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Reaction of the unsaturated cluster $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PCy}_3)$ with the thioketene 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane. X-ray crystal structure of $\text{Os}_3\text{Pt}(\mu_3\text{-S})_2(\text{CO})_9(\text{PCy}_3)(\eta^1\text{-C}=\text{C}_6\text{H}_6\text{Me}_4)$, a cluster containing an unusual terminal η^1 -vinylidene ligand

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Abstract

The reaction of $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PCy}_3)$ with a twofold excess of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane in toluene at 90°C affords as the major product $\text{Os}_3\text{Pt}(\mu_3\text{-S})_2(\text{CO})_9(\text{PCy}_3)(\eta^1\text{-C}=\text{C}_6\text{H}_6\text{Me}_4)$, which has been characterized by a single crystal X-ray diffraction study. Crystal data: triclinic, space group $P\bar{1}$, a 11.935(4), b 12.755(3), c 15.228(3) Å, α 74.84(2), β 80.91(2), γ 84.42(2)°, V 2206(1) Å³ and $Z = 2$, final $R(R_w)$ values 0.038(0.048) for 5695 unique observed ($I > 3\sigma(I)$) absorption corrected data. The cluster contains a spiked triangular Os_3Pt core with two triply bridging sulfido groups spanning an Os_3 and an Os_2Pt face. A terminal η^1 -vinylidene ligand, formed by C=S bond cleavage of the thioketene, is coordinated to an Os center.

Introduction

The unsaturated hydrido cluster $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ (**1**) reacts readily with a wide variety of unsaturated organic compounds [1–3], very often with a formal reduction of the organic substrate by transfer of a hydride forming new C–H or heteroatom–H bonds. For instance the stable sterically hindered thioketene $\text{S}=\text{C}=\text{C}_6\text{H}_6\text{Me}_4$ (**2**) [4] readily reacts with **1** to give the enethiolate cluster $\text{Os}_3(\mu\text{-H})(\mu\text{-SC}(\text{H})=\text{C}_6\text{H}_6\text{Me}_4)(\text{CO})_{10}$ (**3**) by transfer of one hydride to the C_α of the heteroallene [5]. The reactions of the tetranuclear unsaturated cluster $\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)$ (**4**) [6] with unsaturated organic compounds on the other hand have hardly been investigated, though in principle similar products to those formed by **1** may be envisaged. Reaction of **4a** ($\text{R} = \text{Ph}$) with but-2-yne afforded several compounds, including the alkyne complex $\text{OsPt}_2(\mu_3\text{-}\eta^2\text{-C}_2\text{Me}_2)(\text{CO})_5(\text{PPh}_3)_2$, but no products involving hy-

hydride transfer were observed [7]. Likewise the reaction of **4b** (R = Cy) with organic isocyanides [8] resulted only in substitution products, and no hydride insertion was observed. This latter reaction of **4b** contrasts with that observed for **1**, for which hydride insertion readily occurs to give formimidoyl or iminyl species [3]. We report here the reaction of **4b** (R = Cy) with the thioketene **2**.

Results and discussion

Treatment of a toluene solution of complex **4b** with a two molar excess of **2** at 90 °C for 12 h afforded a mixture of complexes, the major product, complex **5**, being isolated as red crystals. The other complexes were not obtained in sufficient yield or purity to allow characterization. The FAB mass spectrum of **5** showed a parent ion envelope with the strongest peak at $m/e = 1513$, consistent with a formulation of $\text{Os}_3\text{PtS}(\text{CO})_9(\text{PCy}_3)(\text{thioketene})$. The ^1H NMR spectrum was not very informative, with a complex set of signals in the region δ 2.36–0.82 due to cyclohexyl and CH_3 groups. No high field signal was observed. A singlet resonance in the ^{31}P NMR spectrum at δ 36.2 ($J(\text{Pt}-\text{P})$ 2770 Hz) indicated the presence of a $\text{Pt}(\text{PCy}_3)$ unit, while the IR spectrum showed eight $\nu(\text{CO})$ stretches between 2069 and 1946 cm^{-1} , indicating that only terminal carbonyls were present. Complex **5** was fully characterized by a single crystal X-ray study as the bis-sulfido vinylidene cluster $\text{Os}_3\text{Pt}(\mu_3\text{-S})_2(\text{CO})_9(\text{PCy}_3)(\eta^1\text{-C}=\text{C}_6\text{H}_6\text{Me}_4)$.

The molecular structure is shown in Fig. 1, while atomic coordinates, selected metrical parameters, and experimental details are given in Tables 1, 2 and 3, respectively. The spiked-triangular metal skeleton is comprised of an Os_2Pt triangle with an *exo*-ligated Os atom Os(1) bonded in a pseudo-axial position on Os(2). The Os(1)...Pt and Os(1)...Os(3) separations of 3.656(1) and 3.618(1) Å, respectively, are non-bonding. Complex **5** has 64 cluster valence electrons, which is consistent with the spiked-triangular metal core [9] if the Pt atom is assumed to behave as an 18 electron centre. The Os(1)–Os(2)–Os(3) and the Os(1)–Pt–Os(3) open faces are capped by two sulfido groups. Complex **5** is closely related to several clusters $\text{Os}_3\text{Pt}(\mu_3\text{-S})_2(\text{CO})_{11-n}(\text{L})_n$ (**6a**: L = PPh_3 , $n = 1$; **6b**: $n = 2$) [10], (**6c**, L = PMe_2Ph , $n = 2$) [11], prepared from triosmium-sulfido precursors by Adams and coworkers. The most significant difference between complexes **5** and **6a–6c** lies in the presence in **5** of a terminal η^1 -vinylidene group ligated to Os(3). This ligand is derived by cleavage of the C=S bond from one molecule of the thioketene **2**, with the sulfur atom remaining coordinated to the cluster as a four electron donor sulfido group. The second sulfido ligand present in **5** must arise from cleavage of a further molecule of **2**. The fate of the residual organic fragment has not been determined, though since no hydride ligands remain in **5** it is likely that this residue has been hydrogenated to give $\text{H}_2\text{C}=\text{C}_6\text{H}_6\text{Me}_4$ or $\text{C}_6\text{H}_7\text{Me}_5$.

The presence of a terminal η^1 -vinylidene ligand in a cluster complex is highly unusual, though Behrens [12] has previously reported the analogous generation of an η^1 -vinylidene ligand in the dinuclear complex $\text{Fe}_2(\mu\text{-}\eta^2\text{-S}_2\text{C}=\text{C}_6\text{H}_6\text{Me}_4)(\text{CO})_4(\text{PPh}_3)(\eta^1\text{-C}=\text{C}_6\text{H}_6\text{Me}_4)$ by treatment of the thioketene complex $\text{Fe}_2(\mu\text{-}\eta^2\text{-S}=\text{C}=\text{C}_6\text{H}_6\text{Me}_4)(\text{CO})_4(\text{PPh}_3)_2$ with an excess of **2**. In polynuclear compounds vinylidene ligands are usually observed in bridging coordination modes, viz. $\mu\text{-}\eta^1$ [13], $\mu_3\text{-}\eta^2$ [14], or $\mu_4\text{-}\eta^2$ [15], although terminal intermediates have been proposed [13a] in fluxional processes.

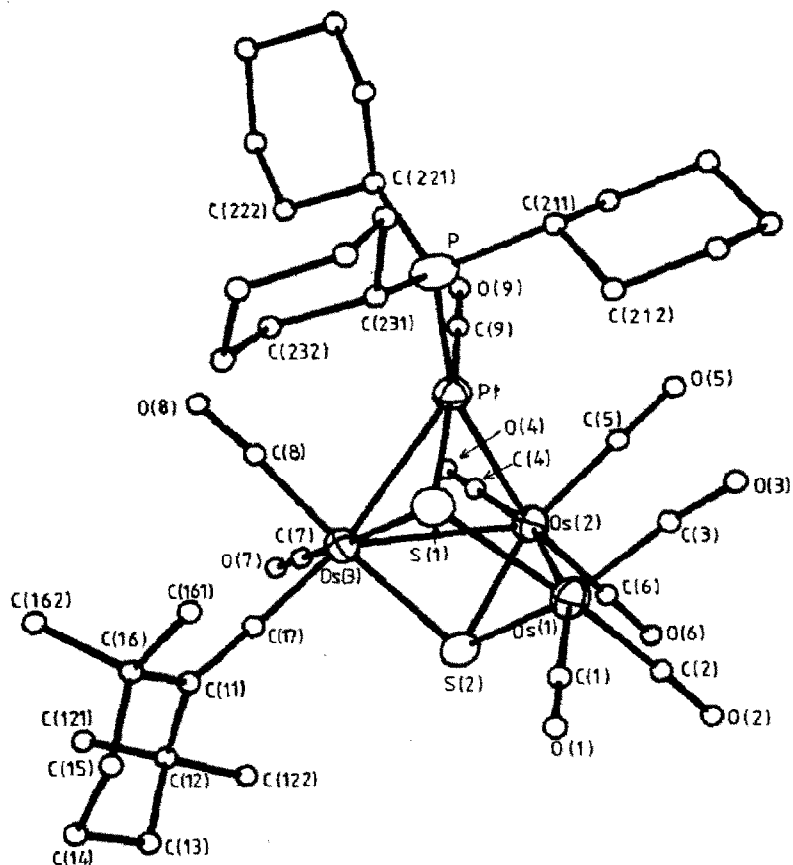


Fig. 1. The molecular structure and atomic labelling scheme for the complex $\text{Os}_3\text{Pt}(\mu_3\text{-S})_2(\text{CO})_9(\text{PCy}_3)(\eta^1\text{-C}_6\text{H}_6\text{Me}_4)$ (5).

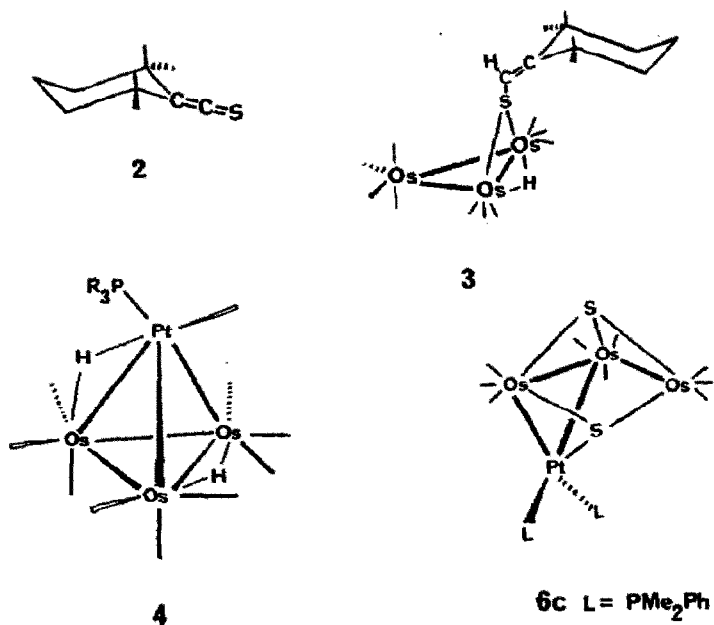


Table 1

Final positional parameters (fractional coordinates) with esd's in parentheses, and equivalent isotropic thermal parameters U_{eq} (\AA^2)^a for $\text{Os}_3\text{Pt}(\mu_3\text{-S})_2(\text{CO})_9(\text{PCy}_3)(\eta^1\text{-C}=\text{C}_6\text{H}_6\text{Me}_4)$ (**5**)

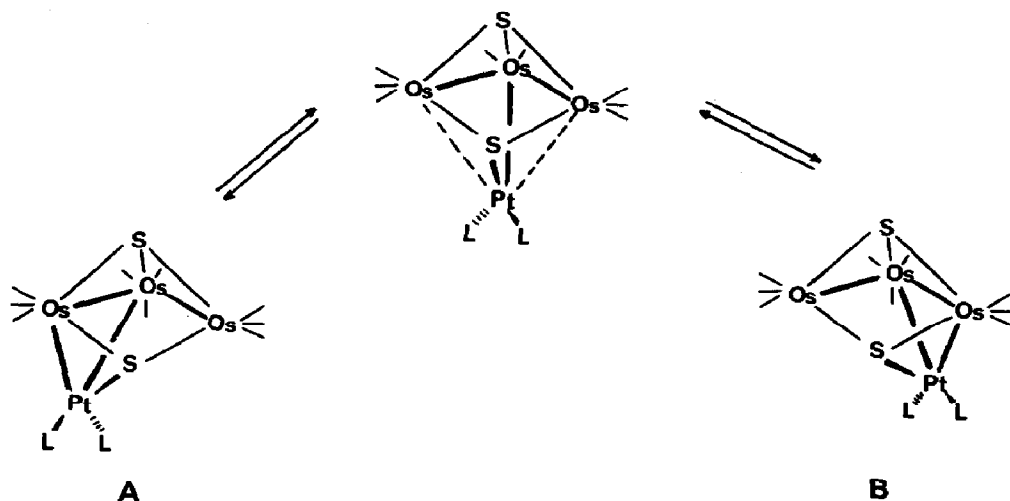
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Pt	0.22537(4)	0.24957(3)	0.68660(3)	0.031
Os(1)	0.40828(5)	0.23670(4)	0.86084(3)	0.036
Os(2)	0.44372(4)	0.33061(3)	0.67065(3)	0.031
Os(3)	0.41430(4)	0.09341(3)	0.68394(3)	0.031
P	0.0289(3)	0.2275(3)	0.7240(2)	0.040
S(1)	0.2811(3)	0.1249(2)	0.8157(2)	0.035
S(2)	0.5427(3)	0.1703(2)	0.7514(2)	0.035
O(1)	0.4243(10)	0.0750(7)	1.0428(6)	0.067
O(2)	0.5936(12)	0.3679(10)	0.8856(8)	0.105
O(3)	0.2294(10)	0.3905(9)	0.9353(9)	0.096
O(4)	0.4967(9)	0.3717(7)	0.4645(6)	0.062
O(5)	0.2743(9)	0.5223(7)	0.6808(8)	0.077
O(6)	0.6416(8)	0.4600(7)	0.6750(7)	0.062
O(7)	0.5701(9)	0.1134(7)	0.5036(7)	0.064
O(8)	0.2474(9)	0.0094(8)	0.5905(8)	0.081
O(9)	0.2027(9)	0.3995(8)	0.5015(7)	0.071
C(1)	0.4153(12)	0.1326(10)	0.9765(11)	0.056
C(2)	0.5216(13)	0.3200(11)	0.8776(8)	0.054
C(3)	0.2912(14)	0.3307(12)	0.9056(12)	0.070
C(4)	0.4736(11)	0.3533(8)	0.5430(8)	0.037
C(5)	0.3392(11)	0.4471(9)	0.6774(7)	0.036
C(6)	0.5681(11)	0.4109(9)	0.6743(8)	0.040
C(7)	0.5104(12)	0.1089(9)	0.5703(10)	0.046
C(8)	0.3047(11)	0.0434(9)	0.6281(9)	0.043
C(9)	0.2115(11)	0.3443(10)	0.5719(11)	0.054
C(11)	0.5110(12)	-0.1507(9)	0.7546(9)	0.051
C(12)	0.6388(12)	-0.1785(10)	0.7245(10)	0.053
C(13)	0.6828(15)	-0.2593(12)	0.8075(10)	0.071
C(14)	0.6141(19)	-0.3552(11)	0.8467(12)	0.086
C(15)	0.4953(19)	-0.3190(11)	0.8847(11)	0.083
C(16)	0.4339(14)	-0.2392(10)	0.8105(9)	0.058
C(17)	0.4703(11)	-0.0520(10)	0.7298(11)	0.057
C(121)	0.6595(15)	-0.2285(12)	0.6433(11)	0.078
C(122)	0.7101(12)	-0.0786(10)	0.7008(11)	0.062
C(161)	0.3295(15)	-0.1887(12)	0.8593(13)	0.084
C(162)	0.3921(16)	-0.3005(12)	0.7494(13)	0.089
C(211)	-0.0423(12)	0.3377(11)	0.7752(11)	0.060
C(212)	-0.0048(14)	0.3281(14)	0.8687(12)	0.082
C(213)	-0.0648(17)	0.4182(18)	0.9114(14)	0.108
C(214)	-0.0449(18)	0.5300(18)	0.8487(16)	0.111
C(215)	-0.0822(16)	0.5370(13)	0.7581(14)	0.088
C(216)	-0.0222(15)	0.4490(12)	0.7120(12)	0.077
C(221)	-0.0373(11)	0.2401(11)	0.6198(9)	0.056
C(222)	0.0190(12)	0.1702(12)	0.5556(11)	0.064
C(223)	-0.0261(18)	0.2016(17)	0.4670(12)	0.104
C(224)	-0.1532(15)	0.2089(15)	0.4722(11)	0.085
C(225)	-0.2033(15)	0.2783(17)	0.5336(13)	0.100
C(226)	-0.1631(15)	0.2391(16)	0.6291(13)	0.093
C(231)	-0.0090(11)	0.1009(11)	0.8123(9)	0.055
C(232)	0.0286(15)	-0.0017(11)	0.7824(12)	0.078
C(233)	0.0089(19)	-0.1028(13)	0.8604(14)	0.100
C(234)	-0.110(2)	-0.103(2)	0.913(1)	0.115
C(235)	-0.1480(17)	-0.0015(20)	0.9380(14)	0.112
C(236)	-0.1355(14)	0.0965(15)	0.8571(12)	0.083

^a $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Steric hindrance may be a factor in preventing the vinylidene ligand in **5** adopting a bridging mode.

As stated above complex **5** is closely related to a series of clusters **6a–6c**. Adams et al. [11] have reported the fluxional behavior of **6c**, and proposed a mechanism involving a novel low-energy metal framework rearrangement (Scheme 1). In complex **5** this would correspond to the reversible breaking of the Pt–Os(3) bond and formation of a Pt–Os(1) bond. For complex **6c** this mechanism results in a time averaged mirror plane and exchange of the diastereotopic methyl groups on both of the PMe_2Ph ligands [11]. In complex **5**, on the other hand, such a process would be nondegenerate, i.e. the two conformations **A** and **B** would be non-equivalent isomers due to the presence of the Os-ligated terminal vinylidene moiety. The ^{31}P spectrum of **5**, consisting of a sharp singlet with ^{195}Pt satellites, is invariant between -60 and $+25^\circ\text{C}$, with no detectable line broadening at the lowest temperature. This negative evidence suggests either that (a) the system is at the fast exchange regime even at -60°C , (b) exchange is rendered degenerate by a concerted migration of the vinylidene and one CO ligand, which is somewhat unlikely, (c) the population of one of the isomers in solution is very low, (d) the ^{31}P resonances of both isomers are accidentally degenerate, or (e) such an exchange process does not occur in complex **5**. We cannot distinguish between these possibilities at present.

In the context of this framework rearrangement it is, however, of interest to compare the metal–metal separations found in complexes **5** and **6a–6c**. These are given in Table 4, with the atomic labeling corresponding to Fig. 1, and arranged in the order of increasing Pt...Os(1) distances. It can be seen that the related Os–Os distances remain reasonably constant in all the clusters, only varying by 0.03–0.04 Å. On the other hand the Pt–Os separations vary quite widely, this being particularly so with the non-bonded Pt...Os(1) distance, which increases from 3.336(1) Å in **6b** to 3.771(1) Å in **6c**. This increase is mirrored by a decrease in the Pt–Os(3) separation, from 2.904(1) to 2.789(1) Å. This evidence strongly suggests that the Pt–Os distances in these clusters are “soft” compared with the Os–Os separations,



Scheme 1.

Table 2

Selected bond lengths (Å) and bond angles (deg) for Os₃Pt(μ₃-S)₂(CO)₉(PCy₃)χ^η¹-C=C₆H₆Me₄) (5)

<i>Bond lengths</i>			
Pt–Os(2)	2.848(1)	Pt–Os(3)	2.862(1)
Pt–P	2.350(4)	Pt–S(1)	2.325(3)
Pt–C(9)	1.867(16)	Os(1)–Os(2)	2.810(1)
Os(1)–S(1)	2.464(3)	Os(1)–S(2)	2.387(3)
Os(1)–C(1)	1.916(16)	Os(1)–C(2)	1.885(15)
Os(1)–C(3)	1.912(17)	Os(2)–Os(3)	3.030(1)
Os(2)–S(2)	2.400(3)	Os(2)–C(4)	1.870(12)
Os(2)–C(5)	1.859(12)	Os(2)–C(6)	1.899(13)
Os(3)–S(1)	2.450(4)	Os(3)–S(2)	2.384(3)
Os(3)–C(7)	1.895(15)	Os(3)–C(8)	1.908(13)
Os(3)–C(17)	1.898(13)	O(1)–C(1)	1.097(18)
O(2)–C(2)	1.14(2)	O(3)–C(3)	1.14(2)
O(4)–C(4)	1.150(16)	O(5)–C(5)	1.179(16)
O(6)–C(6)	1.130(15)	O(7)–C(7)	1.136(18)
O(8)–C(8)	1.138(16)	O(9)–C(9)	1.133(19)
C(11)–C(12)	1.56(2)	C(11)–C(16)	1.515(19)
C(11)–C(17)	1.286(17)	C(12)–C(13)	1.54(3)
C(12)–C(121)	1.51(3)	C(12)–C(122)	1.533(18)
C(13)–C(14)	1.48(3)	C(14)–C(15)	1.52(3)
C(15)–C(16)	1.54(3)	C(16)–C(161)	1.52(3)
C(16)–C(162)	1.53(3)		
<i>Bond angles</i>			
Os(2)–Pt–Os(3)	64.1(1)	Os(2)–Pt–P	161.6(1)
Os(2)–Pt–S(1)	84.0(1)	Os(2)–Pt–C(9)	87.1(5)
Os(3)–Pt–P	31.2(1)	Os(3)–Pt–S(1)	55.2(1)
Os(3)–Pt–C(9)	113.6(5)	P–Pt–S(1)	97.3(2)
P–Pt–C(9)	93.6(5)	S(1)–Pt–C(9)	168.1(5)
Os(2)–Os(1)–S(1)	82.4(1)	Os(2)–Os(1)–S(2)	54.3(1)
Os(2)–Os(1)–C(1)	160.0(5)	Os(2)–Os(1)–C(2)	90.2(4)
Os(2)–Os(1)–C(3)	103.5(6)	S(1)–Os(1)–S(2)	82.0(1)
S(1)–Os(1)–C(1)	91.3(5)	S(1)–Os(1)–C(2)	170.5(5)
S(1)–Os(1)–C(3)	96.4(5)	S(2)–Os(1)–C(1)	106.2(5)
S(2)–Os(1)–C(2)	88.9(5)	S(2)–Os(1)–C(3)	157.8(6)
C(1)–Os(1)–C(2)	93.7(6)	C(1)–Os(1)–C(3)	96.0(7)
C(2)–Os(1)–C(3)	91.1(7)	Pt–Os(2)–Os(1)	80.5(1)
Pt–Os(2)–Os(3)	58.2(1)	Pt–Os(2)–S(2)	100.0(1)
Pt–Os(2)–C(4)	94.9(4)	Pt–Os(2)–C(5)	73.9(4)
Pt–Os(2)–C(6)	165.5(4)	Os(1)–Os(2)–Os(3)	76.5(1)
Os(1)–Os(2)–S(2)	53.8(1)	Os(1)–Os(2)–C(4)	164.3(4)
Os(1)–Os(2)–C(5)	93.9(4)	Os(1)–Os(2)–C(6)	95.1(4)
Os(3)–Os(2)–S(2)	50.5(1)	Os(3)–Os(2)–C(4)	88.3(4)
Os(3)–Os(2)–C(5)	132.0(4)	Os(3)–Os(2)–C(6)	134.4(4)
S(2)–Os(2)–C(4)	113.1(4)	S(2)–Os(2)–C(5)	147.6(4)
S(2)–Os(2)–C(6)	88.1(4)	C(4)–Os(2)–C(5)	99.2(5)
C(4)–Os(2)–C(6)	92.8(6)	C(5)–Os(2)–C(6)	92.8(6)
Pt–Os(3)–Os(2)	57.7(1)	Pt–Os(3)–S(1)	51.2(1)
Pt–Os(3)–S(2)	100.0(1)	Pt–Os(3)–C(7)	115.8(4)
Pt–Os(3)–C(8)	75.4(4)	Pt–Os(3)–C(17)	146.6(5)
Os(2)–Os(3)–S(1)	78.1(1)	Os(2)–Os(3)–S(2)	50.9(1)
Os(2)–Os(3)–C(7)	88.2(4)	Os(2)–Os(3)–C(8)	124.4(4)
Os(2)–Os(3)–C(17)	145.1(5)	S(1)–Os(3)–S(2)	82.3(1)
S(1)–Os(3)–C(7)	165.0(4)	S(1)–Os(3)–C(8)	95.7(4)
S(1)–Os(3)–C(17)	101.8(5)	S(2)–Os(3)–C(7)	94.0(5)

Table 2 (continued)

<i>Bond angles</i>			
S(2)–Os(3)–C(8)	175.2(4)	S(2)–Os(3)–C(17)	94.2(5)
C(7)–Os(3)–C(8)	86.9(6)	C(7)–Os(3)–C(17)	92.9(6)
C(8)–Os(3)–C(17)	90.5(6)	Pt–S(1)–Os(1)	99.5(1)
Pt–S(1)–Os(3)	73.6(1)	Os(1)–S(1)–Os(3)	94.8(2)
Os(1)–S(2)–Os(2)	71.9(1)	Os(1)–S(2)–Os(3)	98.7(2)
Os(2)–S(2)–Os(3)	78.6(1)	Os(1)–C(1)–O(1)	176.5(13)
Os(1)–C(2)–O(2)	177.0(13)	Os(1)–C(3)–O(3)	173.4(15)
Os(2)–C(4)–O(4)	175.8(11)	Os(2)–C(5)–O(5)	178.8(11)
Os(2)–C(6)–O(6)	178.7(11)	Os(3)–C(7)–O(7)	176.9(11)
Os(3)–C(8)–O(8)	173.8(12)	Pt–C(9)–O(9)	178.2(12)
C(12)–C(11)–C(16)	120.6(11)	C(12)–C(11)–C(17)	119.4(13)
C(16)–C(11)–C(17)	120.0(14)	C(11)–C(12)–C(13)	106.8(12)
C(11)–C(12)–C(121)	113.6(12)	C(11)–C(12)–C(122)	112.3(10)
C(13)–C(12)–C(121)	109.2(12)	C(13)–C(12)–C(122)	106.9(12)
C(121)–C(12)–C(122)	107.8(13)	C(12)–C(13)–C(14)	114.0(15)
C(13)–C(14)–C(15)	109.6(13)	C(14)–C(15)–C(16)	112.3(14)
C(11)–C(16)–C(15)	110.7(14)	C(11)–C(16)–C(161)	109.7(11)
C(11)–C(16)–C(162)	111.4(13)	C(15)–C(16)–C(161)	107.4(13)
C(15)–C(16)–C(162)	110.1(12)	C(161)–C(16)–C(162)	107.4(14)
Os(3)–C(17)–C(11)	175.6(14)		

Table 3

Experimental data for crystallographic study

Formula	$C_{38}H_{51}O_9Os_3PtS_2$
M_r	1512.6
Space group	$P\bar{1}$ (No. 2 C_i^1)
Cryst. system	triclinic
a (Å)	11.935(4)
b (Å)	12.755(3)
c (Å)	15.228(3)
α (deg)	74.84(2)
β (deg)	80.91(2)
γ (deg)	84.42(2)
V (Å ³)	2206(1)
Z	2
$D_{\text{calc}}/\text{g cm}^{-3}$	2.28
$F(000)$	1408
$\mu(\text{Mo-K}\alpha)$, cm^{-1}	119.97
T (K)	298
Scan mode	$\theta/2\theta$
θ range/deg	$2 < \theta < 25$
Cryst. size/mm	$0.35 \times 0.35 \times 0.1$
Range of trans. coeff. corr.	0.75–1.45
No. of data collected	8142
No. of unique data	7736
Std. reflections	507, $2\bar{5}4$
Observability criterion n	
$I > n\sigma(I)$	3
No. of data in refinement	5695
No. of refined parameters	325/307
Final R	0.038
R_w	0.048
Largest remaining feature in elec. density map, $e \text{ \AA}^{-3}$	+ 1.69(max) – 1.68(min)
shift (esd) in last cycle	0.19 (max), 0.02 (av)

Table 4

Metal-metal separations (Å) in complexes **5** and **6a–6c** (estimated esd's are 0.001 Å)

	6b	6a	5	6c
Pt... Os(1)	3.336	3.401	3.656	3.771
Pt–Os(2)	2.878	2.858	2.848	2.936
Pt–Os(3)	2.904	2.905	2.862	2.789
Os(1)... Os(3)	3.612	3.585	3.618	–
Os(1)–Os(2)	2.819	2.826	2.810	2.798
Os(2)–Os(3)	2.998	2.990	3.030	3.027

and as such is wholly consistent with the fluxional mechanism proposed by Adams et al. [11].

Experimental

All manipulations were performed under oxygen-free dinitrogen by standard Schlenk tube techniques. Solvents were freshly distilled prior to use; light petroleum refers to the fraction of b.p. 40–60 °C. ¹H and ³¹P NMR spectra were recorded on a Bruker WP200SY and IR spectra on a Perkin–Elmer 983 instrument. FAB mass spectra were obtained at the SERC service at Swansea. Os₃Pt(μ-H)₂(CO)₁₀(PCy₃) was prepared as previously described [6], and a sample of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane was kindly donated by U. Behrens.

Preparation of Os₃Pt(μ₃-S)₂(CO)₉(PCy₃)(η¹-C=C₆H₆Me₄) (**5**)

Os₃Pt(μ-II)₂(CO)₁₀(PCy₃) 0.3 g (0.22 mmol) in 20 cm³ of toluene was heated with a twofold molar excess of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane at 90 °C in a closed vessel under vacuum for 12 h. (Use of less than this amount of the thioetene resulted in substantial amounts of starting material remaining.) Removal of the solvent, followed by chromatography with light petroleum/dichloromethane mixtures as eluents gave a red-orange band containing the major colored product. Crystallisation of the material from this band from light petroleum afforded bright red crystals of complex **5** (0.15 g, 0.10 mmol, 45% yield). Several pale coloured products were observed, but these could not be isolated in sufficient yield or purity to allow characterization.

Complex **5**, Found: C, 30.73; H, 3.35. C₃₈H₅₁O₉Os₃PPtS₂ calcd.: C, 30.17; H, 3.40%. FAB mass spectrum *m/z* 1513 (100% peak in parent ion envelope, calculated 100% peak at *m/z* 1512). IR (ν(CO)_{max} (cm⁻¹), cyclohexane) 2069s, 2045vs, 2032m, 2023s, 1977s, 1971s, 1961w, 1946w. NMR (¹H, CDCl₃, 233 K) δ 2.36 (m, 3H, C₆H₁₁), 1.78–0.82 (complex mult., C₆H₁₁, CH₃ and CH₂ of vinylidene); (³¹P, CDCl₃, 213 K) δ 36.2 (s, *J*(Pt–P) 2770 Hz).

Crystal structure analysis of complex **5**

Crystals of **5** were grown as red prisms from light petroleum. Details of data collection procedures and structure refinement are given in Table 3. Data were collected on an Enraf–Nonius CAD4F automated diffractometer with graphite monochromated X-radiation (λ 0.71069 Å). Unit cell parameters were determined by refinement of the setting angles (θ ≥ 12°) of 25 reflections. Data were collected

at 298 K using the $\theta/2\theta$ scan mode, and standard reflections were measured every 2 h during data collection. Data were corrected for a linear decay (ca. 3%), Lorentz-polarization and absorption (DIFABS [16]) effects. The structure was solved by direct methods (MITHRIL [17]) and subsequent electron density difference syntheses. All non-hydrogen atoms were allowed anisotropic thermal motion. Hydrogen atoms were placed in calculated positions (C–H 1.073 Å) with fixed isotropic thermal parameters (U 0.05 Å²). Refinement was by full matrix least-squares, minimising the function $\sum w(|F_o| - |F_c|)^2$, with the weighting scheme $w = [\sigma^2(F_o)]^{-1}$ used and judged satisfactory. $\sigma(F_o)$ was estimated from counting statistics. Final discrepancy indices R and R_w were 0.038, 0.048 respectively where $R = \sum(|F_o| - |F_c|) / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$. Neutral atom scattering factors were obtained from ref. 18, with corrections applied for anomalous dispersion. All calculations were carried out on a Gould-SEL 32/27 mini computer using the GX suite of programs [19].

Supplementary material

Lists of observed and calculated structure factors, thermal parameters, and a complete list of bond lengths and angles are available from the authors.

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