Carbon–Sulphur and Carbon–Hydrogen Bond Cleavages in the Reactions of Phenyl Vinyl Sulphide with Triosmium Clusters: Crystal Structure Determination of $[Os_3(\mu\text{-}SPh)(\mu\text{-}CH{=}CH_2)(CO)_{10}]$†

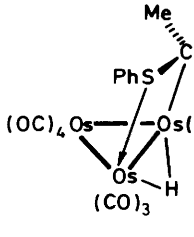
Esther Boyar and Antony J. Deeming*
Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ
Kim Henrick, Mary McPartlin, and Anthony Scott
Department of Chemistry The Polytechnic of North London, Holloway, London N7 8DB

Phenyl vinyl sulphide inserts at room temperature into an Os–H bond of $[Os_3H_2(CO)_{10}]$ to give two diastereomers of the cluster $[Os_3H(\mu\text{-}PhSCHMe)(CO)_{10}]$. However, under similar conditions the sulphide oxidatively adds to $[Os_3(CO)_{10}(MeCN)_2]$ with C–S cleavage to give $[Os_3(\mu\text{-}SPh)(\mu\text{-}CH{=}CH_2)(CO)_{10}]$, the single-crystal *X*-ray structure of which has been determined. The structure relates to the known structure of $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_{10}]$ except that the bridged Os–Os distance [3.328(1) Å] precludes a metal–metal bond. Thermolysis and photolysis products of $[Os_3(\mu\text{-}SPh)(\mu\text{-}CH{=}CH_2)(CO)_{10}]$ are formed by C–H cleavage at the aryl or vinyl groups: $[Os_3H(SPh)(C{=}CH_2)(CO)_9]$, $[Os_4H(SPh)(C{=}CH_2)(CO)_{11}]$, $[Os_2(SPh)(CH{=}CH_2)(CO)_6]$, $[Os_3H(SPh)(CO)_{10}]$, $[Os_3H(SC_6H_4)(CH{=}CH_2)(CO)_9]$, $[Os_3(SPh)(CMe)(CO)_9]$, $[Os_2(SC_6H_4)(CH{=}CH)(CO)_6]$, and $[Os_3H_2(C{=}CH_2)(CO)_9]$.

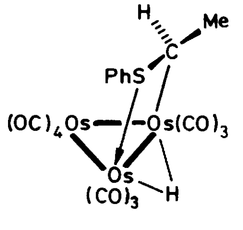
We have previously reported that $MeOCH{=}CH_2$ inserts reversibly into $[Os_3H_2(CO)_{10}]$ to give diastereomers of $[Os_3H(MeOCHMe)(CO)_{10}]$ containing a co-ordinated ether function.[1] Here we report the corresponding reaction of $PhSCH{=}CH_2$ which we carried out expecting stronger Os–S bonds to be generated which would prevent β-elimination to regenerate $[Os_3H_2(CO)_{10}]$. Although oxidative addition reactions of this sulphide with $[Os_3(CO)_{10}(MeCN)_2]$ could have involved aryl or vinyl C–H bond cleavage or S–C bond cleavage, we have established that S–C cleavage occurs initially to give $[Os_3(SPh)(CH{=}CH_2)(CO)_{10}]$. Only subsequently are C–H bonds cleaved. Our present results may be compared with earlier work on $Me_2AsCH{=}CH_2$[2] and PhSR (R = Me or Pr^i)[3] which led to Me_2As- or RS-bridged Os_3 clusters containing $\mu_3\text{-}C_2H_2$ or $\mu_3\text{-}C_6H_4$ bridges.

Results and Discussion

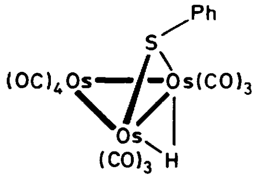
Products derived directly from Phenyl Vinyl Sulphide.—The cluster $[Os_3H_2(CO)_{10}]$ reacts with an excess of $PhSCH{=}CH_2$ in cyclohexane at room temperature to give a good yield of compound $[Os_3H(PhSCHMe)(CO)_{10}]$ (**1**) (90%) together with $[Os_3H(SPh)(CO)_{10}]$ (**2**) (3%), which has previously been formed from $[Os_3(CO)_{12}]$ and PhSH.[4] Compound (**1**) is stable towards β-elimination unlike $[Os_3H(MeOCHMe)(CO)_{10}]$[1] which slowly eliminates $MeOCH{=}CH_2$ to regenerate the dihydride $[Os_3H_2(CO)_{10}]$ in the absence of a large excess of the vinyl ether. The thioether group is more strongly co-ordinated than the ether one. The pyramidal S and the *C*HMe atoms are both asymmetric centres but only two diastereomers, (**1a**) and (**1b**), inseparable by t.l.c., are detected in a 3:2 mol ratio by ^1H n.m.r. spectra of $CDCl_3$ solutions (Table 1). We presume that (**1a**) and (**1b**) have different stereochemistries at carbon, corresponding to the isomers of the MeOCHMe complex, and that inversion at sulphur is either very rapid or that one configuration is strongly preferred.



(**1a**)



(**1b**)



(**2**)

The thioether $PhSCH{=}CH_2$ reacts differently with $[Os_3(CO)_{10}(MeCN)_2]$ to give compound (**3**) of stoicheiometry $Os_3(CO)_{10}PhSCH{=}CH_2$ (elemental analysis and mass spectrum). The ^1H n.m.r. spectrum shows that the vinyl group is intact but this may or may not be still bonded to the PhS group. The same problem arose in considering the structure of $[Os_3(CO)_{10}(Me_2AsCH{=}CH_2)]$ for which we considered the structures (**4a**)—(**4c**).[2] An *X*-ray structure determination of (**4**) could not be carried out because good crystals were unavailable. If there is a $\mu\text{-}\eta^2\text{-}CH{=}CH_2$ ligand in (**3**), the spread of ^1H n.m.r. signals for this group (δ 3.92—5.92) is unexpectedly small compared with that for $[Os_3H(CH{=}CH_2)(CO)_{10}]$ (δ 3.40—7.58)[5,6] and that for compound (**4**) (δ 3.99—7.46).[2] Fortunately good crystals were obtained for (**3**) and a single-crystal *X*-ray structure has been determined.

The molecular structure of compound (**3**) is shown in the Figure, selected bond lengths and angles are given in Table 2,

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† 1,1,1,2,2,2,3,3,3,3-Decarbonyl-1,2-μ-phenylthio-1,2-μ-(σ,η^2-vinyl)-triosmium(2 *Os–Os*).

Supplementary data available (No. SUP 56518, 4 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. I.r.[a] and ^1H n.m.r.[b] data

	Compound	ν(CO)/cm^{-1}		δ/p.p.m.	Assignment
(**1**)	$[Os_3H^w(Ph^xSCH^yMe^z)(CO)_{10}]$	2 101m, 2 059s, 2 047s, 2 019s, 2 004s, 1 993m, 1 980w, 1 973m, 1 948w	*c*	7.28—7.48 (m)	x
				3.79 (q, J_{yz} 7.0)	y
				1.78 (d)	z
				−16.57 (d, J_{wy} 1.0)	w
			d	7.28—7.48 (m)	x
				3.70 (q, J_{yz} 7.1)	y
				1.61 (d)	z
				−16.13 (d), J_{wy} 1.0)	w
(**3**)	$[Os_3(SPh^w)(CH^x{=}CH_2{}^{y,z})(CO)_{10}]$	2 101m, 2 060s, 2 051s, 2 017s, 2 012s, 1 994m, 1 987m, 1 975m		7.2—7.4 (m)	w
				5.92 (dd, J_{xy} 16.3)	x
				4.57 (dd, J_{xz} 10.7)	z
				3.92 (dd, J_{yx} 2.5)	y
(**5**)	$[Os_3H^w(SPh^x)(C{=}CH_2{}^{y,z})(CO)_9]$	2 098w, 2 076s, 2 050s, 2 019m, 2 010m, 2 000w, 1 977w	*c,e*	7.21—7.36 (m)	x
				6.65 (s)	y
				3.87 (s)	z
				−12.27 (s)	w
			d,e	7.2—7.36 (m)	x
				6.88 (s)	y
				3.63 (s)	z
				−12.44 (s)	w
(**6**)	$[Os_4H^w(SPh^x)(C{=}CH_2{}^{y,z})(CO)_{11}]$	2 095w, 2 067s, 2 053m, 2 018s, 2 006m, 1 990w, 1 963w, 1 951w	*c*	7.1—7.6 (m)	x
				5.58 (d, J_{yz} 3.4)	y
				4.92 (d)	z
				−21.99 (s)	w
			d	7.1—7.6 (m)	x
				5.62 (d, J_{yz} 3.4)	y
				4.63 (d)	z
				−21.72 (s)	w
(7)	$[Os_2(SPh^w)(CH^x{=}CH_2{}^{y,z})(CO)_6]$	2 085s, 2 066m,[f] 2 055s, 2 033m, 2 009s, 2 000s, 1 983s, 1 965w, 1 960w, 1 950w	*c*	7.1—7.3 (m)	w
				8.23 (dd, J_{xz} 14.2)	x
				4.70 (dd J_{xy} 10.8)	y
				2.39 (dd, J_{yz} 1.0)	z
			d	7.1—7.3 (m)	w
				8.65 (dd, J_{xz} 14.1)	x
				4.59 (dd, J_{xy} 10.8)	y
				1.87 (dd, J_{yz} 1.0)	z
(**8**)	$[Os_3H^v(SC_6H_4{}^w)(CH^x{=}CH_2{}^{y,z})(CO)_9]$	2 101m, 2 083w,[f] 2 061s, 2 033w,[f] 2 021vs, 2 014s, 2 001m, 1 990w, 1 987m, 1 969m		7.01—7.39 (m)	w
				4.99 (dd, J_{xy} 9.9)	x
				3.98 (dd, J_{xz} 8.8)	z
				2.70 (dd, J_{yz} 1.0)	y
				−16.21 d, J (2.3)	v
(**9**)	$[Os_3(SPh^y)(CMe^z)(CO)_9]$	2 097w, 2 072s, 2 049w,[f] 2 034s, 2 011s, 1 973w		6.88—7.5 (m)	y
				4.73 (s)	z
(**10**)	$[Os_2(SC_6H_4{}^x)(CH^y{=}CH^z)(CO)_6]$	2 087s, 2 057vs, 2 011vs, 2 001vs, 1 988s, 1 913vw, 1 870vw		6.87—7.18 (m)	x
				9.04 (d, J_{yz} 10.5)	y
				6.38 (d)	z

[a] In cyclohexane. [b] In $CDCl_3$, 200 MHz, 27 °C unless stated otherwise; J values in Hz. [c] Major isomer. [d] Minor isomer. [e] At −50 °C. [f] Probably an impurity absorption.

and fractional atomic co-ordinates in Table 3. Oxidative addition has occurred with C–S bond cleavage to give $[Os_3(\mu\text{-}SPh)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$ which has a very similar structure to that of $[Os_3H(\mu\text{-}\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$[6] except that, in the hydride, the bridged Os–Os distance of 2.845(2) Å is much shorter than that in compound (**3**) [Os(1)–Os(3) = 3.328(1) Å], a distance too long to accommodate a direct Os–Os bond. This longer distance may be partly a consequence of Os–S bonds [2.459(4) and 2.446(4) Å in (**3**)] being much longer than Os–H bonds [1.857(4) and 1.813(4) Å in the hydride[6]], but it is expected that a change from a one-electron to a three-electron donor bridge would lead formally to a change from a single Os–Os bond to a non-bond. The greater Os–Os distance has some consequences in the bond lengths and angles associated with the μ-η^2-vinyl but not enough to affect this ligand bridge grossly. For example, the angle Os(1)–C(1)–C(2) opens up from 121.3(2) to 125(1)° on going from the hydride to complex (**3**). The C(1)–Os(3) distance increases from 2.273(3) to 2.343(14) Å and the C(1)–Os(1)–Os(3) angle changes from 52.1(1) to 44.4(4)° on going to compound (**3**). The $CH{=}CH_2$ ligand is stretched out further across the two metal atoms in (**3**) but it is not obvious why there is a much closer bunching of ^1H n.m.r. chemical shifts.

Different configurations have been observed in compounds of type $[Os_3H(CR{=}CHR)(CO)_{10}]$ corresponding to (**3a**) when R = Ph[7] and to (**3b**) when R = H.[6] In crystals of compound (**3**) the observed configuration is (**3b**) and no evidence was observed for (**3a**).

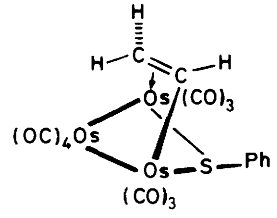
Thermolysis and Photolysis of $[Os_3(SPh)(CH{=}CH_2)(CO)_{10}]$ (**3**).—Attempts to decarbonylate the cluster (**1**) led to decomposition and no isolable products were obtained. In contrast, treatment of $[Os_3(SPh)(CH{=}CH_2)(CO)_{10}]$ in refluxing heptane, in refluxing light petroleum (b.p. 120—160 °C), or by u.v. photolysis in cyclohexane at room temperature gave low to moderate yields of compounds (**5**)—(**10**) and small quantities of

Table 2. Selected bond lengths (Å) and angles (°) for [Os_3(SPh)-($CH{=}CH_2$)$(CO)_{10}$] (**3**)

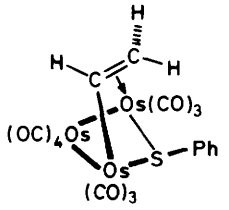
Os(1)–Os(2)	2.898(1)	Os(1)–C(11)	1.909(17)
Os(2)–Os(3)	2.965(1)	Os(1)–C(12)	1.968(17)
		Os(1)–C(13)	1.908(22)
Os(1) ··· Os(3)	3.328(1)	Os(2)–C(21)	2.018(16)
Os(1)–S	2.459(4)	Os(2)–C(22)	1.915(20)
Os(3)–S	2.446(4)	Os(2)–C(23)	1.912(19)
S–C(111)	1.794(20)	Os(2)–C(24)	1.883(17)
Os(1)–C(1)	2.118(13)	Os(2)–C(31)	1.939(23)
Os(3)–C(1)	2.343(14)	Os(3)–C(32)	1.908(17)
Os(3)–C(2)	2.339(14)	Os(3)–C(33)	1.900(15)
C(1)–C(2)	1.39(3)		

Average C–O 1.134(28)
Average C–C(aryl) 1.38(4)

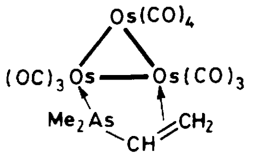
Os(3)–Os(2)–Os(1)	69.2(1)	C(2)–Os(3)–C(1)	34.5(6)
Os(2)–Os(3)–Os(1)	54.5(1)	Os(3)–C(1)–Os(1)	96.4(5)
Os(3)–Os(1)–Os(2)	56.4(1)	C(2)–C(1)–Os(3)	72.6(9)
S–Os(1)–Os(3)	47.1(1)	C(1)–C(2)–Os(3)	72.9(8)
S–Os(3)–Os(1)	47.4(1)	C(2)–C(1)–Os(1)	125(1)
S–Os(1)–Os(2)	80.8(1)	C(11)–Os(1)–Os(2)	168.7(4)
S–Os(3)–Os(2)	79.6(1)	C(13)–Os(1)–S	167.0(6)
Os(3)–S–Os(1)	85.4(1)	C(1)–Os(1)–C(12)	169.7(6)
C(111)–S–Os(1)	112.9(6)	C(31)–Os(3)–Os(2)	172.0(5)
C(111)–S–Os(3)	115.4(6)	C(32)–Os(3)–S	164.9(6)
C(1)–Os(1)–Os(3)	44.4(4)	C(1)–Os(3)–C(33)	153.0(7)
C(1)–Os(3)–Os(1)	39.2(3)	C(2)–Os(3)–C(33)	170.0(8)
C(2)–Os(3)–Os(1)	64.4(4)		



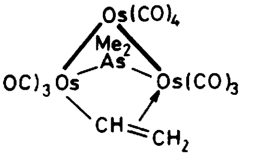
(**3a**)



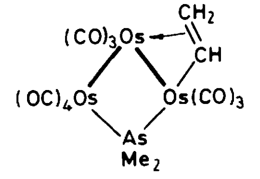
(**3b**)



(**4a**)



(**4b**)



(**4c**)

other species which we were unable to characterise. Compounds (**5**)—(**10**) were characterised by data in Table 1 and the Experimental section. In each case we have established the stoicheiometry but in general we have no firm evidence for structure.

Compound [Os_3H(SPh)($C{=}CH_2$)$(CO)_9$] (**5**) is a simple decarbonylation product of (**3**) formed analogously to [Os_3H_2-($C{=}CH_2$)$(CO)_9$] from [Os_3H($CH{=}CH_2$)$(CO)_{10}$].[5] Compound

Table 3. Fractional atomic co-ordinates for [Os_3(SPh)($CH{=}CH_2$)-$(CO)_{10}$] (**3**)

Atom	*x*	*y*	*z*
Os(1)	0.206 59(4)	0.262 88(6)	0.194 45(4)
Os(2)	0.159 24(4)	−0.000 56(7)	0.269 86(4)
Os(3)	0.234 28(4)	−0.079 18(6)	0.131 76(4)
S	0.330 5(2)	0.111 8(4)	0.217 4(2)
C(11)	0.229 0(9)	0.416 4(17)	0.122 4(11)
O(11)	0.236 5(9)	0.502 1(12)	0.072 7(8)
C(12)	0.265 2(12)	0.351 2(18)	0.314 9(13)
O(12)	0.301 3(9)	0.405 5(14)	0.382 2(8)
C(13)	0.100 2(13)	0.338 7(19)	0.181 8(13)
O(13)	0.038 8(9)	0.387 0(16)	0.177 5(12)
C(21)	0.270 8(11)	0.019 5(19)	0.369 2(13)
O(21)	0.329 6(8)	0.029 6(17)	0.425 8(8)
C(22)	0.108 8(10)	0.106 3(18)	0.342 5(12)
O(22)	0.077 3(9)	0.168 7(17)	0.383 4(10)
C(23)	0.143 2(12)	−0.198 9(21)	0.302 8(12)
O(23)	0.135 6(10)	−0.315 6(15)	0.325 2(10)
C(24)	0.058 1(13)	0.004 5(20)	0.171 6(11)
O(24)	−0.009 0(8)	0.007 9(16)	0.112 4(9)
C(31)	0.292 2(13)	−0.151 1(20)	0.053 7(12)
O(31)	0.321 6(9)	−0.207 7(16)	0.008 9(10)
C(32)	0.138 8(12)	−0.196 4(18)	0.072 7(11)
O(32)	0.082 2(8)	−0.268 6(15)	0.039 0(10)
C(33)	0.280 9(11)	−0.222 6(17)	0.224 4(11)
O(33)	0.309 7(9)	−0.310 9(14)	0.275 9(9)
C(1)	0.157 8(10)	0.135 2(15)	0.073 8(9)
C(2)	0.199 7(10)	0.098 1(16)	0.015 3(9)
C(111)	0.396 6(10)	0.187 0(22)	0.161 8(11)
C(112)	0.416 7(13)	0.338 0(25)	0.174 9(17)
C(113)	0.472 4(15)	0.397 2(33)	0.138 4(20)
C(114)	0.507 8(16)	0.309 2(44)	0.088 7(17)
C(115)	0.491 7(18)	0.165 8(44)	0.082 5(18)
C(116)	0.432 6(14)	0.101 5(33)	0.116 4(17)

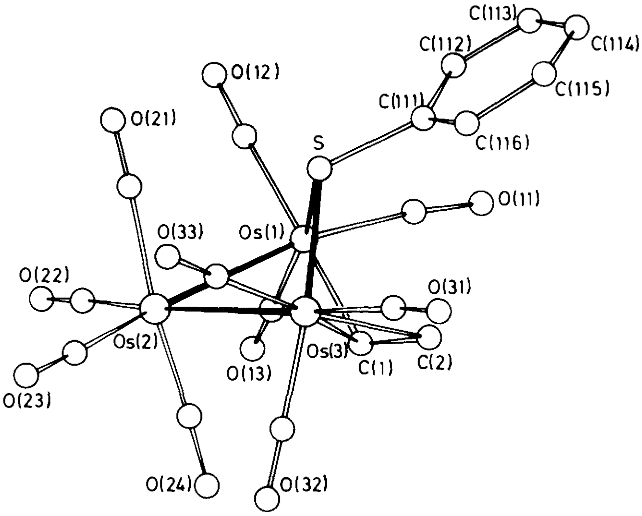
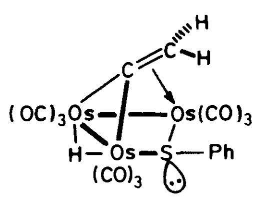


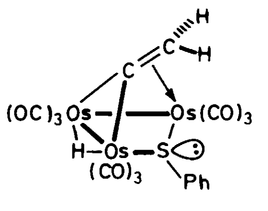
Figure. Molecular structure of [Os_3(SPh)($CH{=}CH_2$)$(CO)_{10}$] (**3**). The Os(1) ··· Os(3) distance is 3.328(1) Å. The numbering of the C atoms is the same as that of the relevant O atoms

(**5**) exists as two isomers in mol ratio 3 : 2 which are rapidly interconverting at 20 °C but which give separate ^1H n.m.r. signals at −50 °C (Table 1). We believe this isomerism is due to inversion at sulphur so that the isomers are (**5a**) and (**5b**), analogous to the interconverting isomers observed for [Os_3H-(SMe)(C_6H_4)$(CO)_9$].[3] The overall structure proposed for (**5**) is based on that established by *X*-ray diffraction for [Os_3H(OH)-($C{=}C{=}CPh_2$)$(CO)_9$].[8]

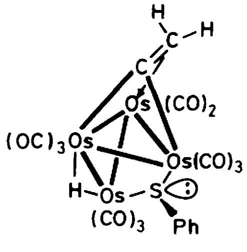
The other two products obtained from (**3**) in refluxing



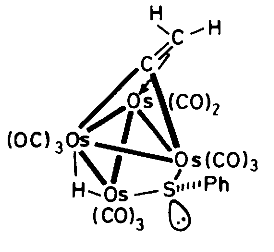
(5a)



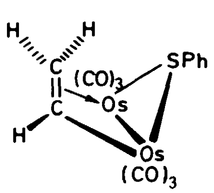
(5b)



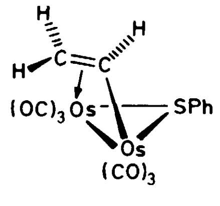
(6a)



(6b)



(7a)



(7b)

heptane, $[Os_4H(SPh)(C{=}CH_2)(CO)_{11}]$ (**6**) and $[Os_2(SPh)(CH{=}CH_2)(CO)_6]$ (**7**), are probably formed together in the transfer of an $Os(CO)_x$ group from one trinuclear cluster to another. Compound (**7**) relates to $[Fe_2(SR)(CH{=}CH_2)(CO)_6]$ (R = Me, Et, *etc.*) formed from $RSCH{=}CH_2$ and $[Fe_3(CO)_{12}]$.[9] Since (**7**) exists as two inseparable isomers (mol ratio 1 : 3) which do not interconvert rapidly enough to give any n.m.r. line-broadening, we propose structures (**7a**) and (**7b**) rather than isomers related by inversion at sulphur. Isomers are also observed for the tetranuclear species (**6**) (mol ratio 5 : 1) and (**6a**) and (**6b**) are tentative suggestions for these. Assuming that SPh is a three-electron donating bridge and that the vinylidene ligand is triply bridging, the Os_4 cluster should adopt an open butterfly rather than a closed tetrahedral arrangement.

Compounds (**8**)—(**10**) were formed by thermolysis at higher temperatures. Their structures are unknown.

Experimental

The starting materials $[Os_3H_2(CO)_{10}]$[10] and $[Os_3(CO)_{10}(MeCN)_2]$[11] were prepared as described previously. Phenyl vinyl sulphide was used as purchased (Aldrich).

Reaction of $[Os_3H_2(CO)_{10}]$ *with* $PhSCH{=}CH_2$.—A solution of $PhSCH{=}CH_2$ (0.30 cm^3, 2.3 mmol) and purple $[Os_3H_2(CO)_{10}]$ (0.20 g, 0.23 mmol) in cyclohexane (50 cm^3) was stirred under nitrogen at room temperature for 2 h to give a clear yellow solution. Removal of the solvent under vacuum and chromatography of the residue [t.l.c., SiO_2; eluant: light petroleum (b.p. 30—40 °C)] gave one main yellow band which was extracted with dichloromethane. Removal of the solvent gave $[Os_3H(PhSCHMe)(CO)_{10}]$ (**1**), as a deep yellow oil (0.199 g, 90%) which crystallised only with difficulty on treating with hexane (Found: C, 22.3; H, 1.1; S, 2.9. $C_{18}H_{10}O_{10}Os_3S$ requires C, 21.85; H, 1.0; S, 3.25%). A trace of the known cluster $[Os_3H(SPh)(CO)_{10}]$ (**2**) was also obtained as yellow crystals (0.006 g, 3%) (Found: C, 20.4; H, 0.8; S, 3.75. $C_{16}H_6O_{10}Os_3S$ requires C, 20.0; H, 0.65; S, 3.35%).

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ *with* $PhSCH{=}CH_2$.—A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.10 g, 0.107 mmol) and $PhSCH{=}CH_2$ (0.20 cm,^{3} 1.5 mmol) in dichloromethane (25 cm^3) was stirred under nitrogen at room temperature for 4 h by which time the starting material had been consumed (i.r. evidence). The solvent was removed under vacuum and the residue separated by t.l.c. [SiO_2; eluant: light petroleum (b.p. 30—40 °C)]. On evaporation of a dichloromethane extract of the major yellow band, bright yellow crystals (0.036 g, 34%) of $[Os_3(SPh)(CH{=}CH_2)(CO)_{10}]$ (**3**) were obtained (Found: C, 21.95; H, 0.85; S, 3.5. $C_{18}H_8O_{10}Os_3S$ requires C, 21.9; H, 0.8; S, 3.25%).

Thermal and Photochemical Degradation of $[Os_3(SPh)(CH{=}CH_2)(CO)_{10}]$ (**3**).—(*a*) *Thermolysis in refluxing n-heptane.* A solution of compound (**3**) (0.148 g) in n-heptane (30 cm^3) was heated under reflux under nitrogen for 4 h. Removal of the solvent gave a residue which was separated by t.l.c. [SiO_2; eluant: light petroleum (b.p. 30—40 °C)] to give four main products. The cluster $[Os_3H(SPh)(C{=}CH_2)(CO)_9]$ (**5**) was obtained as a colourless solid (0.025 g, 17%) (Found: C, 21.4; H, 0.9; S, 3.4. $C_{17}H_8O_9Os_3S$ requires C, 21.3; H, 0.85; S, 3.35%) [*m/e* ($^{192}Os_3$), 964], $[Os_4H(SPh)(C{=}CH_2)(CO)_{11}]$ (**6**) as red needles (0.014 g, 8%) (Found: C, 18.85; H, 0.7; S, 2.8. $C_{19}H_8O_{11}Os_4S$ requires C, 18.95; H, 0.65; S, 2.65%) [*m/e* ($^{192}Os_4$), 1 212], $[Os_2(SPh)(CH{=}CH_2)(CO)_6]$ (**7**) as a pale yellow solid (0.011 g, 11%) [*m/e* ($^{192}Os_2$), 688], and $[Os_3H(SPh)(CO)_{10}]$ (**2**) as yellow crystals (0.002 g, 1%).

(*b*) *Thermolysis in refluxing light petroleum* (*b.p.* 120—160 °C). A solution of compound (**3**) (0.102 g) was heated under reflux under nitrogen for 12 h. Chromatographic separation as above gave four main products: compound $[Os_2(SPh)(CH{=}CH_2)(CO)_6]$ (**7**) was obtained contaminated with $[Os_3H_2(C{=}CH_2)(CO)_9]$ (i.r. and n.m.r. evidence) (0.014 g total), $[Os_3H(SC_6H_4)(CH{=}CH_2)(CO)_9]$ (**8**) as a yellow powder (0.018 g, 18%), $[Os_3(SPh)(CMe)(CO)_9]$ (**9**) as orange crystals (0.007 g, 7%) [*m/e* ($^{192}Os_3$), 954], and $[Os_2(SC_6H_4)(CH{=}CH)(CO)_6]$ (**10**) as an orange solid (0.004 g, 6%) [*m/e* ($^{192}Os_2$), 686].

(*c*) *Photolysis.* Irradiation of a bright yellow solution of compound (**3**) (0.174 g) in cyclohexane (50 cm^3) (Philips 80 W u.v. lamp) under nitrogen for 1 h gave a cloudy orange solution containing none of compound (**3**). Work-up as before gave three identifiable products: $[Os_3H(SPh)(C{=}CH_2)(CO)_9]$ (**5**) as a white solid (0.053 g, 32%), $[Os_4H(SPh)(C{=}CH_2)(CO)_{11}]$ (**6**) as red needles (0.013 g, 6%), and $[Os_2(SPh)(CH{=}CH_2)(CO)_6]$ (**7**), as a pale yellow solid (0.013 g, 11%).

X-*Ray Structure Determination of* $[Os_3(SPh)(CH{=}CH_2)(CO)_{10}]$ (**3**).—*Crystal data.* $C_{18}H_8O_{10}Os_3S$, $M = 986.92$, monoclinic, space group $P2_1/c$ (no. 14), $a = 17.291(4)$, $b = 9.039(3)$, $c = 15.614(3)$ Å, $\beta = 110.40(3)°$, $U = 2\,287.28$ Å^3, $D_c = 2.865$ g cm^{-3}, $Z = 4$, $F(000) = 1\,760$, $\mu(Mo\text{-}K_\alpha) = 161.03$ cm^{-1}.

The crystal selected for data collection was a yellow plate of dimensions *ca.* 0.21 × 0.21 × 0.03 mm. Data were collected in the θ range 3—25° on a Philips PW1100 diffractometer with a scan width of 0.8°. 310 Azimuthal scan data were used in absorption correction and relative transmission factors varied from 1.00 to 0.20. Equivalent reflections were merged to give 3 011 data with $I/\sigma(I) \geqslant 3.0$. The methods of data collection, data processing, and absorption correction have been described previously.[12]

Structure solution and refinement.[13] The osmium atom positions were found from a Patterson synthesis and the non-hydrogen atoms from subsequent difference-Fourier syntheses. Anisotropic thermal parameters were assigned to all atoms in the final cycles of full-matrix least-squares refinement. Refinement converged at R 0.0429 and R' 0.0416 with $w = 1/\sigma^2(F)$. The hydrogen atoms of the phenyl rings were included at calculated positions (C–H 1.08 Å). There were a few relatively high residual peaks (*ca.* 3 e Å^{-3}) in the vicinity of the osmium atoms in the final difference-Fourier map. These are possibly due to the absorption corrections inadequately compensating for the very large variation in transmission factor observed for the plate-like crystals.

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