Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 2138–2147
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Reactivity of $[Os_3(CO)_{10}(NCMe)_2]$ and $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)]$ with 4-mercaptopyridine: X-ray structure of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-SC}_5H_4N)]$ and $[Os_3(CO)_{10}(\mu\text{-AuPPh}_3)(\mu\text{-SC}_5H_4N)]$

Gloria Sánchez-Cabrera [a,*], Francisco J. Zuno-Cruz [a], Berenice A. Ordóñez-Flores [a], María J. Rosales-Hoz [b], Marco A. Leyva [b]

[a] *Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Hidalgo, Ciudad Universitaria, Km 4.5 Carretera Pachuca–Tulancingo, Pachuca Hgo., Mexico*

[b] *Departamento de Química, Centro de Investigación y Estudios Avanzados del I. P. N. Apdo. postal 14-740, 07000 México D.F., Mexico*

Received 3 January 2007; received in revised form 20 January 2007; accepted 20 January 2007
Available online 26 January 2007

Abstract

The compound $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)]$ (**2**) was prepared from the reaction between $[Os_3(CO)_{10}(NCMe)_2]$ (**1**) and $[AuClPPh_3]$ under mild conditions. The reaction of **2** with 4-mercaptopyridine (4-pyS) ligand yielded compounds $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-SC}_5H_4N)]$ (**4**), formed by isolobal replacement of the fragment $[AuPPh_3]^+$ by H^+ and $[Os_3(CO)_{10}(\mu\text{-AuPPh}_3)(\mu\text{-SC}_5H_4N)]$ (**5**). $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-SC}_5H_4N)]$ (**4**) was also obtained by substitution of two acetonitrile ligands in the activated cluster **1** by 4-pyS, at room temperature in dichloromethane. Compounds **2**–**5** were characterized spectroscopically and the molecular structures of **4** and **5** in the solid state were obtained by single crystal X-ray diffraction studies.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Osmium–gold clusters; Mercaptopyridine; Isolobal analogy

1. Introduction

The synthesis of heteronuclear gold clusters has been widely studied [1,2]. Oxidative addition reactions have been used to synthesize these types of compounds from neutral clusters. Clark and co-workers [3] were the first to prepare the compound $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)]$ (**2**) using this methodology; this reaction was carried out in refluxing xylene using $[Os_3(CO)_{12}]$ and $[AuClPPh_3]$ as starting material. Compound **2** has also been prepared by photochemical methods [4]. An additional synthetic method using an anionic precursor $[HOs_3(CO)_{11}]^-$, has been employed to prepare the unsaturated analog compound $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-AuPPh}_3)]$ [5]. Activated metallic clusters have been used to prepare mixed metal clusters under very mild conditions [6,7].

Most of the compounds containing bonds between gold and some other transition metals have been prepared using the isolobal relationship between hydride ligands and $AuPR_3$ fragments [2,8]. Some of them involve the replacement of hydride ligands in homonuclear clusters by $AuPR_3$ groups, and formation of heteronuclear compounds [9,10].

In spite of all advances in the synthesis of these heteronuclear compounds, there are few reports of osmium–gold cluster reactivity studies with donor ligands (nucleophiles) [11,12]. One group of ligands, that have attracted a great deal of attention are those which have different donor atoms and are, therefore, capable of bonding to one or more metal atoms. Mercaptopyridines are a set of such ligands. Studies have shown them to present a thione-thiol tautomerism [13]. Upon coordination to mononuclear

* Corresponding author. Tel.: +52 771 1421144/7172000x2207; fax: +52 771 7172103.
E-mail addresses: gloriasa@uaeh.redaueh.mx, gloriasa@uaeh.edu.mx (G. Sánchez-Cabrera).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.01.032

compounds $[M(CN)_5(4\text{-pyS})]^{4-}$ (M = Ru, Fe), the 4-pyS ligand bonds through the sulfur atom. These complexes have been observed to form monolayers on gold surfaces [14].

Some studies of homometallic osmium and ruthenium clusters with ligands containing both S- and N-atoms have been carried out. The reaction of $[Os_6(CO)_{16}(NCMe)_2]$ with di-2-pyridyl disulfide gave two compounds where the S–S bond has been broken, in the compound $[Os_6(CO)_{16}(\mu_3\text{-}\eta^2\text{-}C_5H_4NS)_2]$ both fragments are coordinated to the osmium cluster through the sulfur and nitrogen atoms [15]. The reaction of $[Os_3(CO)_{12}]$ with 1-hydroxipyridine-2-thione induced cluster fragmentation to produce three mononuclear compounds [16]. The reactions of $[Ru_3(CO)_{12}]$ with 2-mercaptopyridine [17] and mercaptobenzothiazole [18] produced the clusters $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}SNC_5H_4)]$ and $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}S_2NC_7H_4)]$, respectively; in both cases a symmetric sulfur bridge is present while the nitrogen atom is bonded to the third ruthenium atom.

Mixed-metal gold clusters can be important as homogeneous catalysts [19]; it has been proposed [20] that the intrinsic polarity of heterometallic bonds can provide multifunctional activation and direct the selectivity of substrate–cluster interactions, thus, an increase in the polarity of the molecule could result in the enhancement of the catalytic activity. A recent report [21] described the use of polynuclear osmium–gold derivatives as catalysts for the oxidative carbonylation of aniline in methanol to produce carbamate with good activity and selectivity.

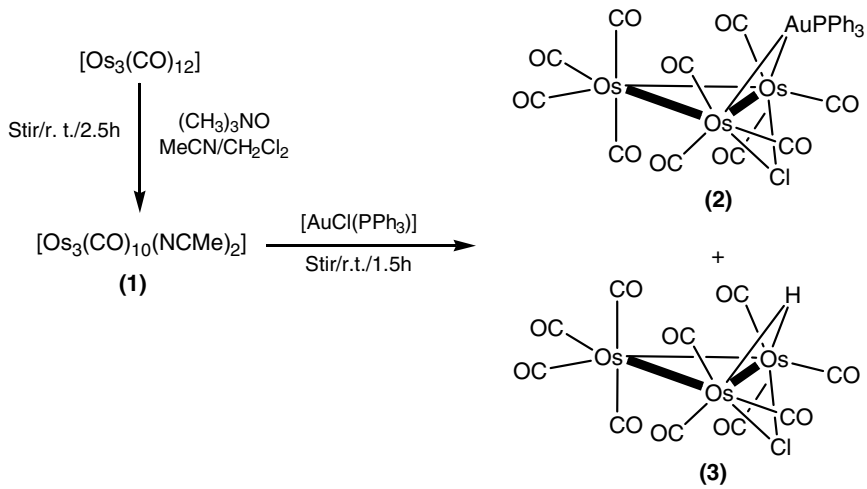
In this paper, we present the results obtained in the reactions of compounds **1** and **2** with 4-mercaptopyridine (4-pyS) and describe an alternative synthetic method to obtain **2** from $[Os_3(CO)_{10}(NCMe)_2]$ (**1**) and $[AuClPPh_3]$. The spectroscopic data of all compounds are described as well as the crystal structures of compounds **4** and **5**.

2. Results and discussion

The equimolar reaction of compound **1**, $[Os_3(CO)_{10}(NCMe)_2]$, with $[AuClPPh_3]$ at room temperature (r.t.) in dichloromethane for 24 h, leads to a mixture of two compounds. Separation by preparative thin-layer chromatography (TLC) gave as the major product, compound **2**, $[Os_3(CO)_{10}(\mu\text{-}Cl)(\mu\text{-}AuPPh_3)]$, in 41% yield. This yield was lower when compared to those reported earlier (54% [3] and 60% [4]). The other product isolated was compound **3**, $[Os_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}]$ [22,23], obtained in 5% yield. To improve yields compound **1** was prepared "in situ" and $[AuClPPh_3]$ was added at r.t. in CH_2Cl_2 for 1.5 h. The TLC separation produced $[Os_3(CO)_{10}(\mu\text{-}Cl)(\mu\text{-}AuPPh_3)]$ (**2**) in 66% yield and $[Os_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}]$ (**3**) in 7% yield (Scheme 1). To keep an excess of Me_3NO in the reaction mixture helps to promote the substitution reaction and diminishes the reaction time.

The NMR spectroscopic data obtained for **2** and **3** at room temperature are shown in Table 1. The ^1H NMR spectrum for **2** only showed signals corresponding to the phenyl ring and in the ^{31}P spectrum we observed a singlet at 82.7 ppm from the phosphine group. The ^{13}C spectrum in the carbonyl region for **2** showed six signals due to mirror symmetry in the molecule for the six different types of CO groups, Fig. 1a, five of them are singlets and we proposed that the signal at 174.0 ppm is a doublet because of coupling with ^{31}P, with a coupling constant $^3J_{^{13}C-^{31}P}$ of 10.8 Hz, which was assigned to the CO(2) in *trans* position to the Au atom. We also observed signals corresponding to the carbon atoms in the phenyl rings as doublets due to the same coupling with ^{31}P at one, two, three and four bonds, Table 1.

The ^{13}C NMR spectrum for **3** just showed six signals in the carbonyl region due to mirror symmetry in the molecule for the six different types of CO groups, Fig. 1b. The signals are shifted to lower frequencies with respect to



Scheme 1. Reaction scheme between $[Os_3(CO)_{10}(NCMe)_2]$ (**1**) and chloro(triphenylphosphine)gold(I) to obtain compounds **2** and **3**.

Table 1
^{1}H, ^{31}P and ^{13}C NMR data for **2**–**5**

Compound	^{1}H δ (ppm) J (Hz)	^{31}P δ (ppm)	^{13}C–^{1}H δ (ppm)	
			J (Hz) [$^{1}J_{^{13}C-^{1}H}$], {$^{2}J_{^{13}C-^{1}H}$}	
2	7.49 (m) (Ph)	82.7 (s)	184.4 (s) CO 183.7 (s) CO 182.5 (s) CO 180.8 (s) CO 177.8 (s) CO 174.0 (d) CO $^{3}J_{^{13}C-^{31}P} = 10.8$	134.1 (ddm) [162.2] C_m $^{3}J_{^{13}C-^{31}P} = 14.6$ 131.4 (ddm) [160.7] C_p $^{4}J_{^{13}C-^{31}P} = 2.4$ 130.1 (dt) C_i $^{1}J_{^{13}C-^{31}P} = 47.7, \{7.0\}$ 129.3 (ddd) [162.2] C_o $^{2}J_{^{13}C-^{31}P} = 10.7, \{6.2\}$
3	−14.30 (s) $^{1}J_{^{1}H-^{187}Os} = 36.8$ $^{2}J_{^{1}H-^{13}C} = 12.0$	–	181.4 (s) CO 180.9 (s) CO 175.4 (d) {2.3} CO 174.8 (s) CO 170.9 (d) {3.1} CO 170.5 (d) {12.0} CO	
4	−17.19 (s) $^{1}J_{^{1}H-^{187}Os} = 33.0$ $^{2}J_{^{1}H-^{13}C} = 11.0$ 8.51 $CH_{XX'}$ 7.19 $CH_{AA'}$ $J_{AA'} = 5.5$ $J_{XX'} = 1.3$ J_{AX}, $J_{A'X'} = 6.2$	–	180.4 CO 179.6 CO 175.6 (d) {2.3} CO 173.4 CO 171.5 (d) {2.3}CO 168.7 (d) {11.0} CO	156.1 (s) C–S 149.8 (dm) [182.7] $CH_{XX'}$ 126.1 (dm) [156.3] $CH_{AA'}$
5	7.51 (m) (Ph) 8.35 $CH_{XX'}$ 7.37 $CH_{AA'}$ $J_{AA'} = 5.5$ $J_{XX'} = 1.3$ J_{AX}, $J_{A'X'} = 6.2$	85.3 (s)	183.4 CO 182.9 CO 182.1 CO 181.6 CO 176.2 CO 172.6 (d) CO $^{3}J_{^{13}C-^{31}P} = 10.0$	156.0 (t) {7.3} C–S 149.4 (dd) [180.0] {12.3} $CH_{XX'}$ 134.0 (ddt) [162.2] C_m $^{3}J_{^{13}C-^{31}P} = 14.6, \{5.8\}$ 131.5 (dtd) [161.8] C_p {6.2}, $^{4}J_{^{13}C-^{31}P} = 2.3$ 131.2 (dt) C_i $^{1}J_{^{13}C-^{31}P} = 47.7, \{6.9\}$ 129.4 (ddd) [163.0] C_o $^{2}J_{^{13}C-^{31}P} = 10.7, \{5.8\}$ 128.1 (dd) [164.9] {9.2} $CH_{AA'}$

(s) singlet, (d) doublet, (t) triplet, (m) multiplet, *o*, *ortho*; *p*, *para*; *m*, *meta*; *i*, *ipso*.

those in compound **2**. The ^{1}H NMR spectrum for **3** exhibited a singlet at −14.30 ppm corresponding to a hydride ligand, this signal has two pairs of satellites, one as a result of coupling with ^{187}Os isotope [24,25], with a coupling constant similar to those described in other hydride-trinuclear osmium derivatives [24]. The second set of satellites is caused by the coupling with ^{13}C due to the CO groups in *trans* position, this set of satellites are unsymmetrically centered around the hydride signal. This is characteristic for an isotopomeric effect $^{n}\Delta^{13/12}$C (secondary isotope effects on the nuclear shielding of a signal) [26–28]. A positive sign on this $^{n}\Delta^{13/12}$C denote a high frequency shift with respect to the lighter isotope; therefore measuring the difference between the proton signal and each one of the satellites we can calculate the $\Delta\delta$ difference, to evaluate the isotopomeric effect $^{2}\Delta^{13/12}$C [24]. The value found for compound **3** was +5.50 ppb. This isotopomeric effect over the chemical shift of any nucleus in NMR has been related to changes in rotational and vibrational states in a compound [27]. Unfortunately these effects cannot be evaluated separately; but it is important to report these isotopomeric data in order to contribute to a better understanding of these values. The ^{1}H–^{13}C coupling was confirmed by a ^{13}C proton coupled experiment (^{13}C–^{1}H), the signal at 170.5 ppm showed coupling with the hydride ligand, with a $^{2}J_{^{13}C-^{1}H}$ of 12.0 Hz, which was assigned to the CO(2). The doublet signals at 170.9 and 175.4 ppm correspond to the CO(1) or CO(3) *cis* to the hydride ligand, Fig. 1e.

The equimolar reaction of 4-mercaptopyridine with complex **1** in dichloromethane solution afforded a mixture of products. Separation by preparative thin layer chromatography (TLC), gave $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_5H_4N)]$ (**4**) in 38% yield, 6% of starting material and two other products that we could not identify due to their low solubility (Scheme 2).

Compound **4** was characterized by the usual spectroscopic methods (Table 1). The ^{13}C NMR spectrum for **4** showed six signals in the carbonyl region corresponding to six different types of CO groups, resembling compounds **2** and **3**, Fig. 1c. The ^{1}H NMR spectrum of **4**, recorded at

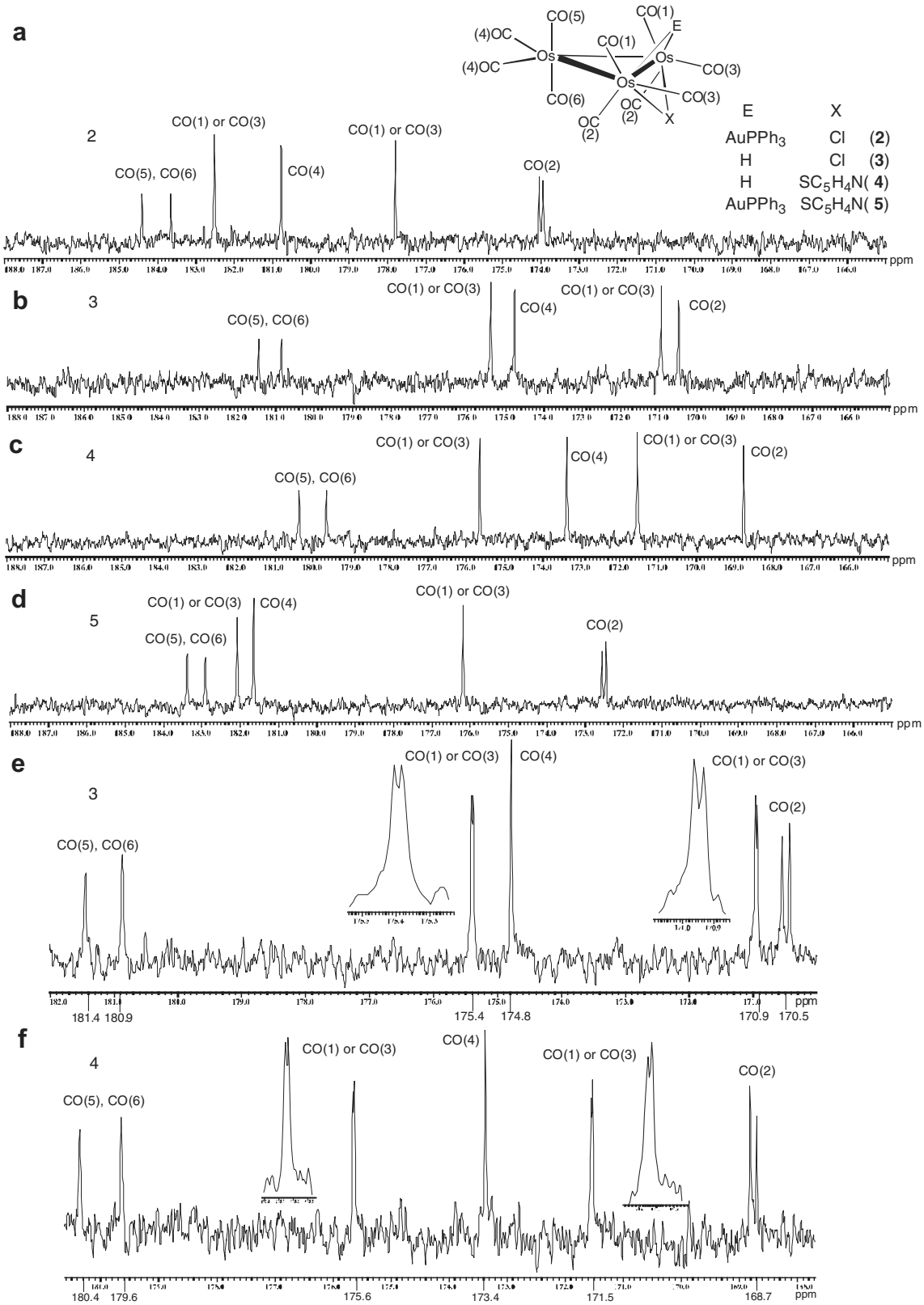
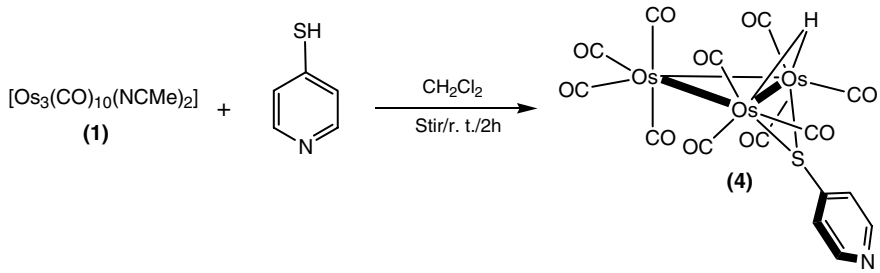


Fig. 1. (a)–(d) ^{13}C NMR and (e) and (f) ^{13}C–^{1}H NMR spectrums of compounds **2**–**5**, in the carbonyl region (in $CDCl_3$) at room temperature.

room temperature, showed a high-field singlet resonance corresponding to a hydride ligand, analogous to **3**; this signal presents two pairs of satellites due to coupling with ^{187}Os and ^{13}C to one and two bonds, respectively. The isotopomeric effect was measured, $^{2}\Delta^{13/12}C = +2.80$ ppb. In addition, the ^{13}C–^{1}H NMR spectrum of the CO groups showed coupling with the hydride ligand, the doublet signal at 168.7 ppm correspond to the CO(2) carbonyls, *trans*



Scheme 2. Reaction scheme between $[Os_3(CO)_{10}(NCMe)_2]$ (**1**) and 4-mercaptopyridine to obtain compound **4**.

to the hydride position with a $^2J_{^{13}C-^1H}$ of 11.0 Hz, doublet signals at 175.6 and 171.5 ppm correspond to the CO(1) or CO(3) *cis* to the hydride ligand, with $^2J_{^{13}C-^1H}$ of 2.3 Hz, Fig. 1f.

The ^{1}H NMR spectrum also showed two signals in the aromatic region as an AA′XX′ system due to the four pyridine hydrogen atoms. This system displays four coupling constants $J_{AA'}$, J_{AX}, $J_{A'X'}$ and $J_{XX'}$, which were determined using a simulation program [29], and full assignment was made by comparison with the literature [30]. The signal at 8.51 ppm corresponds to the H_X and $H_{X'}$ diamagnetic deshielded hydrogen atoms, closer to the nitrogen atom and the signal at 7.19 ppm correspond to the H_A and $H_{A'}$ hydrogen atoms closer to the sulfur atom. The assignment of the carbon atoms of this system was made by a 2D heteronuclear correlation experiment (HETCOR), Table 1.

A single crystal X-ray diffraction study of **4** was carried out to confirm the solid state structure. An ORTEP diagram of the structure is shown in Fig. 2 and some selected bond lengths (Å) and bond and dihedral angles (°) are shown in Table 2. There are two molecules of **4** in the asymmetric unit. The structure has an approximate C_s symmetry and consists of a trigonal array of 3 metallic atoms with the Os(1)–Os(2) bond bridged both by the 4-mercaptopyridine ligand through the sulfur atom and by a hydride ligand. The bridging hydride, which was observed in the ^{1}H NMR spectrum, could not be located in the X-ray diffraction study, however, its position was calculated [31] and the results suggest that it bridges the Os(1)–Os(3) bond. This is also supported by the fact that this M–M bond is slightly longer than the other two. In general, Os–Os distances have shorter values than those reported for $[Os_3(CO)_{12}]$ [32,33]. The pyridine ring is oriented in a semi-parallel fashion to the metal ring, with an angle of 158.8(2)° for molecule 1 and 153.8(3)° for molecule 2. The CO ligands *trans* to the sulfur atom are in pseudo-axial positions according to their bond angles, Table 2.

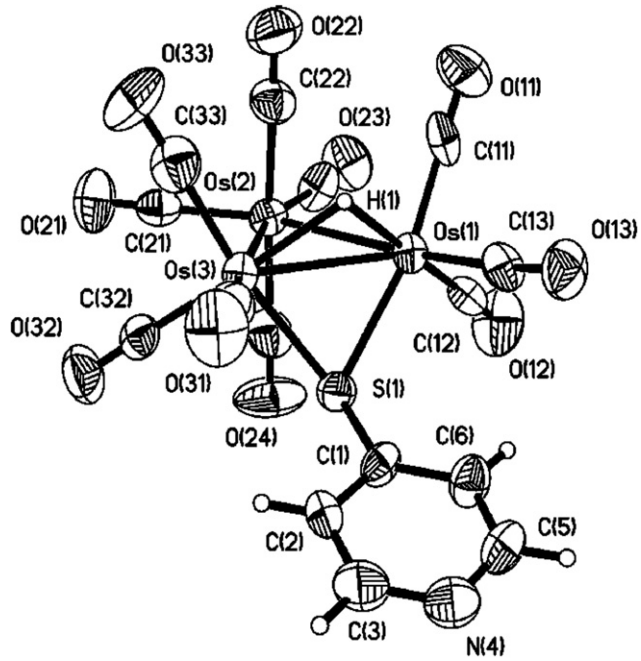


Fig. 2. Molecular structure of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_5H_4N)]$ (**4**). Thermal ellipsoids shown at 50% probability.

The angles made by the Os(1)–Os(2)–Os(3)/Os(1)–Os(3)–S(1) and Os(4)–Os(5)–Os(6)/Os(4)–Os(6)–S(2) planes are 103.5(1)° and 101.8(1)°, respectively. These values are smaller than the angle formed by the planes Os(1)–Os(2)–Os(3) and Os(1)–Os(2)–Cl(1) 110.0° reported for **2** [4], probably due to a less repulsion between the electron pairs of the sulfur and oxygen atoms than between the chlorine and oxygen atoms.

The reaction of **2** with a small excess of 4-mercaptopyridine in refluxing dichloromethane for 2 h afforded compounds $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_5H_4N)]$ (**4**) and $[Os_3(CO)_{10}(\mu\text{-}AuPPh_3)(\mu\text{-}SC_5H_4N)]$ (**5**). Separation by preparative TLC, gave **4** and **5** in 24% and 19% yields, respectively, 26% of starting material and two other unstable products that we have not been able to identify due to their low stability (Scheme 3). The compounds isolated from the reaction of **2** with the mercaptopyridine, indicate that two different reactions took place; in one, the chlorine atom was substituted by the gold fragment while in the other one, an isolobal replacement took place, with the $[AuPPh_3]^+$ fragment being substituted by a proton, presumably coming from the rupture of the H–S bond.

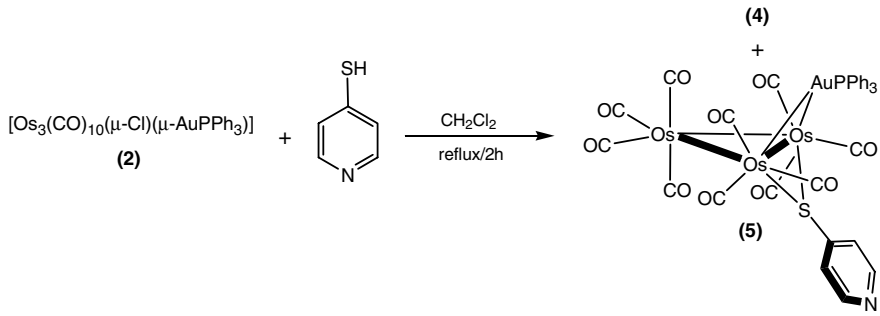
In order to have an alternative synthetic route of compound **5** and using the isolobal principle, we carried out the equimolar reaction of compound **4** with $[AuClPPh_3]$ in refluxing dichloromethane for 2 h and we obtained **5** in 50% yield. Thermolysis of compound **5** in refluxing toluene for 1 h leads to the formation of compound **4** in 45% yield.

Table 2
Selected bond lengths (Å) and bond and dihedral angles (°) for **4** and **5**

Bond lengths (Å)		Bond angles (°)	
*Compound **4***			
Molecule 1			
Os(1)–S(1)	2.413(3)	Os(3)–Os(2)–Os(1)	60.25(3)
Os(3)–S(1)	2.424(3)	Os(2)–Os(3)–Os(1)	59.95(3)
Os(1)–Os(2)	2.8603(9)	Os(2)–Os(1)–Os(3)	59.80(2)
Os(2)–Os(3)	2.8558(8)	Os(1)–S(1)–Os(3)	72.75(8)
Os(1)–Os(3)	2.869(1)	C(11)–Os(1)–S(1)	167.7(3)
C(11)–Os(1)	1.88(2)	C(33)–Os(3)–S(1)	168.7(4)
C(12)–Os(1)	1.91(1)	Dihedral angles (°)	
C(13)–Os(1)	1.92(1)	Os(1)–Os(2)–Os(3)/	103.5(1)
C(31)–Os(3)	1.93(1)	Os(1)–Os(3)–S(1)	
C(32)–Os(3)	1.93(1)	Os(1)–Os(2)–Os(3)/	
C(33)–Os(3)	1.90(2)	C(1)–C(2)–C(3)–N(4)–C(5)–C(6)	158.8(2)
Molecule 2			
Os(4)–S(2)	2.414(3)	Os(6)–Os(5)–Os(4)	60.20(3)
Os(6)–S(2)	2.420(3)	Os(5)–Os(6)–Os(4)	59.92(3)
Os(4)–Os(5)	2.8590(8)	Os(5)–Os(4)–Os(6)	59.88(2)
Os(5)–Os(6)	2.8599(9)	Os(4)–S(2)–Os(6)	72.79(9)
Os(4)–Os(6)	2.868(1)	C(41)–Os(4)–S(2)	167.5(3)
C(41)–Os(4)	1.88(1)	C(62)–Os(6)–S(2)	167.1(4)
C(43)–Os(4)	1.93(1)	Dihedral angles (°)	
C(44)–Os(4)	1.91(1)	Os(4)–Os(5)–Os(6)/	101.8(1)
C(61)–Os(6)	1.93(1)	Os(4)–Os(6)–S(2)	
C(62)–Os(6)	1.90(1)	Os(4)–Os(5)–Os(6)/	
C(63)–Os(6)	1.88(1)	C(71)–C(72)–C(73)–N(2)–C(75)–C(76)	153.8(3)
Bond lengths (Å)		**Bond angles (°)**	
*Compound **5***			
Au(1)–P(1)	2.309(4)	Os(3)–Os(2)–Os(1)	60.78(2)
Au(1)–Os(1)	2.7755(8)	Os(2)–Os(3)–Os(1)	59.83(2)
Au(1)–Os(3)	2.7744(7)	Os(2)–Os(1)–Os(3)	59.39(2)
Os(1)–S(1)	2.420(3)	Os(1)–S(1)–Os(3)	73.6(1)
Os(3)–S(1)	2.411(3)	S(1)–Os(1)–Au(1)	94.81(9)
Os(1)–Os(2)	2.8658(7)	S(1)–Os(3)–Au(1)	95.03(8)
Os(2)–Os(3)	2.8531(8)	P(1)–Au(1)–Os(1)	150.59(9)
Os(1)–Os(3)	2.8932(8)	P(1)–Au(1)–Os(3)	146.50(9)
C(11)–Os(1)	1.89(2)	Os(1)–Au(1)–Os(3)	62.84(2)
C(12)–Os(1)	1.88(2)	C(13)–Os(1)–S(1)	169.2(5)
C(13)–Os(1)	1.89(2)	C(33)–Os(3)–S(1)	167.1(5)
C(31)–Os(3)	1.93(2)	C(11)–Os(1)–Au(1)	167.9(4)
C(32)–Os(3)	1.90(1)	C(32)–Os(3)–Au(1)	170.7(4)
C(33)–Os(3)	1.89(1)	Dihedral angles (°)	
		Os(2)–Os(3)–Os(1)/	
		Os(1)–Os(3)–Au(1)	128.99(2)
		Os(2)–Os(3)–Os(1)/	
		Os(1)–Os(3)–S(1)	105.4(1)
		Os(1)–Os(2)–Os(3)/	
		C(1)–C(2)–C(3)–N(1)–C(4)–C(5)	93.2(4)

The spectroscopic data of compound **5** are described in Table 1. The ^{1}H NMR spectrum for **4** showed the signals corresponding to the phenyl ring and two signals in the aromatic region as an AA′XX′ system due to the four pyridine hydrogen atoms. This system displays four coupling constant $J_{AA'}$, J_{AX}, $J_{A'X'}$ and $J_{XX'}$, similar to the one observed for compound **4**, the signal at 8.35 ppm corresponds to the H_X and $H_{X'}$ hydrogen atoms and the signal at 7.37 ppm corresponds to the H_A and $H_{A'}$ hydrogen atoms. The ^{31}P NMR spectrum showed a singlet at 85.3 ppm from the phosphine group.

The ^{13}C NMR spectrum in the carbonyl region for **5** showed six signals corresponding to six different types of CO groups, similar to compound **2**, five of them are singlets and the signal at 172.6 ppm is a doublet because of coupling with ^{31}P, with a $^{3}J_{^{13}C–^{31}P}$ of 10.0 Hz, which was assigned to the CO(2) in *trans* position to the Au atom, Fig. 1d. All carbon signals corresponding to the phenyl rings are doublets due to ^{31}P coupling at one, two, three and four bond distances. An HETCOR experiment allowed us to assign the carbon atoms of the AA′XX′ system (Table 1). We were able to assign the signals corre-



Scheme 3. Reaction scheme between $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)]$ (**2**) and 4-mercaptopyridine to obtain compounds **4** and **5**.

sponding to CO(2), CO(1) and CO(3) because of their ^{1}H coupling.

A comparison of the ^{13}C spectra of compounds **2** to **5** in the CO region showed that compounds **2** and **5** have a similar displacement pattern while the corresponding pattern of **3** is similar to that of **4**. The CO's chemical shifts for the two gold derivatives (**2** and **5**), Fig. 1a and d, are found at higher frequencies than in the hydride derivatives (**3** and **4**), Fig. 1b and c. We presume that this is caused by a diamagnetic deshielding effect of the gold atom over the carbon atoms.

We carried out an X-ray diffraction study on a single crystal of **5**. Selected bond lengths (Å), bond and dihedral angles (°) for **5** are shown in Table 2 and Fig. 3 shows an ORTEP diagram of this compound. The structure has an approximate C_s symmetry and consists of a "butterfly" array of the metal atoms, with the gold in a wing-tip position of the butterfly. Both the SC_5H_4N and $AuPPh_3$ fragments are bridging the Os(1)–Os(3) bond and this is the longest Os–Os distance in the triangle.

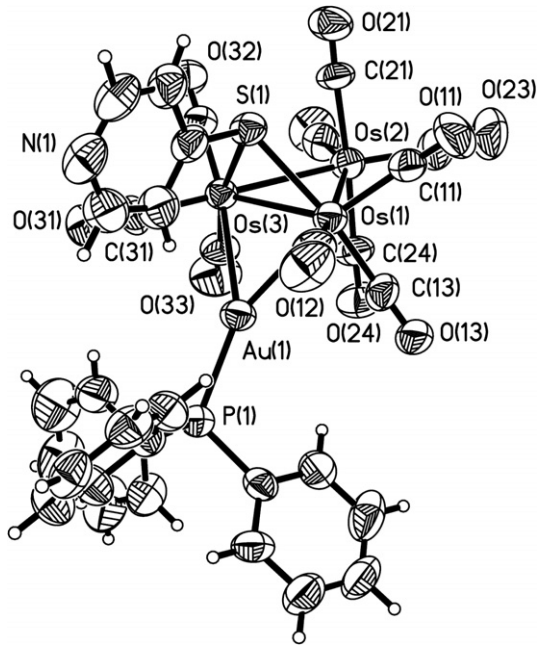


Fig. 3. Molecular structure of $[Os_3(CO)_{10}(\mu\text{-AuPPh}_3)(\mu\text{-SC}_5H_4N)]$ (**5**). Thermal ellipsoids shown at 50% probability.

It has been observed [23], that in molecules with a similar skeleton like $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-X})]$, X = H, CHCH=NEt$_2$, CHCH$_2PMe_2$Ph, AuPPh$_3$ [5], the Os–Os bridged bond is shorter than the nonbridged Os–Os bonds, meanwhile, in compounds of the type $[Os_3(CO)_{10}(\mu\text{-E})(\mu\text{-X})]$, E = AuPPh$_3$, X = Cl (**2**) [4], E = H, X = Cl (**3**) [23], E = H, X = SEt [34], the bridged bond is slightly longer than the other two. This last behavior is similar to the one found in compounds **4** and **5**. The bridged bond corresponding to compound **5** is the largest, probably due to the size of bridging substituents. The Os–Au bond distances in compound **5** are slightly longer than those reported for compound **2** [4] probably due to the steric effect cause by the pyridine ring. No short non-bonding distances were found in compounds **4** and **5** precluding the possible existence of an interaction of the pyridine nitrogen atom with any other atom.

The dihedral angle formed by the planes Os(2)–Os(3)–Os(1) and Os(1)–Os(3)–Au(1) of 128.99(2)° in compound **5** is bigger than the same angle in compounds $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)]$ **2** (120.8°) [4], $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-AuPPh}_3)]$ (109.8°) [5], $[Os_4(CO)_{11}(\mu\text{-H})_3(\mu\text{-AuPPh}_3)(NMe_3)]$ (120.2°) [21] and $[Os_4(CO)_{12}(\mu\text{-H})_3(\mu\text{-AuPPh}_3)]$ (109.5°) [21]. This suggests that the bridging bulky substituents in **5**, force the metal planes to adopt a wider angle between them in comparison to its analogous compound **2** and other similar compounds. The dihedral angle formed by the planes Os(2)–Os(3)–Os(1) and Os(1)–Os(3)–S(1) of 105.4(1)° in compound **5** have an intermediate value to those found in compounds **2** (110.0°) [4] and **4**. The pyridine ring is pointing out of the Os triangle in a perpendicular fashion to the Os_3 ring, with an angle between the rings of 93.2(4)°. The CO ligands *trans* to the sulfur and gold bridging atoms are in pseudo-axial positions according to their bond angles, Table 2.

The *trans* influence caused by the chlorine atom in compound **2**, seems to remain when the chlorine is exchanged by the sulfur atom provided by the 4-mercaptopyridine ligand in compound **4**. The Os–C distances *trans* to either chlorine or sulfur in both **2** and **4**, are similar [4]. However, the effect is less clear in **5** because there are other M–C dis-

tances that are shorter than those almost *trans* to the sulfur atom.

3. Conclusions

The reaction between $[Os_3(CO)_{10}(NCMe)_2]$ (**1**) and $[AuClPPh_3]$ under the mildest condition reported gave the substitution product $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)]$ (**2**) and its isolobal analog $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-H})]$ (**3**). The reaction of compound **2** with 4-mercaptopyridine gave the isolobal products $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-SC}_5H_4N)]$ (**4**) and $[Os_3(CO)_{10}(\mu\text{-AuPPh}_3)(\mu\text{-SC}_5H_4N)]$ (**5**). Compound **5** can also be obtained from **4** with $[AuClPPh_3]$ and compound **4** can be produced from the reaction of bisacetonitrile triosmium derivative **1** with 4-pyS. We proved that compound **5** can be converted into **4** under thermal conditions. These results indicate that the affinity of sulfur to form μ_2-bridges between osmium atoms, avoids a possible interaction between the sulfur and gold atoms.

4. Experimental

4.1. General procedures and materials

All reactions were carried out under nitrogen atmosphere. Commercial TLC plates (silica gel 60 F254, Merck Co.) were used to monitor the progress of the reaction. All chemicals were supplied by Aldrich Company except chloro(triphenylphosphine)gold(I) which was supplied by Strem Chemicals and used without further purifications. Solvents were dried prior to use by standard techniques and trimethylamine *N*-oxide dihydrate was sublimed several times in high-vacuum to remove water. All infrared spectra were recorded in a GX Perkin–Elmer FT-IR system spectrometer; compounds were applied as a solution in chloroform in a CsI window and let them to dry to acquire the spectrum as a solid thin film. NMR spectra were obtained using a JEOL Eclipse 400 spectrometer, with ^1H and ^{13}C spectra relative to $SiMe_4$, and ^{31}P spectra relative to 85% aq. H_3PO_4. All spectra were obtained in $CDCl_3$. Elemental analyses were obtained in a Perkin–Elmer series II Analyzer 2400 and ThermoFinnigan Model Flash 1112 equipments. Melting points were taken in a Büchi B-250 fusiometer and reported without correction.

4.2. Synthesis of compounds $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)]$ (2) and $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-H})]$ (3)

A solution of dry Me_3NO (5.7 mg, 0.076 mmol) in acetonitrile (4 mL) was added dropwise to a solution of $[Os_3(CO)_{12}]$ (30 mg, 0.033 mmol) in dichloromethane (10 mL) over a period of 15 min. After stirring for 2.5 h, complete conversion of $[Os_3(CO)_{12}]$ into $[Os_3(CO)_{10}(MeCN)_2]$ (**1**) (30.8 mg, 0.033 mmol) had occurred (TLC control). The compound $[AuClPPh_3]$ (15.7 mg, 0.032 mmol) was then added "in situ" to the solution of $[Os_3(CO)_{10}(NCMe)_2]$ (**1**) and stirred at r.t. for 1.5 h. The solvent was removed under reduced pressure, the solid residue was redissolved in $CHCl_3$ (2 mL) and it was separated by preparative TLC on silica gel. Elution with hexane/chloroform (1:1) afforded four bands. The first band (yellow) was identified as compound **3**, $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-H})]$ (2.0 mg, 7%), a second band (red) was identified as compound **2**, $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)]$ (29.3 mg, 66%). A third (colorless) and fourth (yellow) bands could not be identified.

Analytical and spectroscopic data for compound 2: $C_{28}H_{15}O_{10}ClPAuOs_3$ (1345.50): Microanalysis: Calc. for **2**: C, 24.99; H, 1.22. Found: C, 25.85; H, 1.12% [35]. Melting point: 134 °C (dec). IR ν(CO): 2095 (m), 2040 (vs), 2008 (vs), 1980 (s), 1961 (s) cm^{-1}.

Analytical and spectroscopic data for compound 3: $C_{10}HO_{10}ClOs_3$ (887.25). Microanalysis: Calc. for **3**: C, 13.54; H, 0.11. Found: C, 14.59; H, 0.36% [35]. Melting point: 156.2–158.0 °C. IR ν(CO): 2116 (m), 2076 (vs), 2067 (vs), 2018 (vs, br), 1980 (s) cm^{-1}.

4.3. Synthesis of compounds $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-SC}_5H_4N)]$ (4) and $[Os_3(CO)_{10}(\mu\text{-AuPPh}_3)(\mu\text{-SC}_5H_4N)]$ (5)

4.3.1. Using $[Os_3(CO)_{10}(NCMe)_2]$ (1) as starting material

A similar procedure as describe before was used to prepare the compound **1**. A solid 4-mercaptopyridine (3.7 mg, 0.033 mmol) was added "in situ" to the solution of $[Os_3(CO)_{10}(NCMe)_2]$ (**1**) (30.8 mg, 0.033 mmol) and stirred at r.t. for 2 h. The reaction mixture was evaporated to dryness under reduced pressure, the dry residue was redissolved in $CHCl_3$ (2 mL) and it was separated by preparative TLC on silica gel. Elution with hexane/chloroform (1:1) afforded four bands. The first band (yellow) afforded compound $[Os_3(CO)_{10}(NCMe)_2]$ (**1**) (1.4 mg, 6%), a second band (yellow) was identified as compound $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-SC}_5H_4N)]$ (**4**). (12.1 mg, 38%), a third and fourth bands (yellow) corresponding to unidentified compounds were discarded.

4.3.2. Using $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)]$ (2) as starting material

The reaction of $[Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)]$ (**2**) (10 mg, 0.007 mmol) and 4-mercaptopyridine (1.2 mg, 0.011 mmol) in 15 mL of refluxing dichlormethane for 2 h. gave a mixture of compounds. The reaction mixture was dried under vacuum and the residue was redissolved in $CHCl_3$ (2 mL) and it was separated by preparative TLC plates using hexane/chloroform (1:1) as eluent. The first band was identified as compound **2** (2.6 mg, 26%), a second band (orange) contained the compounds **4** and **5**, a third and fourth bands (orange), corresponding to unidentified compounds, were discarded. The second band was separated once more by preparative TLC plates using hexane/chloroform (95:5) as eluent. After repeated chromatography the mixture was separated into two bands,

the first band (yellow) was identified as compound $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_5H_4N)]$ (**4**) (1.7 mg, 24%) and the second band (orange) was identified as compound $[Os_3(CO)_{10}(\mu\text{-}AuPPh_3)(\mu\text{-}SC_5H_4N)]$ (**5**) (2.0 mg, 19%).

4.3.3. Using $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_5H_4N)]$ (4) as starting material

Compounds $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_5H_4N)]$ (**4**) (10 mg, 0.010 mmol) and $[AuClPPh_3]$ (5.1 mg, 0.010 mmol) were dissolved in CH_2Cl_2 and heated to reflux for 2 h. The solvent was reduced (2 mL) under vacuum, and it was separated by preparative TLC on silica gel using hexane/chloroform (95:5) as eluent. After repeated chromatography the mixture was separated into two bands, the first band (yellow) was identified as compound $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_5H_4N)]$ (**4**) (5 mg, 50%) and the second band (orange) was identified as compound $[Os_3(CO)_{10}(\mu\text{-}AuPPh_3)(\mu\text{-}SC_5H_4N)]$ (**5**) (7.4 mg, 50%).

4.3.4. Thermolysis of $[Os_3(CO)_{10}(\mu\text{-}AuPPh_3)(\mu\text{-}SC_5H_4N)]$ (5)

The compound $[Os_3(CO)_{10}(\mu\text{-}AuPPh_3)(\mu\text{-}SC_5H_4N)]$ (**5**) (8 mg, 0.006 mmol) was dissolved in 10 mL of toluene and heated to reflux for 1 h. The solvent was removed under reduced pressure and similar procedure of separation to the one describe in 4.3.3 was followed. The two bands obtained afforded compounds yellow **4** (2.4 mg, 45%) and red **5** (3.0 mg, 38%).

Analytical and spectroscopic data for compound **4**: $C_{15}H_5O_{10}NSOs_3$ (961.96): Microanalysis: Calc. for **4**: C, 18.73; H, 0.52; N, 1.46. Found: C, 22.70; H, 0.92; N, 1.35% [35]. Melting point: 153.6–155.6 °C. IR ν(CO): 2111 (m), 2060 (s), 2003 (s, br), 1973 (s, br) cm^{-1}.

Analytical and spectroscopic data for compound **5**: $C_{33}H_{19}O_{10}NSPAuOs_3$ (1420.21): Microanalysis: Calc. for **5**: C, 26.73; H, 1.29; N, 0.94. Found: C, 28.85; H, 1.70; N, 0.99% [35]. Melting point: 174 °C dec. IR ν(CO): 2093 (m), 2070 (w), 2035 (vs), 2005 (vs), 1971 (sh, s), 1960 (s, br) cm^{-1}.

5. Crystallography

Suitable crystals of **4** and **5** were obtained by slow evaporation of $CHCl_3$/hexane and hexane solution, respectively, at low temperature (5 °C) for several days. Relevant crystallographic data for **4** and **5** are summarized in Table 3. The crystals of compounds **4** and **5** were a yellow light flake with $0.05 \times 0.04 \times 0.02$ mm dimensions and a red prism with $0.41 \times 0.23 \times 0.23$ mm dimensions, respectively. Data were collected in an Enraf-Nonius Kappa CCD area detection diffractometer using Mo Kα radiation. The samples were mounted on a glass fiber. The structures were solved by direct methods (DIRDIF-99) [36] using Fourier differences maps and refined by full-matrix least-squares on F^2methodology with SHELXS-97 [37]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms from aromatic groups were fixed in idealized positions and included in the refinement with fixed coordinates. The hydride ligand position in **4** was calculated using the XHYDEX program [31]. The weighting scheme employed for both compounds was $w = (\sigma^2 F_o^2 + (P)^2 + P)^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. All crystallographic programs were used under WINGX program [38].

Table 3
Crystal data and structure refinement parameters for **4** and **5**

Compound	**4**	**5**
Empirical formula	$C_{15}H_5NO_{10}Os_3S$	$C_{33}H_{19}AuNO_{10}Os_3PS$
Formula weight	961.86	1420.09
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions		
a (Å)	9.513(2)	9.2326(1)
b (Å)	27.293(5)	12.1077(1)
c (Å)	16.249(3)	33.5452(4)
α (°)	90.00	90.00
β (°)	95.70(3)	97.652(1)
γ (°)	90.00	90.00
V (Å^3)	4198(1)	3716.48(7)
Z	8	4
ρ_{calc} (Mg/m^{-3})	3.044	2.538
λ (Mo Kα) (Å)	0.71073	0.71073
μ (Mo Kα) (mm^{-1})	18.265	14.312
Scan type	ω–ϕ	$\omega/2\theta$
2θ Range (°)	8.26–54.96	8.26–55.08
Index ranges (h_{min}/h_{max}, k_{min}/k_{max}, l_{min}/l_{max})	−12/11, −35/35, −21/18	−11/11, −15/15, −43/43
Reflections collected	32087	30287
Independent reflections (R_{int})	9553 (0.0128)	8419 (0.0955)
Observed reflections [$F > 4\sigma(F)$]	5568	5505
Final R indices [$F > 4\sigma(F)$]	$R_1 = 0.0473$, $wR_2 = 0.0756$	$R_1 = 0.0615$, $wR_2 = 0.1495$
R indices (all data)	$R_1 = 0.1140$, $wR_2 = 0.0901$	$R_1 = 0.0970$, $wR_2 = 0.1697$
Goodness-of-fit on F^2	0.990	1.032
Largest difference peak/hole (e Å^{-3})	1.866/−1.727	2.162/−2.222

Acknowledgements

The present work was supported through a grant by PROMEP-UAEH-UAEHGO-PTC-256. We also want to thanks to Ana L. Carrasco for her invaluable assistance.

Appendix A. Supplementary material

CCDC 618742 and 618743 contain the supplementary crystallographic data for **4** and **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.01.032.

References

[1] I.D. Salter, in: F.G.A. Stone, R. West (Eds.), Advances in Organometallic Chemistry, vol. 29, Academic Press, London, 1989, p. 249, and references therein.

[2] I.D. Salter, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry II, vol. 10, Pergamon Press, Oxford, 1995, p. 255, and references therein.

[3] C.W. Bradford, W. van Bronswijk, R.J.H. Clark, R.S. Nyholm, J. Chem. Soc. A (1970) 2889.

[4] C.M. Hay, N.E. Leadbeater, J. Lewis, P.R. Raithby, K. Burgess, New J. Chem. 22 (1998) 787.

[5] B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby, J. Organomet. Chem. 215 (1981) C33.

[6] K. Burgess, B.F.G. Johnson, J. Lewis, J. Organomet. Chem. 247 (1983) C42.

[7] A.J. Deeming, S. Donovan-Mtunzi, K. Hardcastle, J. Chem. Soc., Dalton Trans. (1986) 543.

[8] K. Burgess, B.F.G. Johnson, J. Lewis, P.R. Raithby, J. Chem. Soc., Dalton Trans. (1983) 1661.

[9] J.A. Cabeza, V. Riera, R. Trivedi, F. Grepioni, Organometallics 19 (2000) 2043.

[10] M.I. Bruce, P.A. Humprhey, B.W. Skelton, A.H. White, J. Organomet. Chem. 689 (2004) 2558.

[11] K. Burgess, B.F.G. Johnson, D.A. Kaner, J. Lewis, P. Raithby, S.N. Azman, B. Syed-Mustaffa, J. Chem. Soc., Chem. Commun. (1983) 455.

[12] K. Burgess, B.F.G. Johnson, J. Lewis, J. Chem. Soc., Dalton Trans. (1983) 1179.

[13] S. Muthu, J.J. Vittal, Cryst. Growth Design 4 (2004) 1181.

[14] I.C. Nogueira Diógenes, J. Rodrigues de Sousa, I.M. Moreira de Carvalho, M.L. Arruda Temperini, A.A. Tanaka, I. de Sousa Moreira, J. Chem. Soc., Dalton Trans. (2003) 2231.

[15] K.S.-Y. Leung, W.-T. Wong, J. Chem. Soc., Dalton Trans. (1999) 2521.

[16] F.-Y. Lee, J.-J. Huang, Y.-J. Chen, K.-J. Lin, G.-H. Lee, S.-M. Peng, J.R. Hwu, K.-L. Lu, J. Organomet. Chem. (2005) 441.

[17] A.J. Deeming, K.I. Hardcastle, M. Karim, Inorg. Chem. 31 (1992) 4792.

[18] S. Jeannin, Y. Jeannin, G. Lavigne, Inorg. Chem. 17 (1978) 2103.

[19] Y. Li, W.-X. Pan, W.-T. Wong, J. Cluster Sci. 13 (2002) 223.

[20] P. Braunstein, J. Rosé, in: P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Metal Cluster in Chemistry, vol. II, Wiley–VCH, Germany, 1999, p. 616.

[21] Y. Li, W.-T. Wong, Eur. J. Inorg. Chem. (2003) 2651.

[22] A.J. Deeming, S. Hasso, J. Organomet. Chem. 114 (1976) 313–324.

[23] M.R. Churchill, R.A. Lashewycz, Inorg. Chem. 18 (1979) 1926.

[24] E.C. Constable, B.F.G. Johnson, J. Lewis, G.N. Pain, M.J. Taylor, J. Chem. Soc., Chem. Commun. 13 (1982) 754.

[25] J.S. Holmgren, J.R. Shapley, P.A. Belmonte, J. Organomet. Chem. 284 (1985) C5.

[26] C.J. Jameson, J. Chem. Phys. 66 (1977) 4983.

[27] S. Kerschl, A. Sebald, B. Wrackmeyer, Magn. Reson. Chem. 23 (1985) 514.

[28] F.J. Zuno-Cruz, A.L. Carrasco, M.J. Rosales, Polyhedron 21 (2002) 1105.

[29] H.M. Bell, FT-NMR Simulation, Chemistry Department, Virginia Tech., Blacksburg, VA, 2003.

[30] J.B. Lambert, H.F. Shurvell, D.A. Lightner, R. Grahan, Organic Structural Spectroscopy, Prentice-Hall, Englewood Cliffs, NJ, 1998, p. 568.

[31] A.G. Orpen, J. Chem. Soc., Dalton Trans. (1980) 2509.

[32] M.R. Churchill, B.G. DeBoer, Inorg. Chem. 16 (1977) 878.

[33] E.R. Corey, L.F. Dahl, Inorg. Chem. 1 (1962) 521.

[34] V.F. Allen, R. Mason, P.B. Hitchcock, J. Organomet. Chem. 140 (1977) 297.

[35] *Note*: We propose that high errors associated in the elemental analysis measurements could be due to the intrinsic properties of these compounds, which probably decomposed during the performance of the experiments, since we measure several times the microanalysis in two different equipments after several purifications having the same results.

[36] P.T. Beurskens, G. Beurskens, R. de Gelder, S. Garcia-Granada, R. Israel, R.O. Gould, J.M.M. Smits, DIRDIF-99 Program System, Crystallography Laboratory, Univeristy of Ninjmegen, The Netherlands, 1999.

[37] G.M. Sheldrick, SHELX97: Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Göttingen, Germany, 1997.

[38] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.