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Reaction between the thiocarbonyl complex, $Os(CS)(CO)(PPh_3)_3$, and propyne: crystal structure of a new sulfur-substituted osmabenzene

Clifton E.F. Rickard, Warren R. Roper*[1], Scott D. Woodgate, L. James Wright*[2]

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand

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Abstract

Reaction between $Os(CS)(CO)(PPh_3)_3$ and propyne gives a complex mixture of products from which can be isolated the simple oxidative addition product $Os(C{\equiv}CMe)H(CS)(CO)(PPh_3)_2$ (**1**) and the osmabenzene $\overline{Os(\eta^2\text{-}C[S]CMeCHCHC}Me)(CO)(PPh_3)_2$ (**2**), where the two propyne molecules in the osmabenzene ring have linked tail-to-tail. Treatment of **1** with HCl gives, as the ultimate product, the propenylthioacyl complex, $Os(\eta^2\text{-}C[S]CH{=}CHMe)Cl(CO)(PPh_3)_2$ (**3**). The crystal structures of compounds **1**–**3** have been determined. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydride complex; Osmabenzene; Osmium; Propynyl complex

1. Introduction

The first metallabenzenes were prepared by reaction between $Os(CS)(CO)(PPh_3)_3$ [1] and ethyne [2]. Interest continues in this remarkable class of compounds with the development of alternative synthetic routes [3] and the recent demonstration that the osmabenzene compounds exhibit the defining chemical characteristic of 'aromatic' systems in that they undergo the electrophilic aromatic substitution reactions of nitration and halogenation [4]. We have already reported that reaction between $Os(CS)(CO)(PPh_3)_3$ and diphenylacetylene produces osmacyclobutadiene complexes [5]. In this paper we further extend the original synthetic route by exploring the reaction between $Os(CS)(CO)(PPh_3)_3$ and propyne. A new 3,6-dimethyl-substituted osmabenzene has been characterised, albeit in low yield, along with the simple propynyl oxidative addition product, $Os(C{\equiv}CMe)H(CS)(CO)(PPh_3)_2$. Further reaction of this propynyl complex with HCl produced the propenylthioacyl complex, $Os(\eta^2\text{-}C[S]CH{=}CHMe)Cl(CO)(PPh_3)_2$ (**3**) and all three new compounds have been characterised by crystal structure determinations.

2. Results and discussion

*2.1. Preparation and spectroscopic characterisation of $Os(C{\equiv}CMe)H(CS)(CO)(PPh_3)_2$ (**1**) and $\overline{Os(\eta^2\text{-}C[S]CMeCHCHC}Me)(CO)(PPh_3)_2$ (**2**) from reaction between $Os(CS)(CO)(PPh_3)_3$ and propyne*

Propyne was passed through a solution of $Os(CS)(CO)(PPh_3)_3$ in benzene giving ultimately a dark red–brown solution. From this was isolated a crude solid showing at least three $\nu(CO)$ bands in the IR spectrum, suggesting that a number of products had been formed. To separate these complexes the mixture was subjected to column chromatography on silica gel. Two new osmium complexes were isolated, $Os(C{\equiv}CMe)H(CS)(CO)(PPh_3)_2$ (**1**) (in 23% yield) and $\overline{Os(\eta^2\text{-}C[S]CMeCHCHC}Me)(CO)(PPh_3)_2$ (**2**) (in 8% yield) (see Scheme 1). Complex **1** clearly arises from simple oxidative addition of propyne to $Os(CS)(CO)(PPh_3)_3$. The IR spectrum of **1**, which is the major product and pink in colour, reveals a very high $\nu(CO)$

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[1] *Corresponding author. Tel.: +64-9-373 7999 ext. 8320; fax: +64-9-373 7422; w.roper@auckland.ac.nz

[2] *Corresponding author.

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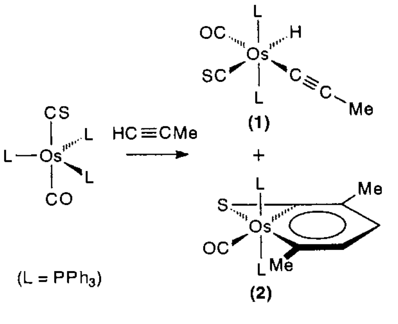
at 2009 cm^{-1}, a feature previously observed in mixed carbonyl, thiocarbonyl osmium(II) complexes [6]. The hydride resonance in the ^1H-NMR spectrum of **1** appears as a high-field triplet at -8.61 ppm ($^2J_{HP} = 21.2$ Hz) with coupling to two equivalent phosphorus nuclei. The protons of the methyl group are also observed as a triplet at 1.36 ppm ($^5J_{HP} = 2.5$ Hz), from long-range coupling to phosphorus. Other spectroscopic data are presented in the Section 4 for all the new compounds.

Complex **2**, the second product isolated from the chromatography described above, was a dark-brown crystalline solid that proved to be the 3,6-dimethyl-substituted osmabenzene, $\overline{Os(\eta^2\text{-}C[S]CMeCHCHC}Me)(CO)(PPh_3)_2$. The IR spectrum of this complex has a $\nu(CO)$ absorption at 1888 cm^{-1}, a position close to that observed for the parent, unsubstituted osmabenzene, $\overline{Os(\eta^2\text{-}C[S]CHCHCHC}H)(CO)(PPh_3)_2$ at 1890 cm^{-1} [2]. The NMR spectroscopic characterisation of this complex involved acquiring ^1H, ^{13}C, as well as ^{13}C–^1H-HMQC and ^{13}C–^1H-HMBC spectra. The spectroscopic data are all consistent with the formulation as a metallabenzene with methyl groups on C3 and C6 only (see Fig. 2 for the metallabenzene ring atom numbering scheme). The carbon and hydrogen atoms of the methyl groups are labeled C3′ and H3′ for the methyl group attached to C3, and C6′ and H6′ for the methyl group attached to C6. The ^1H-NMR spectrum shows a singlet resonance at 1.64 ppm with an integral of three protons that is assigned to H3′. A similar resonance at 2.23 ppm is assigned to H6′. These assignments were made by examination of the ^{13}C–^1H-HMQC and ^{13}C–^1H-HMBC spectra and by the chemical shift positions for H3′ and H6′. The H6′ resonance will be downfield from the H3′ resonance because it is attached to C6, which is in turn bonded directly to the osmium, whereas H3′ is more remote from the metal. The ring protons are both observed as doublets, coupling to each other at 6.65 ppm ($^3J_{HH} = 8.1$ Hz) for H5, and 7.59 ppm ($^3J_{HH} = 8.0$ Hz) for H4. The ^{13}C-NMR spectrum shows resonances at 21.91 ppm for C3′ and at 47.65 ppm for C6′. The resonances for the ring carbon atoms, C4 and C5, are observed at 147.98 ppm and 129.22 ppm respectively. The quaternary carbon resonances appear at 119.89 ppm for C3 (singlet), and as triplets at 257.43 ppm ($^2J_{CP} = 9.1$ Hz) for C2 and 220.07 ppm ($^2J_{CP} = 6.2$ Hz) for C6. The carbonyl resonance is observed at 203.06 ppm ($^2J_{CP} = 11.3$ Hz). It is noteworthy that the chemical shifts for C3, C4, and C5 in the ^{13}C-NMR spectrum all fall within the region expected for ‘aromatic’ carbon atoms.



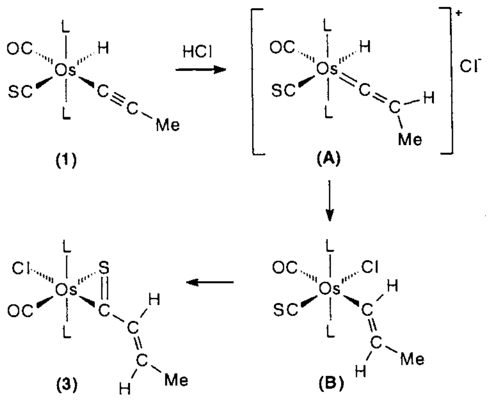
Scheme 1. Synthesis of the new 3,6-dimethyl-substituted osmabenzene, $\overline{Os(\eta^2\text{-}C[S]CMeCHCHC}Me)(CO)(PPh_3)_2$ (**2**).

The ring position of the methyl groups in the isolated complex indicate that the two propyne units have linked together in a tail-to-tail manner, i.e. the new C–C bond has been formed by linkage of the two CH termini. A possible route for the formation of this metallabenzene could be through initial combination of coordinated propyne with the CS ligand to form a four-membered metallacyclic ring, followed by addition of a second molecule of propyne with ring expansion from four to six. There is precedent for the formation of a four-membered ring complex from a coordinated di-*p*-tolylacetylene and a CS ligand [5]. We have no further evidence relating to the mechanism of this reaction. In view of the fact that **2** is formed in such low yield, and that we cannot exclude the possibility that other isomers were also formed but not isolated, further speculation about the mechanism based upon the observed regiochemistry for **2** is unwarranted.

2.2. Preparation and spectroscopic characterisation of $Os(\eta^2\text{-}C[S]CH{=}CHMe)Cl(CO)(PPh_3)_2$ (3)

Treatment of **1** with HCl results in the rapid formation of the dark-red coloured dihapto-propenylthioacyl complex, $Os(\eta^2\text{-}C[S]CH{=}CHMe)Cl(CO)(PPh_3)_2$ (**3**). The IR spectrum of this complex shows a $\nu(CO)$ at 1901 cm^{-1} but no band appropriate for a terminal CS ligand. The ^1H-NMR spectrum of **3** shows a doublet at 0.85 ppm ($^3J_{HH} = 6.8$ Hz) (assigned to the protons of the terminal methyl group), a doublet of quartets at 6.08 ppm ($^3J_{HH} = 14.9$ Hz, $^3J_{HH} = 6.9$ Hz) (assigned to the proton on the carbon atom of the double bond that bears the methyl group), and a second doublet at 5.85 ppm ($^3J_{HH} = 15.0$ Hz) (assigned to the proton on the other carbon atom of the double bond). The large value of the coupling between the vicinal protons on the double bond suggests a trans orientation for these protons about the double bond, and this arrangement has been confirmed by the X-ray crystal structure determination described in Section 2.3.

A plausible mechanism for this reaction is depicted in Scheme 2. Although no definitive evidence for the proposed intermediate vinylidene ligand has been obtained, there is ample precedent for the formation of vinylidene ligands through protonation of the β-carbon



(L = PPh_3; **(A)** and **(B)** not isolated)

Scheme 2. Conversion of the propynyl, thiocarbonyl complex, $Os(C{\equiv}CMe)H(CS)(CO)(PPh_3)_2$ (**1**), to the propenylthioacyl complex, $Os(\eta^2\text{-}C[S]CH{=}CHMe)Cl(CO)(PPh_3)_2$ (**3**).

atoms of alkynyl ligands [7]. The hydrido, vinylidene intermediate then rearranges to a propenyl ligand, which in turn migrates onto the thiocarbonyl ligand. The migratory aptitude of the propenyl ligand is clearly greater than that of *o*-halophenyl ligands, since we have recently described that migration reactions of the complexes $Os(o\text{-halophenyl})Cl(CS)(CO)(PPh_3)_2$ require heating to 70–80°C for some hours [8].

2.3. Crystallographic studies of 1, 2, and 3

The molecular geometries of **1**, **2**, and **3** derived from X-ray crystallographic studies (see Table 1) are depicted in Figs. 1–3 respectively, and selected bond lengths and angles are presented in Tables 2–4 respectively. All three complexes have approximately octahedral coordination geometry with mutually trans triphenylphosphine ligands. Complex **1** crystallises with two independent molecules in the unit cell, both having cis carbonyl and thiocarbonyl ligands with the propynyl ligand trans to carbonyl. The hydride position was not located, but its position can be inferred from the open coordination site. The Os–C distances for the carbonyl and thiocarbonyl ligands are not significantly different. The coordinated propynyl ligand is approximately linear with the angle C(4–C(3)–Os(1) being 170.0(4)°, and the angle C(3)–C(4)–C(5) being 175.7(5)°. The distance C(3) – C(4), 1.188(6) Å, is appropriate for a C≡C bond.

The structure of complex **2** is very similar to that of the parent, unsubstituted osmabenzene,

Table 1
Data collection and processing parameters

	1	2	3
Formula	$C_{41}H_{33}OOsP_2S$	$C_{44}H_{38}OOsP_2S$	$C_{41}H_{35}ClOOsP_2S$
Molecular weight	825.87	866.94	863.34
Temperature (K)	203	203	203
Wavelength (Å)	0.710 73	0.710 73	0.710 73
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$	$Abm2$
a (Å)	10.2376(1)	11.0376(2)	9.1890(18)
b (Å)	16.0348(2)	12.1891(3)	24.608(5)
c (Å)	22.1572(3)	28.4102(7)	16.032(3)
α (°)	101.180(1)		
β (°)	99.132(1)		
γ (°)	96.918(1)		
V (Å^3)	3479.84(7)	3822.26(15)	3625.2(12)
Z	4	4	4
d_{calc} (g cm^{-3})	1.576	1.507	1.582
$F(000)$	1636	1728	1712
μ (mm^{-1})	3.85	3.507	3.769
Crystal size (mm)	0.54 × 0.18 × 0.13	0.24 × 0.07 × 0.06	0.22 × 0.085 × 0.05
2θ (min–max) (°)	0.95–28.24	1.43–28.19	1.66–28.21
h,k,l range	$-13 \leq h \leq 12$, $-20 \leq k \leq 20$, $0 \leq l \leq 29$	$-14 \leq h \leq 14$, $0 \leq k \leq 15$, $0 \leq l \leq 37$	$-12 \leq h \leq 11$, $0 \leq k \leq 32$, $0 \leq l \leq 17$
Reflections collected	28 418	23 873	10 925
Independent reflections, R_{int}	15 576, 0.0235	8558, 0.0372	3487, 0.0463
A (min, max)	0.230, 0.635	0.486, 0.817	0.491, 0.834
Function minimised	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$
Goodness of fit on F^2	1.109	1.010	1.071
R (observed data)[a]	$R_1 = 0.0357$, $wR_2 = 0.0762$	$R_1 = 0.0320$, $wR_2 = 0.0477$	$R_1 = 0.0438$, $wR_2 = 0.0956$
R (all data)	$R_1 = 0.0494$, $wR_2 = 0.0832$	$R_1 = 0.0441$, $wR_2 = 0.0510$	$R_1 = 0.0585$, $wR_2 = 0.1029$
Diff. map (min, max) (e Å^{-3})	+2.35, −1.44	+1.34, −0.77	+1.33, −1.35

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1.0/[\sigma^2(F_o^2) + aP^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

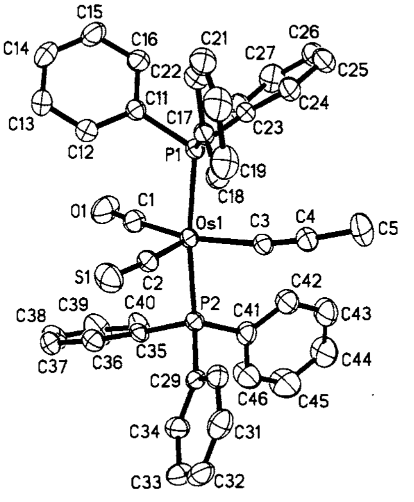


Fig. 1. Molecular geometry of Os(C$\equiv$CMe)H(CS)(CO)(PPh$_3$)$_2$ (**1**).

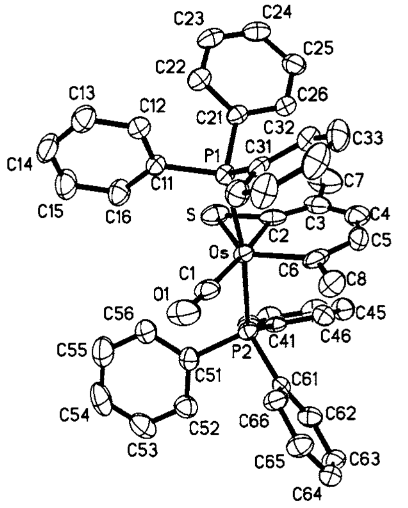


Fig. 2. Molecular geometry of Os(η^2-C[S]CMeCHCHCMe)(CO)(PPh$_3$)$_2$ (**2**).

Os(η^2C[S]CHCHCHCH)(CO)(PPh$_3$)$_2$ [2]. The two Os–C distances within the osmabenzene ring are almost identical at 2.022(5) and 2.027(4) Å. Furthermore, the carbon–carbon bond lengths around the ring are closely similar: C(2)–C(3), 1.365(6); C(3)–C(4), 1.400(7); C(4)–C(5), 1.385(7); C(5)–C(6), 1.415(6) Å. These values are typical for aromatic C–C distances and, together with the identical Os–C distances, point to effective electron delocalisation around the ring. The six-membered ring is almost perfectly planar, with only very small deviations from the RMS plane of best fit through the six ring atoms (Os, 0.014; C(2), −0.025; C(3), 0.012; C(4), 0.014; C(5), −0.016; C(6), 0.001 Å) being observed.

The molecular structure of complex **3** confirms the presence of a dihapto-thioacyl ligand and, in general, terms the ligand arrangements are closely similar to those found for the related complexes Os(η^2-C[S]C$_6$H$_4$X-2)Cl(CO)(PPh$_3$)$_2$ (X = Cl or Br) [8]. In the propenyl group the arrangement about the double bond between C(3) and C(4) is trans and the C(3)–C(4) distance is 1.32(2) Å, appropriate for a double bond.

3. Conclusions

A new dimethyl-substituted osmabenzene, Os(η^2-C[S]CMeCHCHCMe)(CO)(PPh$_3$)$_2$, has been prepared in low yield from reaction between Os(CS)(CO)(PPh$_3$)$_3$ and propyne, showing that there is some generality associated with this synthetic route. Crystal structure determination reveals the positions of methyl substitution and indicates that the presence of these substituents does not perturb the ‘aromatic’ nature of the ring, since ring planarity, equivalence of Os–C distances, and ring C–C distances appropriate for an aromatic system are all observed. A major by-product of the synthesis proves to be the oxidative addition product, Os(C$\equiv$CMe)H(CS)(CO)(PPh$_3$)$_2$. This is protonated by HCl to an intermediate propenylylidene complex which rearranges via two migration processes to the dihapto-propenylthioacyl complex, Os(η^2-C[S]CH=CHMe)Cl(CO)(PPh$_3$)$_2$. Structure determination of this complex confirms a trans arrangement about the double bond of the propenyl group.

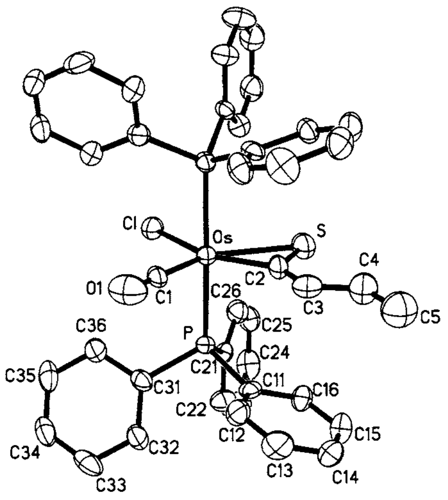


Fig. 3. Molecular geometry of Os(η^2-C[S]CH=CHMe)Cl(CO)(PPh$_3$)$_2$ (**3**).

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Os(1)–C(2)	1.894(5)
Os(1)–C(1)	1.917(5)
Os(1)–C(3)	2.088(4)
Os(1)–P(1)	2.3672(11)
Os(1)–P(2)	2.3849(11)
S(1)–C(2)	1.563(5)
O(1)–C(1)	1.150(6)
C(3)–C(4)	1.188(6)
C(4)–C(5)	1.489(7)
Os(2)–C(6)	1.889(5)
Os(2)–C(7)	1.908(5)
Os(2)–C(8)	2.097(4)
Os(2)–P(3)	2.3661(11)
Os(2)–P(4)	2.3778(11)
S(2)–C(7)	1.559(5)
O(2)–C(6)	1.164(6)
C(8)–C(9)	1.206(6)
C(9)–C(10)	1.474(7)
C(2)–Os(1)–C(1)	97.6(2)
C(2)–Os(1)–C(3)	97.72(19)
C(1)–Os(1)–C(3)	164.0(2)
C(2)–Os(1)–P(1)	92.46(13)
C(1)–Os(1)–P(1)	91.84(15)
C(3)–Os(1)–P(1)	82.77(12)
C(2)–Os(1)–P(2)	95.31(13)
C(1)–Os(1)–P(2)	90.85(15)
C(3)–Os(1)–P(2)	92.45(12)
P(1)–Os(1)–P(2)	171.37(4)
C(4)–C(3)–Os(1)	170.0(4)
C(3)–C(4)–C(5)	175.7(5)
C(6)–Os(2)–C(7)	94.4(2)
C(6)–Os(2)–C(8)	168.4(2)
C(7)–Os(2)–C(8)	96.88(19)
C(6)–Os(2)–P(3)	91.86(15)
C(7)–Os(2)–P(3)	93.35(14)
C(8)–Os(2)–P(3)	85.09(12)
C(6)–Os(2)–P(4)	90.11(15)
C(7)–Os(2)–P(4)	95.29(14)
C(8)–Os(2)–P(4)	91.24(12)
P(3)–Os(2)–P(4)	170.96(4)
C(9)–C(8)–Os(2)	174.9(4)
C(8)–C(9)–C(10)	178.1(5)

4. Experimental

4.1. General procedures and instruments

Standard laboratory procedures were followed, as have been described previously [9]. The compound $Os(CS)(CO)(PPh_3)_3$ [1] was prepared according to the literature method.

Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol mulls between KBr plates on a Perkin Elmer Paragon 1000 spectrometer. NMR spectra were obtained on a Bruker DRX 400 spectrometer at 25°C. ^{1}H- and ^{13}C-NMR spectra were obtained operating at 400.1 MHz (^{1}H) and 100.6 MHz (^{13}C). Resonances are quoted in parts per million and ^{1}H-NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for $CHCl_3$). ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.00 ppm). Mass spectra were recorded using the fast atom bombardment technique with a Varian VG 70-SE mass spectrometer. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

4.2. Preparation of $Os(C{\equiv}CMe)H(CS)(CO)(PPh_3)_2$ (**1**)

A 100 ml round-bottomed flask was fitted with a reflux condenser, and dry, deoxygenated benzene (50 ml) was added. Propyne gas was bubbled through the benzene for 5 min; the stream of gas was stopped temporarily, and $Os(CO)(CS)(PPh_3)_3$ (1.00 g, 0.953 mmol) was added. The mixture was heated to 40°C for 10 min with a constant flow of propyne bubbling through the solution. During this period the

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Os–C(1)	1.908(4)
Os–C(6)	2.022(5)
Os–C(2)	2.027(4)
Os–P(1)	2.3732(10)
Os–P(2)	2.3816(11)
Os–S	2.4990(12)
S–C(2)	1.689(6)
O(1)–C(1)	1.155(4)
C(2)–C(3)	1.365(6)
C(3)–C(4)	1.400(7)
C(3)–C(7)	1.520(6)
C(4)–C(5)	1.385(7)
C(5)–C(6)	1.415(6)
C(6)–C(8)	1.516(6)
C(1)–Os–C(6)	98.8(2)
C(1)–Os–C(2)	173.8(2)
C(6)–Os–C(2)	87.5(2)
C(1)–Os–P(1)	86.59(12)
C(6)–Os–P(1)	93.39(12)
C(2)–Os–P(1)	92.99(11)
C(1)–Os–P(2)	89.31(13)
C(6)–Os–P(2)	94.95(12)
C(2)–Os–P(2)	90.23(11)
P(1)–Os–P(2)	171.19(4)
C(1)–Os–S	131.53(15)
C(6)–Os–S	129.68(15)
C(2)–Os–S	42.23(16)
P(1)–Os–S	89.22(4)
P(2)–Os–S	87.65(4)
C(2)–S–Os	53.77(14)
C(3)–C(2)–S	138.4(4)
C(3)–C(2)–Os	137.5(4)
S–C(2)–Os	84.0(2)

Table 4
Selected bond lengths (Å) and angles (°) for **3**

Os–C(1)	1.885(16)
Os–C(2)	1.927(13)
Os–P	2.3808(16)
Os–Cl	2.493(3)
Os–S	2.542(3)
S–C(2)	1.656(16)
O(1)–C(1)	1.072(18)
C(2)–C(3)	1.44(2)
C(3)–C(4)	1.32(2)
C(4)–C(5)	1.49(3)
C(1)–Os–C(2)	103.4(7)
C(1)–Os–P	89.99(12)
C(2)–Os–P	90.80(11)
P–Os–P # 1	178.4(3)
C(1)–Os–Cl	107.2(5)
C(2)–Os–Cl	149.3(4)
P–Os–Cl	89.22(17)
C(1)–Os–S	144.1(5)
C(2)–Os–S	40.7(5)
P–Os–S	90.49(4)
Cl–Os–S	108.7(2)
C(2)–S–Os	49.3(5)
O(1)–C(1)–Os	179.8(17)
C(3)–C(2)–S	128.8(10)
C(3)–C(2)–Os	141.1(11)
S–C(4)–Os	90.1(7)
C(4)–C(3)–C(2)	122.7(15)
C(3)–C(4)–C(5)	123.9(17)

tan-coloured starting material dissolved and a black solution formed. The solution was then heated under reflux for a further 30 min, during which time a dark red–brown colour appeared. The benzene was removed in vacuo and the mixture was dissolved in the minimum amount of dichloromethane (ca 1 ml). The solution was then placed on a silica gel column (2.5 cm × 1.5 cm) and eluted using dichloromethane as the eluant. The fast-running dark brown band was collected and from this solution complex **2** was isolated (see Section 4.3). A slower-moving light pink band was also collected from the column, whereas a large black band did not elute with dichloromethane. Addition of ethanol to the pink eluate, followed by removal of the dichloromethane, afforded pure complex **1** as bronze-coloured crystals (181 mg, 23%). *m*/*z* 829; $C_{41}H_{34}OOsP_2S$ requires 829. Anal. Found: C, 59.44; H, 4.24. Calc. for $C_{41}H_{34}OOsP_2S$: C, 59.55; H, 4.14%. IR (cm^{-1}): 2009 ν(CO); 1259 ν(CS); 720. ^{1}H-NMR ($CDCl_3$; δ) −8.61 (t, 1H, Os*H*, $^2J_{HP} = 21.2$ Hz); 1.36 (t, 3H, C*Me*, $^5J_{HP} = 2.5$ Hz); 7.77–7.83 (m, P*Ph*$_3$). ^{13}C-NMR (C_6D_6; δ) (resonances between 127 and 128 ppm not observed because of solvent) 6.34 (s, c*Me*)); 77.86 (s, ≡*C*Me); 107.45 (s, Os–*C*≡); 129.74 (s, P*Ph*$_3$ *para*); 134.54 (t′, [9] P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 11.1$ Hz).

4.3. Preparation of $\overline{Os(\eta^2\text{-}C[S]CMeCHCHCMe)}(CO)(PPh_3)_2$ (2)

Material from the brown band collected in the synthesis of complex **1** described in Section 4.2 was dissolved in the minimum amount of dichloromethane (ca 1 ml) and placed on a silica gel column (2.5 cm × 1.5 cm). The fast-moving reddish-brown band was eluted using hexane:dichloromethane (1:3). Ethanol (20 ml) was added to the eluate and the dichloromethane was removed using a rotary evaporator. The resulting product was recrystallised from dichloromethane:ethanol (25 ml:10 ml) to yield pure complex **2** as dark brown crystals (7 mg, 8%). *m*/*z* 868.1705; $C_{44}H_{38}OOsP_2S$ requires 868.1734. Anal. Found: C, 56.77; H, 4.43. Calc. for $C_{44}H_{38}OOsP_2S{\cdot}CH_2Cl_2$: C, 56.77; H, 4.24%.

IR (cm^{-1}): 1888 ν(CO); 1378, 1250, 1235. ^{1}H-NMR ($CDCl_3$; δ): 1.64 (s, 3H, *Me*-3); 2.23 (s, 3H, *Me*-6); 6.65 (d, *H*-5, $^3J_{HH} = 8.1$ Hz); 7.59 (d, *H*-4, $^3J_{HH} = 8.0$ Hz); 7.20–7.40 (m, P*Ph*$_3$). ^{13}C-NMR ($CDCl_3$; δ): 21.91 (s, *Me*-3); 47.65 (s, *Me*-6); 119.89 (s, *C*-3); 129.22 (s, *C*-5); 147.98 (s, *C*-4); 203.06 (t, *C*O, $^2J_{CP} = 11.3$ Hz); 220.07 (t, *C*-6, $^2J_{CP} = 6.2$ Hz); 257.43 (t, *C*-2, $^2J_{CP} = 9.1$ Hz); 127.00 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 10.1$ Hz); 129.40 (s, P*Ph*$_3$, *para*); 132.80 (t′, P*Ph*$_3$ *ipso* $^{1,3}J_{CP} = 51.3$ Hz); 134.44 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 10.1$ Hz).

4.4. Preparation of $Os(\eta^2\text{-}C[S]CH=CHMe)Cl(CO)(PPh_3)_2$ (3)

Os(C≡CMe)H(CS)(CO)(PPh_3)$_2$ (100 mg, 0.119 mmol) was dissolved in dichloromethane (20 ml) and concentrated aqueous HCl (two drops) was added. The colour changed instantly from pink to dark red. Ethanol (10 ml) was added to the reaction mixture and the product was isolated after removal of the dichloromethane using a rotary evaporator. The dark-red product was recrystallised from dichloromethane: ethanol (25 ml:10 ml) to yield pure complex **3** as dark-red crystals (96 mg, 93%). *m*/*z* 864.1154 $C_{41}H_{35}ClOOsP_2S$ requires 864.1127. Anal. Found: C, 56.74; H, 4.01. Calc. for $C_{41}H_{35}ClOOsP_2S$: C, 57.04; H, 4.09%. IR (cm^{-1}): 1901 ν(CO); 1605, 1310, 1276, 1252, 871, 589. ^{1}H-NMR ($CDCl_3$; δ): 0.85 (d, 3H, =CH*Me*, $^3J_{HH} = 6.8$ Hz); 5.85 (d, 1H, –C*H*=, $^3J_{HH} = 15.0$ Hz); 6.08 (dq, 1H, =C*H*Me, $^3J_{HH} = 14.9$ Hz, $^3J_{HH} = 6.9$ Hz); 7.36–7.88 (m, PPh$_3$). ^{13}C-NMR ($CDCl_3$; δ): 19.36 (s, *Me*); 127.80 (t′, PPh$_3$ *ortho*, $^{2,4}J_{CP} = 10.1$ Hz); 129.89 (s, PPh$_3$ *para*); 131.44 (t′, PPh$_3$ *ipso*, $^{1,3}J_{CP} = 51.2$ Hz); 134.46 (t′, PPh$_3$ *meta*, $^{3,5}J_{CP} = 9.1$ Hz); 140.11 (s, =*C*HMe); 146.38 (s, –*C*H=).

*4.5. X-ray crystal structure determinations for complexes **1**, **2**, and **3***

X-ray data collection for **1**, **2**, and **3** was on a Siemens SMART diffractometer with a CCD area detector, using graphite-monochromated Mo–K_α radiation (λ = 0.710 73 Å). Data were integrated and Lorentz and polarisation correction applied using SAINT [10] software. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS [11]. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares on F^2 using programs SHELXS [12] and SHELXL [13]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions and refined with a riding model with thermal parameter 20% greater than the U_{iso} of the carrier atom. Crystal data and refinement details are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 146361, 146362, 146363 for **1**, **2**, and **3** respectively. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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