8(2)	C(4A)–Os(2A)–Os(3A)	109.0(2)
C(5)–Os(2)–Os(1)	96.7(2)	C(5A)–Os(2A)–Os(3A)	135.2(2)
C(6)–Os(2)–Os(1)	164.56(19)	C(6A)–Os(2A)–Os(3A)	118.5(2)
S(1)–Os(2)–Os(1)	82.00(4)	S(1A)–Os(2A)–Os(3A)	54.06(4)
Os(3)–Os(2)–Os(1)	64.883(10)	Os(1A)–Os(2A)–Os(3A)	59.976(10)
C(7)–Os(3)–Os(2)	101.10(19)	C(7A)–Os(3A)–Os(2A)	112.8(2)
C(8)–Os(3)–Os(2)	89.5(2)	C(8A)–Os(3A)–Os(2A)	115.7(2)
C(9)–Os(3)–Os(2)	159.7(2)	C(9A)–Os(3A)–Os(2A)	133.7(2)
S(1)–Os(3)–Os(2)	55.25(4)	S(1A)–Os(3A)–Os(2A)	54.39(4)
C(7)–Os(3)–Os(1)	89.24(19)	C(7A)–Os(3A)–Os(1A)	93.6(2)
C(8)–Os(3)–Os(1)	148.2(2)	C(8A)–Os(3A)–Os(1A)	172.1(2)
C(9)–Os(3)–Os(1)	117.4(2)	C(9A)–Os(3A)–Os(1A)	80.6(2)
S(1)–Os(3)–Os(1)	78.54(4)	S(1A)–Os(3A)–Os(1A)	81.55(4)
Os(2)–Os(3)–Os(1)	59.511(10)	Os(1A)–Os(3A)–Os(2A)	59.423(10)
Os(2)–S(1)–Os(3)	68.43(4)	Os(3A)–S(1A)–Os(2A)	71.56(4)
C(10)–N(1)–Os(1)	122.6(4)	C(10A)–N(1A)–Os(1A)	123.0(5)
C(11)–N(1)–Os(1)	130.5(5)	C(11A)–N(1A)–Os(1A)	130.0(5)

Molecule 1		Molecule 2	
Os–C–O[a]	177.9(1)	Os–C–O[a]	176.4(2)

[a]Average values

Within the heterocyclic ligand, the exocyclic C–S bond distances {C(10)–S(1) = 1.742(7) Å in molecule 1 and C(10A)–S(1A) = 1.750(7) Å in molecule 2} are close to that expected for a C–S single bond.[11,40,45] The C–C bond distances {C(11)–C(12) = 1.340(11) Å in molecule 1 and C(11A)–C(12A) = 1.359(10) Å in molecule 2} are very similar to C–C double bond distances. The C(13)–N(2) and C(13A)–N(2A) bond distances in molecule 1 {1.462(9) Å} and molecule 2 {1.465(9) Å} are similar to that observed for a C–N single bond whereas the other C–N distances {C(10)–N(1) = 1.326(9) Å, C(11)–N(1) = 1.377(9) Å, C(10)–N(2) = 1.355(9) Å, C(12)–N(1) = 1.372(9) Å in molecule 1 and C(10A)–N(1A) = 1.315(9) Å, C(11A)–N(1A) = 1.366(9) Å, C(10A)–N(2A) = 1.358(8) Å, C(12A)–N(1A) = 1.386(9) Å in molecule 2} are in between the C–N single and double bond distances which indicate appreciable double bond character.[9,10,11,45]

All other structural features of both molecules are within the expected range. The Os–C distances {1.893(7) − 1.942(7) Å, average 1.913(9) Å (molecule 1); 1.892(7) − 1.944(8) Å, average 1.915(5) Å (molecule 2)} and Os–C–O angles {175.5(6) − 179.3(7)°, average 177.9(1)° (molecule 1); 172.4(7) − 178.6(8)°, average 176.4(2)° (molecule 2)} are comparable to the corresponding values in the related triosmium nonacarbonyl compounds containing a 3,3,3-carbonyl ligand distribution and in which the hydride and the heterocyclic ligand bridge the same Os–Os edge (corresponds to molecule 1) or the different Os–Os edge (corresponds to molecule 2).[9,18]

The spectroscopic data of the two isomers of **2** are consistent with the solid-state structures being maintained in solution. The infrared spectrum in the carbonyl stretching region is very similar to that of $[Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}SN_2C_3H_3)]$,[1] indicating that they have very similar distribution of the carbonyl ligands. The ^1H NMR spectrum (Fig. 2) clearly indicates the presence of two isomers in solution, the asymmetric form (**2a**) and the symmetric form (**2b**), in 1:1 ratio. In addition to two equal intensity singlets at δ −12.47 and −14.70 due to the hydride ligand, the aromatic region of the ^1H NMR spectrum shows four doublets at δ 6.99 (J = 1.5 Hz), 6.87 (J = 1.5 Hz), 6.53 (J = 1.4 Hz), 6.44 (J = 1.4 Hz) in a relative intensity of 1:1:1:1 indicating the presence two equally populated isomers. Consistent with this the aliphatic region of the spectrum shows two singlets at δ 3.62 and 3.60 (each integrating for 3 H), attributed to the methyl protons of the heterocyclic ligand. The mass spectrum of **2** exhibits a molecular ion peak at m/z 938, which agrees with the molecular formula with ion peaks corresponding to 9 CO loses.

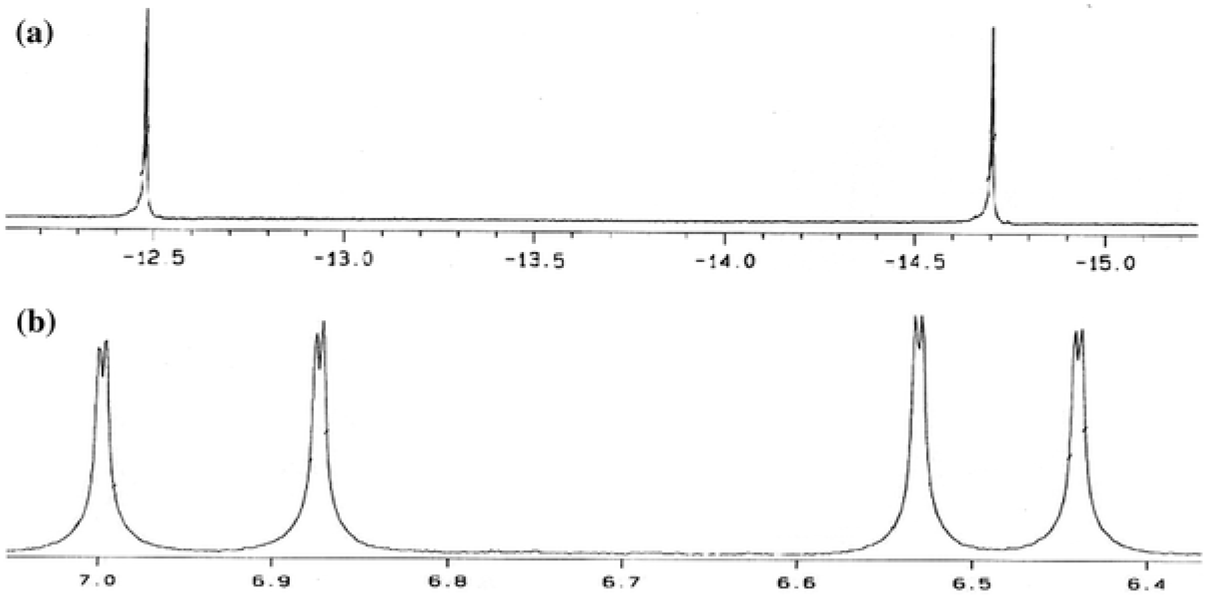


Fig. 2

^{1}H NMR spectrum of $[Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_5)]$ (**2**): **a** hydride region; **b** aromatic region

Supplementary Material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number 669776 (space group *P*-1). Copies of this information can be obtained free of charge on application to 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).

Notes

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References

[1] D'Ornelas L, Castrillo T, Hernández de LB, Narayan A, Atencio R (2003) Inorg Chim Acta 342:1. doi: 10.1016/S0020-1693(02)01134-9

[2] Au Y-K, Cheung K-K, Wong W-T (1995) J Chem Soc, Dalton Trans 1047. doi: 10.1039/dt9950001047

[3] Au Y-K, Cheung K-K, Wong W-T (1995) Inorg Chim Acta 228:267. doi: 10.1016/0020-1693(94)04184-W

[4] Brodie AM, Holden HD, Lewis J, Taylor MJ (1986) J Chem Soc, Dalton Trans 633. doi: 10.1039/dt9860000633

[5] Eisenstadt A, Giandomenico CM, Frederick MF, Laine RM (1985) Organometallics 11:2033. doi: 10.1021/om00130a018

[6] Laine RM (1987) N J Chem 11:543

[7] Laine RM (1983) New York Ann Acad Sci 415:271

[8] Sánchez-Delgado R (1994) J Mol Catal 86:287. doi: 10.1016/0304-5102(93)E0159-E

[9] Akther M, Azam KA, Azad SM, Kabir SE, Malik KMA, Mann R (2003) Polyhedron 22:355. doi: 10.1016/S0277-5387(02)01337-2

[10] Azam KA, Dilshad R, Kabir SE, Mottalib MA, Hursthouse MB, Malik KMA (2000) Polyhedron 19:1081. doi: 10.1016/S0277-5387(00)00354-5

[11] Kabir SE, Malik KMA, Molla E, Mottalib MA (2000) J Organomet Chem 616:157. doi: 10.1016/S0022-328X(00)00696-3

[12] Azam KA, Dilshad R, Kabir SE, Khatoon K, Nessa L, Rahman MM, Rosenberg E, Hursthouse MB, Malik KMA, Deeming AJ (1996) J Chem Soc, Dalton Trans 1731

[13] Azam KA, Hursthouse MB, Hussain SA, Kabir SE, Malik KMA, Rahman MM, Rosenberg E (1998) J Organomet Chem 559:81. doi: 10.1016/S0022-328X(98)00416-1

[14] Hanif KM, Hursthouse MB, Kabir SE, Malik KMA, Rosenberg E (1999) J Organomet Chem 580:60. doi: 10.1016/S0022-328X(98)01090-0

[15] Dilshad R, Hanif KM, Hursthouse MB, Kabir SE, Malik KMA, Rosenberg E (1999) J Organomet Chem 585:100. doi: 10.1016/S0022-328X(99)00201-6

[16] Azam KA, Hursthouse MB, Kabir SE, Malik KMA, Tesmer M, Vahrenkamp H (1998) Inorg Chem Commun 1:402. doi: 10.1016/S1387-7003(98)00110-5

[17] Akter J, Azam KA, Das AR, Hursthouse MB, Kabir SE, Malik KMA, Rosenberg E, Tesmer M, Vahrenkamp H (1999) J Organomet Chem 588:100

[18] Kabir SE, Kolwaite DS, Rosenberg E, Scott LG, McPhillips T, Duque R, Day M, Hardcastle KI (1996) Organometallics 15:1979. doi: 10.1021/om9507235

[19] Angelici RJ (1988) Acc Chem Res 21:387. doi: 10.1021/ar00155a001

[20] Friend CM, Roberts JT (1988) Acc Chem Res 21:394. doi: 10.1021/ar00155a002

[21] Oglivy AE, Draganjac M, Rauchfuss TB, Wilson SR (1988) Organometallics 7:2411. doi: 10.1021/om00101a023

[22] Luo S, Oglivy AE, Rauchfuss TB, Rheingold AL, Wilson SR (1991) Organometallics 10:1002. doi: 10.1021/om00050a035

[23] Deeming AJ, Hardcastle KI, Karim M (1992) Inorg Chem 31:371. doi: 10.1021/ic00049a015

[24] Arce AJ, Deeming AJ, Sanctis YD, Machado R, Manzur J, Rivas C (1990) J Chem Soc Chem Commun 1568. doi: 10.1039/c39900001568

[25] Adam RD, Pompco MP, Wu W, Yamamato JH (1993) J Am Chem Soc 115:8207. doi: 10.1021/ja00071a033

[26]Adam RD, Belinski JA, Yamamato JH (1992) Organometallics 11:3422. doi: 10.1021/om00046a048

[27]Day MW, Hardcastle KI, Deeming AJ, Arce AJ, Sanctis YD (1990) Organometallics 9:6. doi: 10.1021/om00115a002

[28]Rosenberg E, Kabir SE, Hardcastle KI, Day M, Wolf E (1990) Organometallics 9:2214. doi: 10.1021/om00158a018

[29]Adam RD, Chen G (1993) Organometallics 12:2070. doi: 10.1021/om00030a017

[30]Casella L (1984) Inorg Chem 23:2781. doi: 10.1021/ic00186a014

[31]Dance IG (1986) Polyhedron 5:1037. doi: 10.1016/S0277-5387(00)84307-7

[32]Blower PG, Dilworth JR (1987) Coord Chem Rev 76:121. doi: 10.1016/0010-8545(87)85003-8

[33]Krebs B, Henkel G (1991) Angew Chem Int Ed Engl 30:769. doi: 10.1002/anie.199107691

[34]Freeman HC (1980) In: Laurent JP (ed) Coordination Chemistry-21. Pergamon, New York, p 29

[35]Ashworth CC, Bailey NA, Johnson M, McCleverty JA, Morrison N, Tabbiner B (1976) J Chem Soc Chem Commun 743. doi: 10.1039/c39760000743

[36]Raper ES (1985) Coord Chem Rev 61:115. doi: 10.1016/0010-8545(85)80004-7

[37]Jeannin S, Jeannin Y, Lavigne G (1976) Trans Met Chem (Weinh) 1:186

[38]Jeannin S, Jeannin Y, Lavigne G (1976) Trans Met Chem (Weinh) 1:192

[39]Alper R, Chan ASK (1974) Inorg Chem 13:225. doi: 10.1021/ic50131a044

[40]Azam KA, Hanif KM, Ghosh AC, Kabir SE, Karmakar SR, Malik KMA, Parvin S, Rosenberg E (2002) Polyhedron 21:885. doi: 10.1016/S0277-5387(02)00869-0

[41]SAINT (2005) Software for CCD diffractometer, V.7.23A, Bruker AXS

[42]Sheldrick GM (1996) SADBS 5, Program for empirical absorption correction of area-detector data, Institüt für Anorganische Chemie der Universität, Göttingen

[43]Program XS from SHELXTL package (2001) V. 6.12, Bruker AXS

[44]Program XL from SHELXTL package (2001) V. 6.10, Bruker AXS

[45]Zabicky J (ed) (1970) The Chemistry of Amides. Interscience, London, p 388