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Triosmium carbonyl complexes containing bridging ligands derived from *ortho*-functionalized anilines

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Abstract

The trinuclear carbonyl clusters $[Os_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}HNC_6H_2Me_2NH_2)(CO)_9]$ (**1**) ($o\text{-}H_2NC_6H_2Me_2NH_2$ = 1,2-diamino-4,5-dimethylbenzene), $[Os_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}OC_6H_4NH_2)(CO)_9]$ (**2**) ($o\text{-}HOC_6H_4NH_2$ = 2-aminophenol) and $[Os_3(\mu\text{-}H)(\mu,\eta^1\text{-}o\text{-}SC_6H_4NH_2)(CO)_{10}]$ (**3**) ($o\text{-}HSC_6H_4NH_2$ = 2-aminothiophenol) have been prepared by reacting $[Os_3(CO)_{10}(MeCN)_2]$ with the appropriate *ortho*-functionalized aniline in THF solvent. Compounds **1** and **2** are isostructural, having an Os–Os edge spanned by a hydride ligand and by the amido (**1**) or alkoxy (**2**) fragment of the monodeprotonated 1,2-diamino-4,5-dimethylbenzene or 2-aminophenol ligands. In both complexes, one of the metal atoms of the bridged Os–Os edge is also attached to the NH_2 group of the organic ligand. The structure of complex **3** is related to those of **1** or **2**, in that an Os–Os edge is spanned by a three-electron donor ligand (the thiolate fragment of monodeprotonated 2-aminothiophenol), but differs in that the NH_2 group is uncoordinated. The X-ray structure of compound **3** is also reported. The results are discussed taking into account the hard–soft character of the bridging ligands.

Keywords: Osmium; Triosmium clusters; Carbonyl; Substituted anilines; X-ray structure

1. Introduction

The reaction of $[Ru_3(CO)_{12}]$ with aniline under thermal conditions gives the amido derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}NHPh)(CO)_{10}]$ [1]. This complex is an intermediate [2] in the $[Ru_3(CO)_{12}]$-promoted catalytic hydrogenation of nitrobenzene to aniline [3]. It is curious that this interesting ruthenium chemistry has prompted very few studies involving reactions of $[Os_3(CO)_{12}]$ or any of its activated derivatives $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and $[Os_3(CO)_{12-n}(MeCN)_n]$ (n = 1, 2) with anilines. Podberezskaya et al. [4] have reported that $[Os_3(CO)_{12}]$ reacts with pentafluoroaniline to give $[Os_3(\mu\text{-}H)(\mu\text{-}NHC_6F_5)(CO)_{10}]$. Bruce and coworkers [5] and Brodie and coworkers [6] have studied the reactivity of $[Os_3(CO)_{12-n}(MeCN)_n]$ (n = 1, 2) with 2-diphenylphosphinoaniline. The reactions of $[Os_3(CO)_{12}]$ with primary and secondary alkyl amines have been studied in more detail [7,8].

In previous works, we have reported the reactivity of $[Ru_3(CO)_{12}]$ with 1,2-diaminobenzene [9], 2-aminophenol and 2-aminothiophenol [10]. We have also shown that the 1,2-diamino-4,5-dimethylbenzene derivative $[Ru_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}HNC_6H_2Me_2NH_2)(CO)_9]$ is an efficient catalyst precursor for the homogeneous hydrogenation of internal alkynes to alkenes under mild conditions [11]. We report and discuss here our findings on the reactions of these *ortho*-functionalized aniline ligands with $[Os_3(CO)_{10}(MeCN)_2]$.

2. Results

2.1. Reativity studies

The reactions of $[Os_3(CO)_{10}(MeCN)_2]$ with the *ortho*-functionalized ligands 1,2-diamino-4,5-dimethylbenzene and 2-aminophenol proved to be very slow at room temperature in THF solvent, but they readily afforded the compounds $[Os_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}HNC_6H_2Me_2NH_2)(CO)_9]$ (**1**) ($o\text{-}H_2NC_6H_2Me_2NH_2$ = 1,2-

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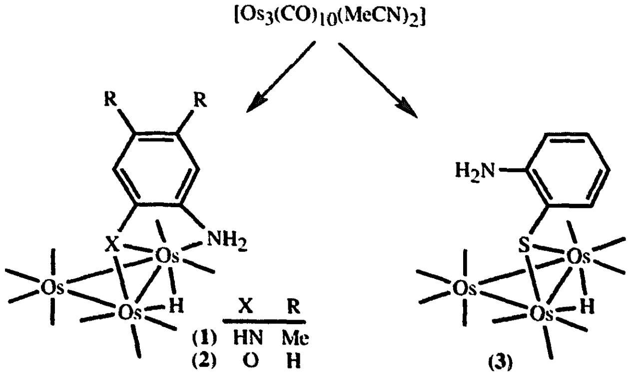
diamino-4,5-dimethylbenzene) and $[Os_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}OC_6H_4NH_2)(CO)_9]$ (**2**) ($o\text{-}HOC_6H_4NH_2$ = 2-aminophenol) respectively when heated to reflux temperature.

An analogous reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 2-aminothiophenol at room temperature gave the decacarbonyl derivative $[Os_3(\mu\text{-}H)(\mu,\eta^1\text{-}o\text{-}SC_6H_4NH_2)(CO)_{10}]$ (**3**) ($o\text{-}HSC_6H_4NH_2$ = 2-aminothiophenol). Compound **3** remained unchanged when it was heated in THF at reflux temperature for 2 h.



Scheme 1.

2.2. Structural characterization of the compounds

The structure proposed for compounds **1** and **2** in Scheme 1 is based on their spectroscopic data. Both compounds gave the corresponding molecular ions in their mass spectra and have similar IR and NMR spectra. The most interesting features of their ^1H NMR spectra are the presence of a hydride resonance and the presence of an AB spin system corresponding to the NH_2 protons. This indicates that both compounds contain an intact NH_2 group; therefore, the hydride ligand of **2** arises from the oxidative addition of an O–H bond and not from that of an N–H bond. Moreover, the diastereotopic character of the hydrogen atoms of the NH_2 groups confirms that they are coordinated to one of the bridged osmium atoms (uncoordination or coordination of the NH_2 group to the unique osmium atom would result in structures of C_s symmetry, which would give a singlet for the NH_2 protons). All these spectroscopic data can be compared with those reported for the ruthenium analogue of complex **1** $[Ru_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}HNC_6H_2Me_2NH_2)(CO)_9]$ [9] and for $[M_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}HNC_6H_4PPh_2)(CO)_9]$ (M = Ru [5], Os [6]). The structures of these compounds have been unambiguously determined by X-ray diffraction methods and are

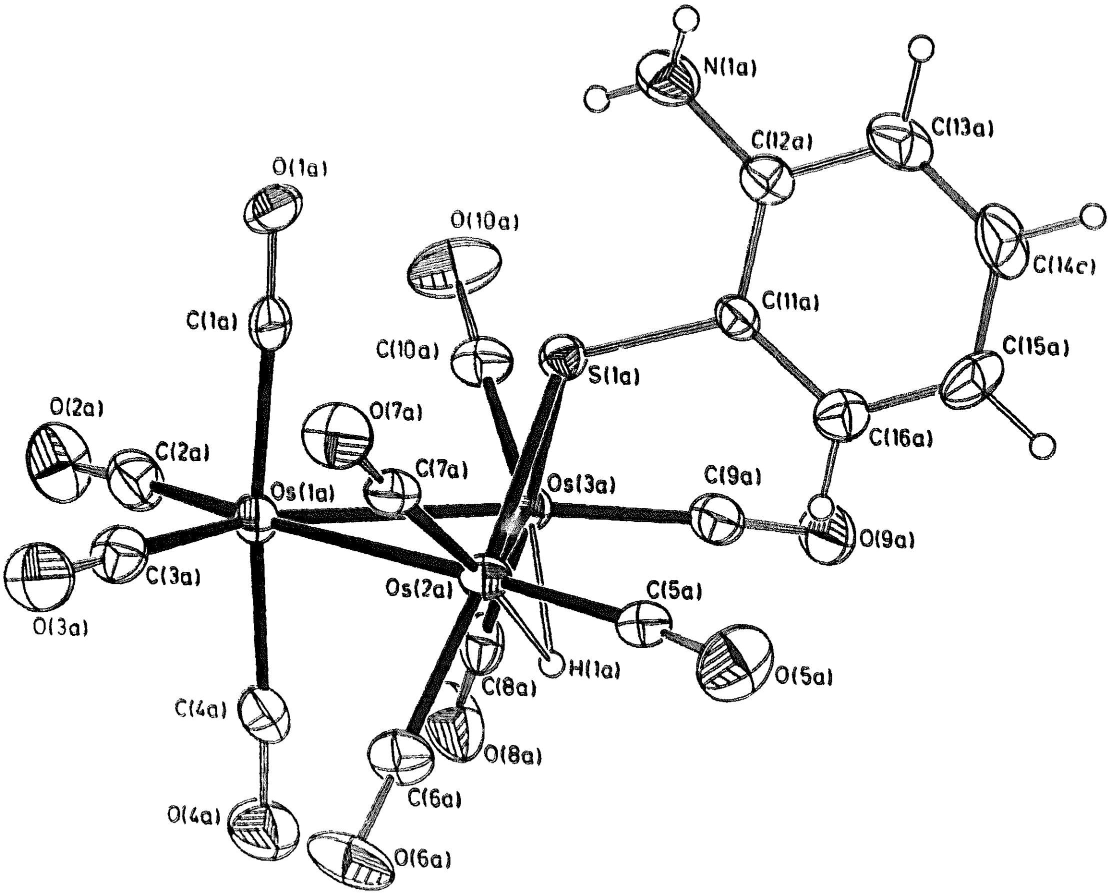


Fig. 1. A view of the molecular structure of one of the two crystallographically independent molecules found in one crystal of compound **3**. Thermal ellipsoids are drawn at the 30% probability level.

Table 1
Selected bond lengths and angles in compound 3

Molecule A		Molecule B	
Os(1A)–Os(2A)	2.861(3)	Os(1B)–Os(2B)	2.870(3)
Os(1A)–Os(3A)	2.867(2)	Os(1B)–Os(3B)	2.862(3)
Os(2A)–Os(3A)	2.862(2)	Os(2B)–Os(3B)	2.866(3)
Os(2A)–S(1A)	2.411(5)	Os(2B)–S(1B)	2.417(5)
Os(3A)–S(1A)	2.415(5)	Os(3B)–S(1B)	2.411(5)
Os(1A)–C(2A)	1.91(2)	Os(1B)–C(2B)	1.93(2)
Os(1A)–C(3A)	1.94(2)	Os(1B)–C(3B)	1.92(2)
Os(1A)–C(4A)	1.94(2)	Os(1B)–C(4B)	1.93(2)
Os(1A)–C(1A)	1.95(2)	Os(1B)–C(1B)	1.95(2)
Os(2A)–C(5A)	1.89(2)	Os(2B)–C(5B)	1.93(2)
Os(2A)–C(6A)	1.93(2)	Os(2B)–C(6B)	1.93(2)
Os(2A)–C(7A)	1.89(2)	Os(2B)–C(7B)	1.87(2)
Os(3A)–C(8A)	1.91(2)	Os(3B)–C(8B)	1.90(2)
Os(3A)–C(9A)	1.91(2)	Os(3B)–C(9B)	1.92(2)
Os(3A)–C(10A)	1.86(2)	Os(3B)–C(10B)	1.92(2)
C(1A)–O(1A)	1.13(2)	C(1B)–O(1B)	1.12(2)
C(2A)–O(2A)	1.15(2)	C(2B)–O(2B)	1.14(2)
C(3A)–O(3A)	1.12(2)	C(3B)–O(3B)	1.14(2)
C(4A)–O(4A)	1.14(2)	C(4B)–O(4B)	1.15(2)
C(5A)–O(5A)	1.16(2)	C(5B)–O(5B)	1.12(2)
C(6A)–O(6A)	1.12(2)	C(6B)–O(6B)	1.13(2)
C(7A)–O(7A)	1.14(2)	C(7B)–O(7B)	1.15(2)
C(8A)–O(8A)	1.12(2)	C(8B)–O(8B)	1.13(2)
C(9A)–O(9A)	1.15(2)	C(9B)–O(9B)	1.14(2)
C(10A)–O(10A)	1.18(2)	C(10B)–O(10B)	1.12(2)
Os(1A)–Os(2A)–Os(3A)	60.13(6)	Os(1B)–Os(2B)–Os(3B)	59.86(7)
Os(2A)–Os(1A)–Os(3A)	59.96(6)	Os(2B)–Os(1B)–Os(3B)	60.00(7)
Os(2A)–Os(3A)–Os(1A)	59.91(6)	Os(2B)–Os(3B)–Os(1B)	60.14(7)
Os(2A)–S(1A)–Os(3A)	72.7(2)	Os(2B)–S(1B)–Os(3B)	72.8(1)

very similar to that depicted in Scheme 1 for **1** and **2**. They all have the hydride ligand spanning the same M–M edge as the other bridging ligand.

The ^1H NMR spectrum of compound **3** contained four multiplets for the aromatic protons, one singlet resonance for the hydride ligand and one broad singlet which could be assigned to the NH_2 group. These data suggest a symmetric structure which would make equivalent the hydrogen atoms of the NH_2 group but cannot unambiguously determine whether the amino group is coordinated or not because its chemical shift (4.42 ppm) is close to those observed for the NH_2 groups of compounds **1** (5.35, 5.01 ppm) and **2** (5.59, 5.44 ppm). Therefore, the structure of compound **3** was established by an X-ray diffraction study.

Fig. 1 shows a view of one of the two crystallographically independent molecules found in one crystal of compound **3**. Selected bond distances and angles are given in Table 1. The cluster consists of a nearly equilateral triangle of osmium atoms with one edge doubly bridged by a hydride and an *S*-coordinated 2-aminothiophenolate ligand. The cluster shell is completed by ten terminal carbonyl ligands. The phenyl group of the bridging 2-aminothiophenolate ligand is nearly perpendicular to the Os_3 plane and adopts an *exo* configuration (it points outwards from the metal triangle). Similar structures have been reported previously for other μ-hydrido-μ-thiolatotriosmium clusters (see for example Ref. [12]).

3. Discussion

Osmium is a soft metal and, therefore, it prefers soft over hard ligands. On the contrary, the hardness of the ligands used in this work decreases in the series *o*-hydroxy- > *o*-amino- > *o*-mercaptoaniline, corresponding to *O*-, *N*- and *S*-donor ligands respectively [13]. This explains why 2-aminothiophenol (a soft ligand) reacts readily with $[Os_3(CO)_{10}(MeCN)_2]$ at room temperature, whereas the reactions of the other two ligands (which are hard) with the same triosmium cluster require higher temperatures.

Another point which needs to be addressed is why the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 2-aminothiophenol gives a stable decacarbonyl complex (**3**) which cannot be transformed into a nonacarbonyl derivative (analogous to **1** and **2**) in refluxing THF, whereas the reactions of the *o*-amino- and *o*-hydroxyaniline ligands end in the nonacarbonyl compounds **1** and **2** respectively under similar conditions. One would expect the decacarbonyl derivatives of the *o*-amino- and *o*-hydroxyaniline ligands to be intermediates in the transformations of $[Os_3(CO)_{10}(MeCN)_2]$ into compounds **1** and **2**, but they should have very short lives in refluxing THF.

These experimental results also seem to be related to the hard–soft character of their bridging ligands. In fact, it is known that the harder the ligand in a carbonyl complex the easier the substitution of a *cis*-CO ligand by another ligand (see for example Ref. [14]). Therefore, amido and alkoxy ligands are expected to be better *cis*-labilizers than thiolate ligands, and this explains why the nonacarbonyl derivatives of the hard amido and alkoxy ligands (complexes **1** and **2**, which have the NH_2 groups and the bridging atoms in *cis* arrangements) are formed more easily than that of the soft 2-aminothiophenolate ligand (which remains unknown).

4. Experimental

4.1. General data

Solvents were dried and distilled under nitrogen prior to use. The reactions were carried out under nitrogen using Schlenk–vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and by spot thin layer chromatography (TLC). $[Os_3(CO)_{12}]$ was made from OsO_4 by a published procedure [15]. Anhydrous Me_3NO was prepared by sublimation of $Me_3NO \cdot 2H_2O$ and was stored under nitrogen. OsO_4 was obtained from Johnson Matthey, all other starting materials and TLC plates were purchased from Aldrich and used as received. Infrared spectra were recorded on a Perkin–Elmer FT 1720-X spectrophotometer, using 0.1 mm CaF_2 cells. ^1H NMR spectra were run at 18 °C with Bruker AC-200 and AC-300 instruments, using internal $SiMe_4$ as standard ($\delta = 0$ ppm). Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan Mat-95 spectrometer, using nitrobenzyl alcohol as matrix and cesium as bombarding gas. Correct microanalyses (C, H, N) were obtained for all compounds; they were performed by the University of Oviedo Analytical Service.

4.2. $[Os_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}HNC_6H_2Me_2NH_2)(CO)_9]$ (1)

A solution of acetonitrile (2 ml), anhydrous Me_3NO (9.5 mg, 0.127 mmol) and $[Os_3(CO)_{12}]$ (50 mg, 0.055 mmol) in dichloromethane (15 ml) was stirred at room temperature for 1 h. The solution was passed through a column ($5 \times 2\,cm^2$) of neutral alumina (activity I) to remove excess Me_3NO. The resulting solution, which contained the complex $[Os_3(CO)_{10}(MeCN)_2]$ (IR identification [16]), was evaporated to dryness under reduced pressure. The residue was dissolved in THF (10 ml) and treated with 1,2-diamino-4,5-dimethylbenzene (75 mg, 0.055 mol). The solution was stirred at room temperature for 2.5 h, but its IR spectrum indicated that most of the $[Os_3(CO)_{10}(MeCN)_2]$ remained unreacted; therefore it was heated to reflux temperature for a further 2.5 h. The solvent was removed under reduced pressure and the residue was separated by TLC (silica gel). Hexane eluted a pale yellow band which was discarded. Hexane–dichloromethane (5:3) eluted complex **1**, which was obtained as a yellow–orange solid (34 mg, 65%). MS (*m/e*): 959 ($C_{17}H_{12}N_2O_9Os_3$, M^+). IR ν(CO) (THF): 2086 (m), 2045 (vs), 2001 (s), 1994 (sh), 1984 (s), 1978 (sh), 1918 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 6.97 (s, 1H), 6.89 (s, 1H), 5.40 (s, br, 1H, NH), 5.35 (d, br, $J = 12$ Hz, 1H, NH), 5.01 (d, br, $J = 12$ Hz, 1H, NH), 2.24 (s, 3H), 2.21 (s, 3H), −14.31 (d, $J = 2.7$ Hz, 1H, μ-H) ppm.

4.3. $[Os_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}OC_6H_4NH_2)(CO)_9]$ (2)

2-Aminophenol (6.0 mg, 0.055 mmol) was added to a THF solution (10 ml) of $[Os_3(CO)_{10}(MeCN)_2]$ (prepared in situ, as described above, from 0.055 mmol of $[Os_3(CO)_{12}]$). The solution was stirred at room temperature for 2.5 h, to give a mixture of compounds (IR and

Table 2
Crystallographic and refinement data for compound **3**

Formula	$C_{16}H_7NO_{10}Os_3S$
Formula weight	975.89
Crystal system	Triclinic
Space group	$P\bar{1}$
a, b, c (Å)	8.670(5), 13.61(1), 19.42(2)
α, β, γ (°)	80.99(8), 89.98(6), 71.51(8)
V ($Å^3$)	2145(3)
Z	4
$F(000)$	1736
D_{calc} ($g\,cm^{-3}$)	3.023
μ (mm^{-1})	17.881
Crystal size (mm^3)	$0.30 \times 0.26 \times 0.20$
Radiation, λ (Å)	Mo Kα, 0.71073
Diffractometer	Enraf–Nonius CAD4
Monochromator	Graphite
Temperature (K)	293(2)
Scan method	$\omega - 2\theta$
θ limits (°)	1.06 to 24.98
h, k, l ranges	−10 to 10, −15 to 16, 0 to 23
Reflections collected	7770
Independent reflections	7518
$R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I$	0.0264
Reflections with $I > 2\sigma(I)$	7517
Restraints, parameters	0, 572
$R(F)_{I > 2\sigma(I)}$ [a]	0.035
$R_w(F^2)_{all\ data}$ [b]	0.089
GOF [c]	1.048
Δ/σ	0.013
Max, min $\Delta\rho$ ($e\,Å^3$)	0.957, −2.246

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R_w(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.
[c] Goodness of fit (GOF) $= [\Sigma w(F_o^2 - F_c^2)^2/(N - P)]^{1/2}$.

Table 3
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for the non-H atoms of compound **3**

Atom	x	y	z	U_{eq} [a]
Os(1A)	−584(1)	2848(1)	2204(1)	39(1)
Os(2A)	−200(1)	2288(1)	840(1)	35(1)
Os(3A)	1342(1)	3703(1)	1237(1)	32(1)
S(1A)	2647(5)	1871(3)	1165(2)	35(1)
N(1A)	5963(25)	314(16)	1294(11)	62(6)
O(1A)	2514(18)	1041(12)	2771(7)	63(4)
O(2A)	−671(20)	3812(13)	3526(9)	74(5)
O(3A)	−2905(20)	1614(14)	2665(10)	81(5)
O(4A)	−3444(21)	4792(13)	1568(9)	77(5)
O(5A)	28(22)	1891(14)	−663(9)	82(5)
O(6A)	−3900(18)	3161(13)	662(10)	82(5)
O(7A)	−128(19)	83(13)	1450(9)	68(4)
O(8A)	−761(20)	5909(11)	1364(9)	72(5)
O(9A)	3021(18)	4684(12)	66(8)	66(4)
O(10A)	3744(22)	3648(14)	2394(9)	91(6)
C(1A)	1383(25)	1688(16)	2541(9)	41(5)
C(2A)	−587(26)	3459(18)	3023(12)	60(6)
C(3A)	−2041(27)	2049(16)	2490(11)	53(5)
C(4A)	−2378(26)	4066(18)	1785(11)	55(6)
C(5A)	44(23)	2038(15)	−91(10)	43(5)
C(6A)	−2540(27)	2848(17)	718(11)	52(5)
C(7A)	−193(23)	919(16)	1212(10)	47(5)
C(8A)	−3(24)	5094(15)	1309(9)	40(5)
C(9A)	2443(24)	4260(17)	498(10)	50(5)
C(10A)	2804(24)	3674(15)	1948(10)	47(5)
C(11A)	3991(20)	1641(14)	471(8)	32(4)
C(12A)	5501(22)	874(14)	639(10)	40(4)
C(13A)	6607(26)	672(17)	131(11)	59(6)
C(14A)	6183(29)	1251(21)	−543(12)	71(7)
C(15A)	4681(28)	2023(17)	−704(10)	56(6)
C(16A)	3617(24)	2200(15)	−196(10)	45(5)
Os(1B)	−2263(1)	2848(1)	−2796(1)	39(1)
Os(2B)	−5045(1)	3703(1)	−3763(1)	32(1)
Os(3B)	−2087(1)	2289(1)	−4161(1)	35(1)
S(1B)	−4516(5)	1868(3)	−3833(2)	34(1)
N(1B)	−6321(29)	340(13)	−3703(11)	59(5)
O(1B)	−3534(22)	1039(13)	−2231(7)	73(5)
O(2B)	1291(20)	1608(14)	−2328(9)	80(5)
O(3B)	−3175(20)	3813(13)	−1476(9)	76(5)
O(4B)	−1370(21)	4801(15)	−3436(9)	82(5)
O(5B)	−7700(19)	4712(12)	−4924(8)	65(4)
O(6B)	−5164(20)	5932(12)	−3639(9)	75(5)
O(7B)	−7395(21)	3657(14)	−2618(9)	84(6)
O(8B)	735(18)	3155(12)	−4354(11)	85(6)
O(9B)	−1928(20)	1880(13)	−5663(8)	73(5)
O(10B)	43(19)	78(11)	−3550(9)	71(5)
C(1B)	−3086(26)	1693(17)	−2467(10)	51(5)
C(2B)	−36(28)	2058(17)	−2489(11)	53(5)
C(3B)	−2878(24)	3442(17)	−1966(11)	50(5)
C(4B)	−1685(26)	4061(18)	−3200(11)	54(5)
C(5B)	−6705(24)	4280(14)	−4513(9)	39(4)
C(6B)	−5071(25)	5097(18)	−3674(9)	49(5)
C(7B)	−6483(26)	3680(17)	−3047(11)	53(6)
C(8B)	−334(25)	2845(15)	−4284(12)	50(5)
C(9B)	−2070(24)	2060(16)	−5110(10)	50(5)
C(10B)	−696(24)	909(18)	−3770(11)	50(5)
C(11B)	−5631(20)	1650(14)	−4522(9)	34(4)
C(12B)	−6349(22)	871(14)	−4362(10)	41(5)
C(13B)	−7299(24)	681(16)	−4879(11)	52(5)
C(14B)	−7468(27)	1249(18)	−5548(11)	59(6)
C(15B)	−6721(27)	2003(19)	−5703(11)	59(6)
C(16B)	−5826(22)	2184(16)	−5198(9)	44(5)

^1H NMR), and then it was heated to reflux temperature for 1 h. The solvent was removed under reduced pressure and the residue was separated by TLC (silica gel). Hexane–dichloromethane (1:1) eluted two yellow bands. The second band afforded complex **2**, which was obtained as a yellow solid (39 mg, 76%). MS (m/e): 932 ($C_{15}H_7NO_{10}Os_3$, M^+). IR ν(CO) (THF): 2094 (m), 2054 (s), 2009 (vs), 1994 (sh), 1985 (sh), 1923 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 7.18 (m, 1H), 6.99 (d, $J = 7.2$ Hz, 1H), 6.78 (m, 2H), 5.59 (d, br, $J = 10$ Hz, 1H, NH), 5.44 (d, br, $J = 10$ Hz, 1H, NH), −10.77 (s, 1H, μ-H) ppm.

4.4. $[Os_3(\mu\text{-}H)(\mu,\eta^1\text{-}o\text{-}SC_6H_4NH_2)(CO)_{10}]$ (3)

2-Aminothiophenol (7.1 μl, 0.066 mmol) was added to a THF solution (10 ml) of $[Os_3(CO)_{10}(MeCN)_2]$ (prepared in situ, as described above, from 0.055 mmol of $[Os_3(CO)_{12}]$). The solution was stirred at room temperature for 2 h. The IR spectrum showed the presence of a new compound and the absence of the starting material. The solution was then stirred at reflux temperature for 2 h, but the IR spectrum remained unchanged with respect to that obtained at room temperature. The solvent was removed under reduced pressure and the residue was washed with hexane (2 ml) to give compound **3** as a yellow solid (46 mg, 86%). MS (m/e): 976 ($C_{16}H_7NO_{10}Os_3S$, M^+). IR ν(CO) (THF): 2107 (w), 2069 (s), 2057 (m), 2019 (vs), 2000 (sh), 1979 (m), 1942 (w) cm^{-1}. ^1H NMR ($CDCl_3$): 7.03 (td, $J = 7.1$ and 1.2 Hz, 1H), 6.79 (td, $J = 7.1$ and 1.0 Hz, 1H), 6.70 (dd, $J = 7.1$ and 1.2 Hz, 1H), 6.58 (dd, $J = 7.1$ and 1.0 Hz, 1H), 4.42 (s, br, 2H, NH_2), −16.96 (s, 1H, μ-H) ppm.

4.5. Crystal structure of compound 3

A yellow crystal, obtained by keeping a pentane solution of the complex at −20°C for one week, was used for the X-ray diffraction study. A selection of crystal and refinement data is given in Table 2.

The cell dimensions were determined by least-squares refinement of 25 reflections with $0° < \theta < 13°$. Space group $P\bar{1}$ from structure determination. Intensities were measured with a variable scan rate and a maximun scan time of 60 s per reflection. Three standard reflections were monitored every 60 min, revealing no intensity fluctuations. Final drift correction factors were between 0.984 and 1.035. Profile analysis was performed on all reflections [17]. Lorentz and polarization corrections were applied and data were reduced to $|F_0|$ values.

Note to Table 3:
[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The structure was solved by Patterson methods and phase expansion using DIRDIF [18]. Isotropic least-squares refinement on F^2, using SHELXL93 [19], was followed by an empirical absorption correction using XABS [20] (min, max correction factors 0.49, 1.00). After anisotropic refinement of the positional and thermal parameters of the non-hydrogen atoms, the hydrogen atoms of the bridging ligands were geometrically placed. The hydride H atoms of both crystallographically independent molecules were detected by a low angle difference Fourier synthesis and were refined isotropically. The function minimized was $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.038P)^2]$, with $\sigma(F_o^2)$ from counting statistics and $P = [\max(F_o^2,0) + 2F_c^2]/3$. Atomic scattering factors were taken from the literature [21]. Geometrical calculations were made with PARST [22]. The structure plot was drawn with the EUCLID package [23]. Final atomic coordinates are given in Table 3. All calculations were carried out on DIGITAL workstations at the Scientific Computer Center of the University of Oviedo.

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