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Triosmium and triruthenium clusters containing the 4-methylthiazolide ligand: crystal structures of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})]$, $[Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(PPh_3)]$ and $[Os_3(\mu\text{-}H)(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(PPh_3)_2]$

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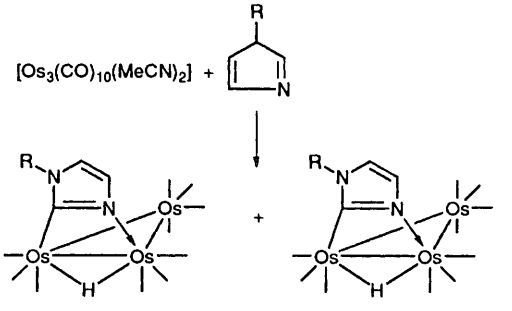
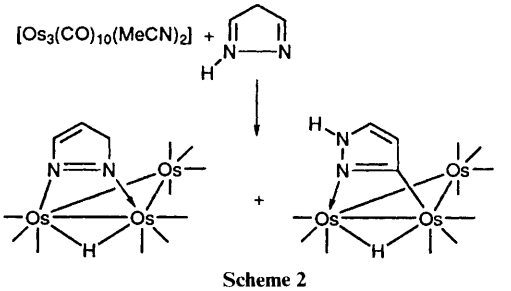
The reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 4-methylthiazole at room temperature gave $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})]$ **1**, in which the thiazolide ligand is co-ordinated to the cluster through the nitrogen and carbon atoms of the C=N bond, in high yield. Compound **1** reacted with PPh_3 at 110 °C to give $[Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(PPh_3)]$ **2** and $[Os_3(\mu\text{-}H)(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(PPh_3)_2]$ **3**. Compound **2** exists as two isomers in solution whereas **3** exists as four. The reaction of **2** with PPh_3 at 110 °C yielded **3** in good yield. Compound **1** reacted with 4-methylthiazole at 110 °C to give $[Os_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(\mu\text{-}1,5\text{-}\eta^2\text{-}\overline{CH{=}NCMe{=}CS})]$ **4** and $[Os_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})_2]$ **5**. In **4** the second thiazolide ligand is co-ordinated through the sulfur and C(5) carbon atoms whereas in **5** both ligands are co-ordinated through the nitrogen and C(2) carbon atoms. The reaction of $[Ru_3(CO)_{12}]$ with 1 equivalent of 4-methylthiazole in the presence of sodium–benzophenone at 67° C gave $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})]$ **6** whereas with 2 equivalents it gave $[Ru_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})_2]$ **7**. Compounds **6** and **7** are the structural analogues of **1** and **4** respectively. The reaction of **6** with 1 equivalent of 4-methylthiazole in the presence of sodium–benzophenone gave **7**. All the compounds were characterized by ^1H NMR and infrared spectroscopy and elemental analysis. In addition, the solid-state structures for **1**–**3** were determined.

In recent years the reactions of $[Ru_3(CO)_{12}]$, $[Os_3(CO)_{12}]$ and the lightly stabilized cluster $[Os_3(CO)_{10}(MeCN)_2]$ with a wide variety of aromatic and aliphatic nitrogen heterocycles to give C–H and N–H activated products have extensively been investigated.[1–16] These reactions continue to attract interest and have been the subject of numerous studies, as the sequence and factors controlling the rate of activation of C–H and N–H bonds of nitrogen-containing heterocycles by trinuclear clusters of ruthenium and osmium have relevance to modelling important industrial catalytic processes.[1] The analogous reactions of S-containing heterocycles with triosmium and triruthenium clusters have also received attention because these have relevance to the hydrodesulfurization process.[17] However, there are very few studies of the interaction of such clusters with N- and S-containing heterocycles.

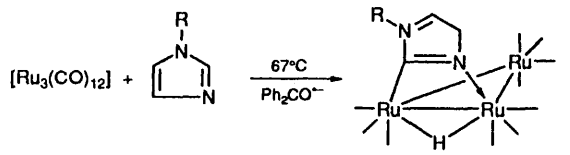
We[16] and others[15] have previously reported that the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with imidazole and related ligands afforded two isomeric compounds $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}3,4\text{-}\eta^2\text{-}\overline{CH{=}NCH{=}CHNR}\}]$ and $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCH{=}CHNR})]$ (Scheme 1), formed by activation of one of the two C–H bonds adjacent to the imino nitrogen atom. On the other hand, when this bis(acetonitrile)triosmium cluster was treated with pyrazole two isomeric compounds $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}1,2\text{-}\eta^2\text{-}\overline{CH{=}CHCH{=}NN})]$ and $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}CHCHNHN})]$ were obtained by the activation of the N–H and C(3)–H bonds respectively (Scheme 2). In contrast, with $[Ru_3(CO)_{12}]$ in the presence of sodium–benzophenone the C(2)–H activated cluster $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCH{=}CHNR})]$ was the only product (Scheme 3).[16]



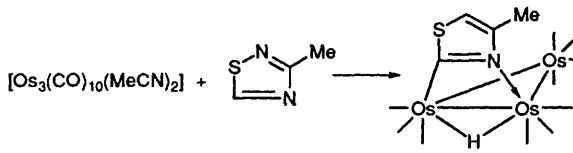
Scheme 1 R = $CH{=}CH_2$ or H



Scheme 2



Scheme 3



Scheme 4

The reactivities of organic heterocycles containing N and S atoms such as pyridine-2-thione,[18] thioamide[19] and pyrimidine-2-thione[20] towards metal carbonyl clusters have been reported. To our knowledge the reactions of thiazoles with triosmium clusters has not been explored so far. The co-ordination of a thiazolyl to a diiron cluster has recently been reported.[21] We report here the results of our investigation of the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ and $[Ru_3(CO)_{12}]$ with 4-methylthiazole, a heterocycle containing both nitrogen and sulfur as heteroatoms. We also describe the reaction of the 4-methylthiazolide cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})]$ **1** with 4-methylthiazole and PPh_3 as well as the crystal structure of **1** and its mono- and bis-phosphine derivatives.

Results and Discussion

The lightly stabilized cluster $[Os_3(CO)_{10}(MeCN)_2]$ readily reacts with 4-methylthiazole at room temperature leading to the formation of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})]$ **1** in 78% yield (Scheme 4). The infrared spectrum of **1** in the ν(CO) stretching region indicates that only terminal carbonyl groups are present. The structure of **1** can be partially inferred from the ^1H NMR spectrum which in addition to the singlet hydride resonance at δ −14.76 exhibits two signals, a quartet at δ 6.57 and a doublet at δ 2.21 with a relative integrated intensity of 1 : 3 respectively. The observation of the ring proton signal as a quartet and the methyl signal as a doublet is consistent with the activation of the C(2)–H proton of the ligand because for the C(5)–H activated product the C(2)–H proton is isolated by the nitrogen and would not exhibit coupling. Although the ^1H NMR data indicate activation of the C(2)–H proton and subsequent co-ordination of the C(2) carbon to the metal, we could not be certain that heteroatom was co-ordinated to the metal.

Confirmation of the proposed structure of compound **1** based on the ^1H NMR data has been obtained by a crystal structure determination. The solid-state structure is shown in Fig. 1, and selected bond distances and angles are in Table 1. The molecule consists of a triangular metal core with three distinct metal–metal bond lengths [Os(1)–Os(2) 2.8849(8), Os(2)–Os(3) 2.9340(8) and Os(1)–Os(3) 2.8590(7) Å]. The organic ligand is η^2-co-ordinated to the longest Os–Os edge bridged by the hydride through a metal–carbon σ bond and a two-electron donor bond from the nitrogen. The C(11)–N bond length of 1.30(2) Å is typical of carbon–nitrogen double bonds in the related triosmium and triruthenium decarbonyl μ-imidoyl complexes[11,14] while the C(12)–N bond length of 1.41(2) Å is consistent with it being a single bond. The Os(2)–C(11) distance of 2.105(12) Å and the Os(3)–N distance of 2.166(11) Å are also similar to those of the μ-imidoyl clusters $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}\eta^2\text{-}\overline{C{=}N(CH_2)_n}\}]$ (n = 3 or 4)[14] and $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}RC{=}NMe)]$[22] (R = Me or Ph). Thus, the overall structure of **1** including the disposition of the carbonyl groups and the probable position of the hydride ligand is similar to those of the previously reported μ-imidoyl decarbonyl clusters of osmium and ruthenium.[11,14]

In contrast to the μ-imidoyl triosmium clusters which decarbonylate both thermally and photochemically to the μ_3-imidoyls, compound **1** is remarkably resistant to thermal and photochemical decarbonylation (see Experimental section).

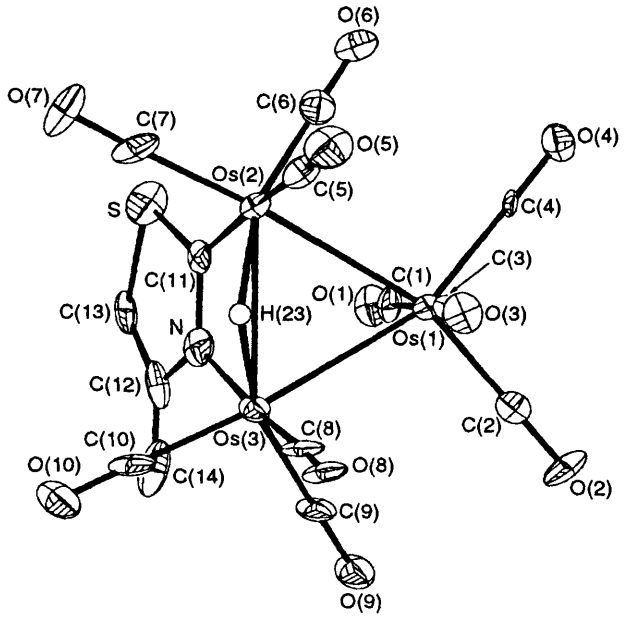
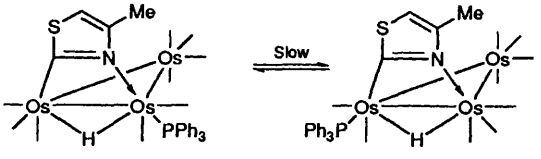


Fig. 1 Molecular structure of the cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})]$ **1** showing the possible position of the hydride (located but not refined)



2a **2b**

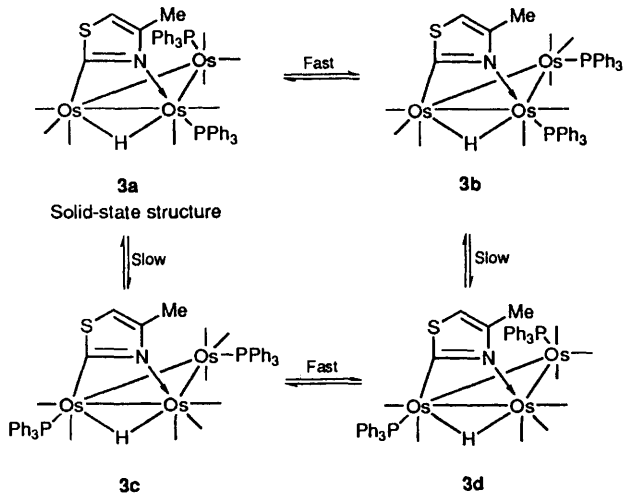
Solid-state structure

Scheme 5

Table 1 Selected bond distances (Å) and angles (°) for compound **1**[a]

Os(1)–Os(2)	2.8849(8)	Os(3)–H(23)	1.81
Os(2)–Os(3)	2.9340(8)	C(11)–N	1.30(2)
Os(1)–Os(3)	2.8590(7)	C(11)–S	1.717(12)
Os(2)–C(11)	2.105(12)	C(13)–S	1.772(13)
Os(3)–N	2.166(11)	C(13)–C(12)	1.38(2)
Os–C(CO)[b]	1.92(12)	C(12)–N	1.41(2)
C–O(CO)[b]	1.145(13)	C(12)–C(14)	1.23(2)
Os(2)–H(23)	1.91		
Os(3)–Os(1)–Os(2)	61.43(2)	Os(2)–Os(3)–N	67.7(3)
Os(1)–Os(3)–Os(2)	59.72(2)	C(11)–S–C(13)	89.1(6)
Os(1)–Os(2)–Os(3)	58.85(2)	S–C(13)–C(12)	112.4(10)
Os–C–O(CO)[b]	177.7(10)	C(13)–C(12)–N	108.3(13)
Os(3)–Os(2)–C(7)	116.6(4)	C(12)–N(1)–C(11)	117.4(11)
Os(2)–Os(3)–C(10)	114.9(3)	N–C(11)–S	112.7(9)
Os(3)–Os(2)–C(11)	67.2(3)	Os–C–O(CO)[b]	117.7(10)

[a] Numbers in parentheses are estimated standard deviations. [b] Average value.



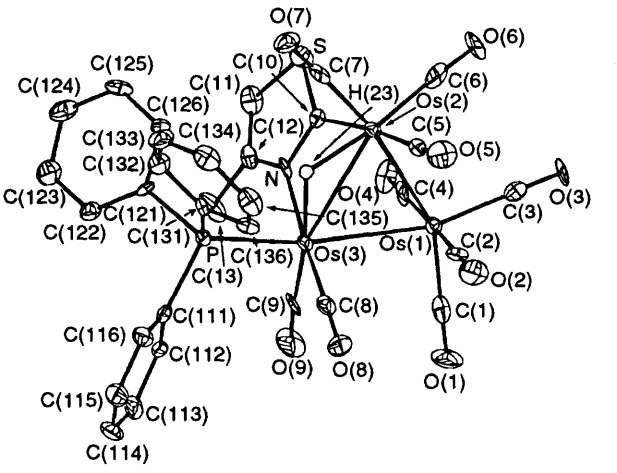


Fig. 2 Molecular structure of the cluster $[Os_3(\mu\text{-H})(CO)_9(\mu\text{-2,3-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(PPh_3)]$ **2** showing the possible position of the hydride (located but not refined)

However, it reacts with triphenylphosphine at 110 °C to give the mono- and bis-phosphine-substituted products $[Os_3(\mu\text{-H})(CO)_9(\mu\text{-2,3-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(PPh_3)]$ **2** and $[Os_3(\mu\text{-H})(CO)_8(\mu\text{-2,3-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(PPh_3)_2]$ **3** in 25 and 40% yields respectively (Schemes 5 and 6). The ^1H NMR spectrum of **2** exhibits two sets of hydride doublets at δ −14.24 and −13.95 as well as two sets of signals for the ring proton (δ 6.20 and 6.26) and methyl protons (δ 1.52 and 2.14) of the organic ligand in a relative intensity 5.6:1 indicating the presence of two isomers (**2a** and **2b**) in solution. The appearance of the hydride signals as doublets and the nearly equal and relatively large phosphorus–hydrogen coupling[23,24] (11.6, **2a**; 11.4 Hz, **2b**) suggests that the phosphine occupies stereochemically similar positions relative to the hydride and therefore that the two isomers probably differ by substitution at the nitrogen-bound (**2a**) *versus* the carbon-bound osmium atom (**2b**). This type of isomerism has been reported in related phosphine substituted imidoyl clusters.[24] Although the ^1H NMR data indicate the relationship between the hydride ligand and the phosphine, we could not be certain that the relationship between the hydride and the organic ligand is the same in **2** as in **1**. We therefore undertook a solid-state structural investigation of the crystals obtained from this isomeric mixture.

The solid-state structure of this isomeric product revealed it to indeed have the structure proposed for isomer **2a**. The structure of **2a** is shown in Fig. 2 and selected bond distances and angles are in Table 2. As proposed from the ^1H NMR data, the phosphine is cisoid to the hydride and substituted on the same osmium as that bound to the nitrogen of the thiazolide ligand. The overall structure is similar to that of **1** with only slight elongation in the Os(2)–Os(3) bond [2.9674(9) in **2** and 2.9340(8) Å in **1**]. The phosphine substitution on the nitrogen-bound osmium causes a slight shortening of the Os(3)–N bond [2.143(7) in **2a** and 2.166(11) Å in **1**] while the osmium–carbon and carbon–nitrogen bonds are very similar to those of **1**. The hydride ligand was located and found to bridge along the Os(2)–Os(3) edge which is also bridged by the thiazolide ligand. We assume that **2a** is the major isomer in solution. Its structure is virtually identical to those of $[Os_3(\mu\text{-H})(CO)_9(\mu\text{-}\eta^2\text{-}\overline{C{=}NCH_2CH_2CH_2})(PPh_3)]$,[24] $[Os_3(\mu\text{-H})(CO)_9(\mu\text{-}\eta^2\text{-PhN=CH})\{P(OMe)_3\}]$[25] and $[Os_3(\mu\text{-H})(CO)_9(\mu\text{-}\eta^2\text{-}F_3CC{=}NH)(PMe_2Ph)]$.[26] The cluster $[Os_3(\mu\text{-H})(CO)_9(\mu\text{-}\eta^2\text{-}\overline{C{=}NCH_2CH_2CH_2})(PPh_3)]$ was obtained from the reaction of $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^2\text{-}\overline{C{=}NCH_2CH_2CH_2})]$ with PPh_3 at 100 °C as well as from the thermal rearrangement of its isomer in which the phosphine was substituted on the unbridged osmium atom,[24] whereas $[Os_3(\mu\text{-H})(CO)_9(\mu\text{-}\eta^2\text{-PhN=CH})\{P(OMe)_3\}]$[25] and $[Os_3(\mu\text{-H})(CO)_9(\mu\text{-}\eta^2\text{-}F_3CC{=}NH)(PMe_2Ph)]$[26] were obtained from the reaction of $[Os_3(\mu\text{-H})(CO)_9(\mu_3\text{-}\eta^2\text{-PhC=NH})]$ with $P(OMe)_3$ and of $[Os_3(\mu\text{-H})_2(CO)_9(PMe_2Ph)]$ with CF_3CN respectively. In the former, the triphenylphosphine and trimethyl phosphite are substituted at the carbon-bound osmium atom while in the latter the dimethylphenylphosphine is substituted at the nitrogen-bound osmium atom. Prior studies suggest that isomers such as **2a** and **2b** are interconverted by a relatively slow phosphine dissociation–association process.[14]

Table 2 Selected bond distances (Å) and angles (°) for compound **2**

Os(1)–Os(2)	2.8779(9)	C–O(CO)*	1.139(12)
Os(2)–Os(3)	2.9674(9)	C(10)–N	1.330(11)
Os(1)–Os(3)	2.8619(13)	C(10)–S	1.715(10)
Os(3)–N	2.143(7)	C(12)–N	1.417(12)
Os(2)–C(10)	2.111(9)	C(12)–C(13)	1.484(13)
Os(3)–P	2.376(3)	C(11)–S	1.744(10)
Os(3)–H(23)	1.84	C(12)–C(11)	1.315(14)
Os(2)–H(23)	1.71	P–C(Ph)*	1.853(4)
Os–C(CO)*	1.931(12)		
Os(1)–Os(2)–Os(3)	58.61(3)	C(10)–S–C(11)	90.2(5)
Os(3)–Os(1)–Os(2)	62.26(3)	C(10)–N(1)–C(12)	113.0(8)
Os(1)–Os(3)–Os(2)	59.14(3)	Os(3)–P–C(121)	117.8(2)
Os(2)–Os(3)–N	58.3(2)	Os(3)–P–C(131)	113.6(2)
Os(3)–Os(2)–C(10)	66.4(3)	Os(3)–P–C(111)	113.3(2)
C(12)–C(11)–S	111.8(8)	C(121)–P–C(111)	104.2(3)
N–C(10)–S	112.0(7)	C(121)–P–C(131)	101.7(3)
C(11)–C(12)–N	121.2(9)	Os–C–O(CO)*	176.5(9)

* Average value.

The ^1H NMR spectrum of compound **3** at −50 °C revealed the presence of four isomers in solution. We performed an X-ray crystallographic investigation of **3** in order to ascertain the disposition of the hydride, the thiazolide ligand and the phosphine ligands of the isomer that crystallized. The solid-state structure of **3** is represented in Fig. 3, and selected bond lengths and angles are in Table 3. The structure reveals that one phosphine ligand is substituted on the osmium atom bound to the nitrogen of the thiazolide ligand while the other is substituted on the unbridged osmium atom Os(2) and occupies an equatorial position along with three carbonyl ligands. The molecule consists of an osmium triangle with three distinctly different metal–metal bonds [Os(1)–Os(2) 2.9050(6), Os(2)–Os(3) 2.9528(6) and Os(1)–Os(3) 2.8795(6) Å]. The overall structure is identical to that of **2**. The substitution of a second phosphine ligand at the remote metal atom causes a significant elongation of the Os(1)–Os(2) bond and a shortening of the Os(2)–C (thiazolide) bond. The hydride ligand bridges the Os(2)–Os(3)

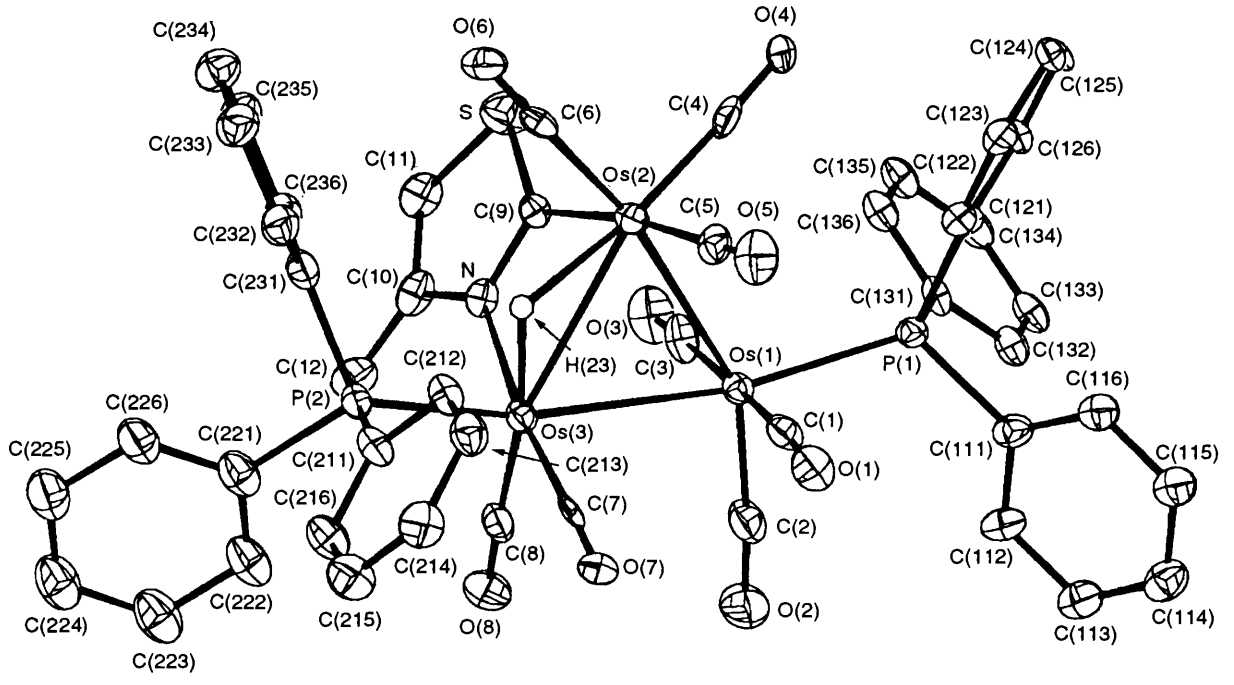


Fig. 3 Molecular structure of the cluster $[Os_3(\mu\text{-H})(CO)_8(\mu\text{-2,3-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(PPh_3)_2]$ **3** showing the possible position of the hydride (located but not refined)

Table 3 Selected bond distances (Å) and angles (°) for compound **3a**

Os(1)–Os(2)	2.9050(6)	Os–C(CO)*	1.906(12)
Os(2)–Os(3)	2.9528(6)	C–O(CO)*	1.150(12)
Os(1)–Os(3)	2.8795(6)	C(9)–S	1.716(10)
Os(2)–C(9)	2.082(10)	C(9)–N	1.328(11)
Os(3)–N	2.166(7)	C(10)–N	1.413(13)
Os(1)–P(1)	2.364(3)	C(10)–C(11)	1.369(13)
Os(3)–P(2)	2.395(3)	C(11)–S	1.749(11)
Os(3)–H(23)	1.87	P(1)–C(Ph)*	1.846(5)
Os(2)–H(23)	1.92	P(2)–C(Ph)*	1.838(5)
Os(3)–Os(1)–Os(2)	61.39(2)	Os(3)–P(2)–C(231)	116.8(2)
Os(1)–Os(3)–Os(2)	59.73(1)	Os(1)–P(1)–C(111)	113.1(2)
Os(1)–Os(2)–Os(3)	58.88(1)	Os(1)–P(1)–C(121)	119.6(2)
Os(3)–Os(2)–C(9)	67.3(3)	Os(1)–P(1)–C(131)	115.1(2)
Os(2)–Os(3)–N	67.6(2)	C(221)–P(2)–C(231)	102.4(3)
C(9)–N(1)–C(10)	116.4(8)	C(231)–P(2)–C(211)	104.3(3)
C(9)–S–C(11)	91.1(5)	C(221)–P(2)–C(221)	102.9(3)
N–C(9)–S	110.8(7)	C(131)–P(1)–C(111)	104.2(3)
S–C(11)–C(10)	111.7(8)	C(111)–P(1)–C(121)	100.9(3)
C(11)–C(10)–N	110.0(9)	C(131)–P(1)–C(121)	101.9(3)
Os(3)–P(2)–C(211)	108.4(3)	Os–C–O(CO)*	176.2(9)
Os(3)–P(2)–C(221)	120.2(3)		

* Average value.

edge and the phosphine at the remote metal atom is *syn* to the carbon atom of the thiazolide ligand. Utilizing this structure we can now interpret the ^{1}H NMR data for **3**. The low-temperature limiting ^{1}H NMR spectrum at 400 MHz in $CDCl_3$ at −50 °C contains four hydride doublets at δ −14.04 ($J_{PH} \approx 12.0$), −14.02 ($J_{PH} = 12.0$), −13.88 ($J_{PH} = 11.6$) and −13.58 ($J_{PH} = 11.6$ Hz) [Fig. 4(*a*)] with relative intensities 1 : 6.4 : 1 : 0.6 as well as four singlets at 6.14, 6.16, 6.18 and 6.24 ppm for the ring proton [Fig. 4(*b*)] and four methyl proton resonances at δ 1.37, 1.42, 2.01 and 2.05 in similar relative integrated intensities. The ring and methyl proton resonances are slightly broadened rendering coupling between them unresolvable. As the temperature is increased to +25 °C the doublet resonances at δ −14.04 and −14.02 average to a doublet at δ −14.03 while the doublets at δ −13.88 and −13.58 broaden into the baseline [Fig. 4(*a*)]. The ring proton signals at δ 6.14 and 6.18 average to a singlet at δ 6.15 and the singlets at 6.16 and 6.24 average to a

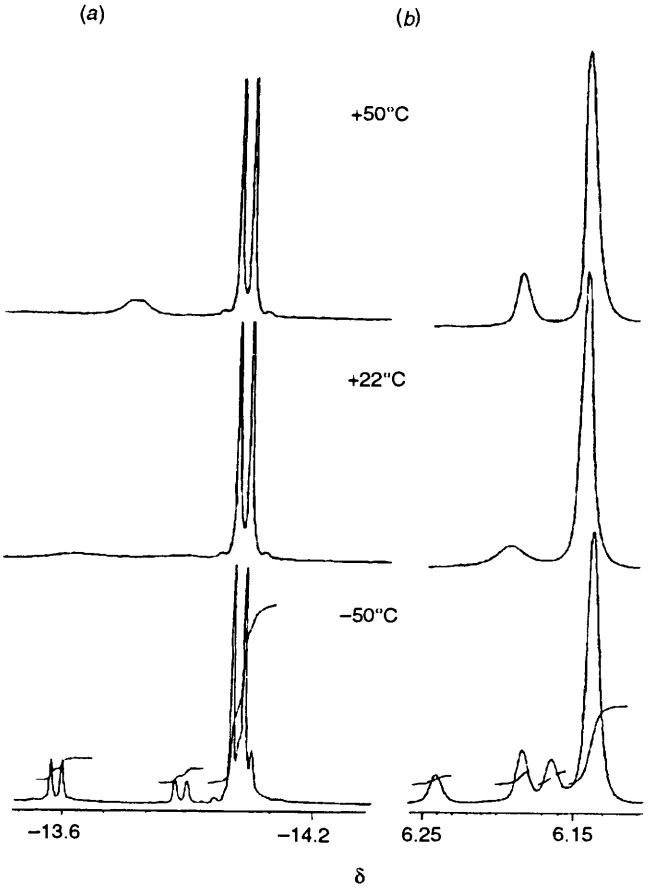


Fig. 4 Variable-temperature ^{1}H NMR spectra of compound **3**: (*a*) in the hydride region; (*b*) in the aromatic region

singlet at δ 6.19 [Fig. 4(*b*)]. Similarly, the methyl singlets at δ 1.37 and 1.42 average to a singlet at δ 1.41 while those at δ 2.01 and 2.04 average to a singlet at δ 2.03. Increasing the temperature to +50 °C, the broadened hydride resonances at δ −13.58 and −13.88 average to a broadened doublet at δ −13.70 while the doublet at δ −13.88 and the singlets at δ 6.15, 6.19, 1.41 and 2.03 remain unchanged. On the basis of the solid-

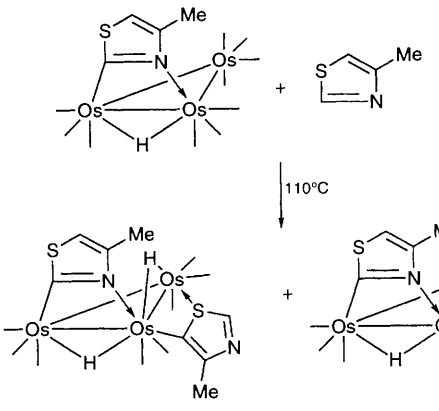
state structure of compound **3**, and the variable-temperature ^1H NMR data, we can tentatively make structural assignments of the four observed isomers (Scheme 6). The major isomer **3a** which exhibits the doublet hydride resonance at δ −14.02 can be assigned the same structure as that observed in the solid state; having one phosphine ligand on the osmium atom bound to the nitrogen atom of the thiazolide ligand cisoid to the hydride and the second phosphine on the unbridged osmium atom, Os(1), *syn* to the carbon atom of the thiazolide ligand. Since the hydride resonance at δ −14.04 has the same phosphorus–hydrogen coupling constant (12.0 Hz) as that of the major isomer and exchanges with it, we assign this resonance to an isomer which has a phosphine on the hydride-bridged edge as in **3a** but with the phosphine on the unbridged osmium *anti* to the carbon of the thiazolide ligand (**3b**, Scheme 6). The existence of two radial isomers in solution has been reported for the cluster $[Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}\eta^2\text{-}\overline{C{=}NCH_2CH_2CH_2})(PPh_3)]$ in which the phosphine is also substituted on the unbridged osmium atom.[24]

Based on the magnitude of the phosphorus–hydrogen coupling constants and their coalescence behaviour compared with that of the phosphine-substituted triosmium imidoyl clusters,[24] we can assign the hydride doublet resonances at δ −13.58 and −13.88 to isomers **3c** and **3d** (Scheme 6) where one phosphine ligand now resides on the osmium bound to the carbon and *cis* to the hydride while the second phosphine ligand is substituted on the unbridged osmium atom. Again as mentioned above for **3a** and **3b**, the isomers **3c** and **3d** must differ by an *anti versus syn* orientation between the unbridged metal-bound phosphine and the carbon atom of the thiazolide ligand. That **3a** and **3b** do not interchange with **3c** and **3d** up to +60 °C is also consistent with these assignments, since this would require phosphine dissociation, a much higher-energy process.[14]

A further reaction of compound **1** with 4-methylthiazole in refluxing toluene affords $[Os_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(\mu\text{-}1,5\text{-}\eta^2\text{-}\overline{CH{=}NCMe{=}CS})]$ **4** and $[Os_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})_2]$ **5** (Scheme 7) each containing two thiazolide ligands. Compounds **4** and **5** obtained in 27 and 42% yields respectively were characterized by ^1H NMR, infrared and elemental analysis. We were unable to obtain suitable crystals for structural analysis. The ^1H NMR spectrum of **4** shows two aromatic proton resonances, a quartet at δ 6.48 and a singlet at δ 6.58, two methyl proton resonances, a doublet at δ 2.17 and a singlet at δ 2.29 and two hydride resonances at δ −11.08 and −12.58 with an integrated ratio of 1:1:3:3:1:1 respectively. As observed for **1**, the quartet at δ 6.48 and the doublet at δ 2.17 can be interpreted as signals due to the N-co-ordinated thiazolide ligand while the singlet resonances at δ 6.58 and 2.29 are assignable to the S-co-ordinated thiazolide ligand. Since the C(2)–H proton is isolated by the nitrogen atom in the S-co-ordinated thiazolide ligand it does not exhibit coupling to the methyl group. On the other hand, the C(4)–H does show coupling to the methyl group in the N-co-ordinated thiazolide. The ^1H NMR spectrum of **5** shows two sets of quartets for the ring protons at δ 6.97 and 6.50, two doublets for the methyl protons at δ 2.45 and 2.17 and two hydride resonances at δ −11.37 and −12.53 indicating the presence of two thiazolide ligands. The coupling of the proton residing on the C(2) carbon with the methyl protons allows us to propose that both the ligands in **5** are N-co-ordinated. This general type of structure has been found in the reactions of other heterocycles with triosmium clusters which have been structurally characterized.[1,27]

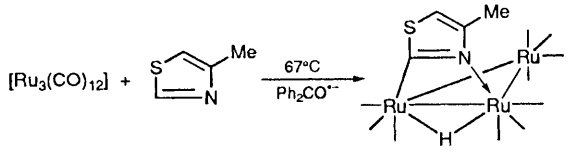
The reaction of $[Ru_3(CO)_{12}]$ with 1 equivalent of 4-methylthiazole in the presence of sodium–benzophenone as the reaction promoter at 67 °C gives $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})]$ **6** (Scheme 8) in 15% yield. The mass spectrum (parent ion at *m/z* 685) and the elemental analysis are consistent with the proposed molecular formula. The infrared spectrum contains a ν(CO) band pattern similar to that of the osmium analogue **1** indicating that the two compounds are structurally similar. The ^1H NMR spectrum shows a quartet at δ 6.76 for the ring proton, a doublet at δ 2.29 for the methyl protons and a singlet hydride resonance at δ −14.23. Comparison of these spectroscopic data with those of **1** provides sufficient evidence to propose that the thiazolide ligand in **6** is co-ordinated through the nitrogen and C(5) carbon atom. The reaction of $[Ru_3(CO)_{12}]$ with 2 equivalents of 4-methylthiazole in the presence of sodium–benzophenone affords the 1:2 compound $[Ru_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})_2]$ **7** (Scheme 9) in 18% yield. Compound **7** has been characterized by ^1H NMR, infrared, and mass spectroscopy (parent ion at *m/z* 728) as well as elemental analysis. The infrared spectrum in the carbonyl stretching region is similar to that of $[Ru_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}\eta^2\text{-}NC_5H_4)_2]$[3] and the osmium analogue **5**. The ^1H NMR spectrum shares a common feature with that of **5** in that the ring proton for both the thiazolide ligands exhibits coupling to the methyl protons. Thus, two quartets due to the ring protons are observed at δ 6.75 and 6.66 as well as two doublets for the methyl protons at δ 2.37 and 2.28. Signals for the two bridging hydrides were observed as doublets at δ −12.04 and −12.94. The hydride chemical shifts are virtually identical to those of $[Ru_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}\eta^2\text{-}NC_5H_4)_2]$ (δ 12.1 and 13.1).[3] Thus, compound **7** has the same basic structure as that of **5** and the pyridine analogue $[Ru_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}\eta^2\text{-}NC_5H_4)_2]$.[3] Treatment of **6** with 1 equivalent of 4-methylthiazole in the presence of sodium–benzophenone at 61 °C produces only **7** in 37% yield. We obtained no evidence for the formation of a ruthenium analogue of **4**. This result is in contrast with that obtained from the reaction of **1** with 4-methylthiazole which gives two isomeric compounds **4** and **5**.

These studies clearly show that an imidoyl-type nitrogen atom is preferred by both osmium and ruthenium to a thiophene type of sulfur. The realization of some sulfur-bound thiazolide in compound **4** is attributed to initial co-ordination



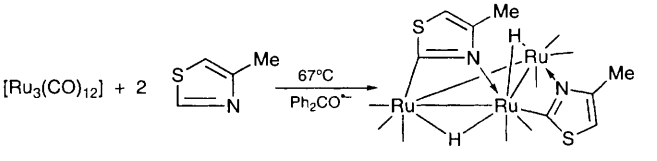
4 **5**

Scheme 7



6

Scheme 8



7

Scheme 9

Table 4 Crystal data and details of data collection and structure refinement for compounds **1**–**3**

	1	**2**	**3**
Empirical formula	$C_{14}H_5NO_{10}Os_3S$	$C_{31}H_{20}NO_9Os_3PS$	$C_{48}H_{35}NO_8Os_3P_2S$
M	949.85	1184.11	1418.37
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
a/Å	9.486(2)	20.834(8)	12.927(1)
b/Å	11.478(2)	16.452(5)	19.652(1)
c/Å	18.516(3)	19.659(5)	17.956(1)
β/°	103.42(1)	104.35(3)	99.20(1)
U/Å^{-3}	1960.8(7)	6528(4)	4502.9(5)
Z	4	8	4
D_c/g cm^{-3}	3.218	2.410	2.092
μ(Mo-Kα)/cm^{-1}	195.51	118.16	86.17
F(000)	1680	4352	2672
Crystal size/mm	0.10 × 0.08 × 0.06	0.15 × 0.10 × 0.08	0.18 × 0.08 × 0.06
θ Range for data collection/°	2.10–25.09	1.78–24.98	1.81–25.06
hkl Ranges	−11 to 11, −13 to 13, −13 to 21	−23 to 22, −14 to 17, −22 to 23	−13 to 15, −23 to 17, −21 to 19
Total reflections collected	8285	13 664	15 605
Total unique reflections (merging R)	3037 (0.0703)	4962 (0.0787)	6566 (0.0629)
Absorption correction factors	0.692–0.998	0.801–1.000	0.769-0.999
Data, parameters in the refinement	3037, 263	4962, 380	6566, 497
Final $R1$, $wR2$*	0.0447 (0.0350), 0.0790 (0.0772)	0.0464 (0.0351), 0.0826 (0.0811)	0.0541 (0.0348), 0.0822 (0.0800)
Largest difference peak and hole/e Å^{-3}	2.879, −1.285	2.209, −1.276	1.905, −0.984
Goodness of fit	0.981	0.982	0.899

* $R1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (qP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$, and $q = 0.0343$, 0.0292 and 0.0253 for compounds **1**, **2** and **3** respectively. Values given for all data with those calculated for data with $I > 2\sigma(I)$ [2563 (**1**), 3987 (**2**), 4749 (**3**)] in parentheses.

Table 5 Atomic coordinates (× 10^4) for compound **1**

Atom	x	y	z
Os(1)	4171.4(4)	1446.6(4)	1725.2(3)
Os(2)	1239.2(4)	2199.2(4)	1650.4(3)
Os(3)	2209.2(4)	1611.7(4)	301.2(3)
S	1450(3)	5140(3)	1212(2)
N	2144(9)	3475(8)	476(6)
O(1)	4987(7)	3998(7)	1510(5)
O(2)	6929(8)	627(7)	1264(5)
O(3)	3115(8)	−1069(7)	1827(5)
O(4)	5304(8)	1669(7)	3402(5)
O(5)	491(9)	−80(8)	2345(5)
O(6)	2505(8)	3306(8)	3156(5)
O(7)	−1889(8)	3051(8)	1460(6)
O(8)	1998(7)	−1037(8)	167(4)
O(9)	4895(8)	1581(8)	−343(5)
O(10)	−56(8)	1972(9)	−1156(5)
C(1)	4644(11)	3071(10)	1588(7)
C(2)	5885(12)	921(9)	1442(6)
C(3)	3479(11)	−145(10)	1801(6)
C(4)	4885(10)	1568(9)	2783(6)
C(5)	773(11)	751(10)	2069(7)
C(6)	2002(12)	2873(10)	2583(7)
C(7)	−709(12)	2731(10)	1515(7)
C(8)	2119(11)	−70(12)	236(6)
C(9)	3871(12)	1608(10)	−100(6)
C(10)	784(12)	1830(11)	−606(7)
C(11)	1692(10)	3681(10)	1074(7)
C(12)	2392(12)	4444(11)	53(8)
C(13)	2070(10)	5445(10)	400(6)
C(14)	2855(12)	4378(11)	−514(9)

on the more crowded **1** of the less sterically encumbered sulfur of the second thiazole ligand. That the ruthenium analogue of **4** is not observed could be due to the much greater stereochemical non-rigidity of ruthenium carbonyl clusters which could allow for rearrangement of sterically encumbered intermediates.

Experimental

Reactions were performed under a dry nitrogen atmosphere. Dichloromethane was distilled from CaH_2 and thf from sodium–benzophenone prior to use. 4-Methylthiazole was obtained from Aldrich and used as received. Water was removed from $Me_3NO{\cdot}2H_2O$ by distilling the azeotrope of toluene. The cluster $[Os_3(CO)_{10}(MeCN)_2]$ was prepared according to the published procedure.[12] Sodium–benzophenone was prepared according to the known procedure.[28] Infrared spectra were recorded on a Perkin-Elmer 1420 spectrophotometer, ^{1}H NMR spectra on a Varian Unity Plus 400 MHz spectrometer. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, New York.

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 4-methylthiazole

To a dichloromethane solution (30 cm^3) of $[Os_3(CO)_{10}(MeCN)_2]$ (0.200 g, 0.214 mmol) was added 4-methylthiazole (96 μl, 1.069 mmol) and the reaction mixture allowed to stir at room temperature for 16 h. The solvent was removed under reduced pressure and the residue dissolved in the minimum volume of CH_2Cl_2 and applied to silica gel preparative TLC plates. Elution was with hexane–CH_2Cl_2 (5:1, v/v). Only one major band was eluted from which the cluster $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-2,3-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})]$ **1** was isolated as yellow crystals after recrystallization from hexane–CH_2Cl_2 at −20 °C (0.159 g, 78%) (Found: C, 17.85; H, 0.75; N, 1.50. Calc. for $C_{14}H_5NO_{10}Os_3S$: C, 17.70; H, 0.55; N, 1.45%). IR [ν(CO), hexane]: 2107m, 2066s, 2056s, 2025s, 2014s, 2006m, 1996s, 1989w and 1979m cm^{-1}. NMR ($CDCl_3$): ^{1}H (400 MHz), δ 6.57 (q, 1 H, J_{HH} = 1.2), 2.21 (d, 3 H, J_{HH} = 1.2 Hz) and −14.76 (s, 1 H); ^{15}N (with reference to nitromethane), δ −11.67 (s).

Reaction of compound **1** with PPh_3

To a solution of compound **1** (0.058 g, 0.061 mmol) in toluene (40 cm^3) in a flame-dried Schlenk tube was added PPh_3 (0.032 g, 0.122 mmol) and the reaction mixture was heated to reflux for 12 h, changing from yellow to orange. The solvent was rotary evaporated and the residue chromatographed on silica TLC plates eluting with hexane–CH_2Cl_2 (5:1, v/v) to give three bands. The first band gave unreacted **1** (0.010 g), the second band $[Os_3(\mu\text{-H})(CO)_9(\mu\text{-2,3-}\eta^2\text{-}\overline{C{=}NCMe{=}CHS})(PPh_3)]$ **2** as orange crystals (0.018 g, 25%) from hexane–CH_2Cl_2 at −20 °C while the third afforded $[Os_3(\mu\text{-H})(CO)_8(\mu\text{-}$

Table 6 Atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	4126.1(2)	5698.1(2)	1355.5(2)	C(9)	2748(5)	5813(6)	2077(5)
Os(2)	3429.1(2)	4757.4(2)	166.9(2)	C(10)	3218(5)	3941(6)	911(5)
Os(3)	2723.6(2)	5521.2(2)	1141.3(2)	C(11)	2976(6)	2939(7)	1735(5)
S	3354(2)	2918(2)	1037(1)	C(12)	2778(5)	3674(6)	1847(5)
P	1571(1)	5292(2)	684(1)	C(13)	2447(6)	3910(7)	2405(5)
O(1)	4213(4)	6974(5)	2513(4)	C(111)	1044(3)	6002(3)	1036(3)
O(2)	3924(4)	7125(4)	305(4)	C(112)	1150(3)	6068(4)	1760(3)
O(3)	5583(4)	5486(4)	1346(4)	C(113)	786(3)	6623(4)	2045(2)
O(4)	4246(4)	4217(5)	2358(4)	C(114)	317(3)	7112(4)	1606(3)
O(5)	3573(4)	6037(4)	−940(4)	C(115)	211(3)	7047(4)	882(3)
O(6)	4774(4)	3958(5)	220(4)	C(116)	575(3)	6492(4)	597(2)
O(7)	2462(4)	3824(4)	−1001(4)	C(121)	1243(3)	4280(3)	813(3)
O(8)	2546(4)	7318(5)	812(4)	C(122)	748(3)	4169(3)	1165(3)
O(9)	2799(4)	6021(5)	2645(4)	C(123)	526(3)	3390(4)	1259(3)
N	2898(4)	4253(5)	1359(4)	C(124)	799(4)	2722(3)	1000(3)
C(1)	4184(5)	6480(7)	2111(5)	C(125)	1294(3)	2834(3)	647(3)
C(2)	3984(5)	6581(6)	678(5)	C(126)	1516(3)	3613(4)	554(3)
C(3)	5045(6)	5565(6)	1334(5)	C(131)	1291(3)	5410(4)	−289(2)
C(4)	4192(5)	4743(7)	1986(6)	C(132)	869(3)	4849(3)	−703(3)
C(5)	3534(5)	5584(6)	−509(5)	C(133)	698(3)	4931(4)	−1429(3)
C(6)	4266(7)	4243(6)	186(5)	C(134)	950(4)	5574(4)	−1742(2)
C(7)	2834(6)	4161(6)	−566(5)	C(135)	1372(3)	6135(3)	−1329(3)
C(8)	2607(5)	6626(7)	914(5)	C(136)	1543(3)	6053(3)	−602(3)

Table 7 Atomic coordinates (× 10^4) for compound **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	706.0(3)	2271.6(2)	7194.7(2)	C(115)	4979(4)	1477(3)	8241(4)
Os(2)	146.6(3)	3452.6(2)	6242.2(2)	C(116)	4234(5)	1721(3)	7658(3)
Os(3)	−1065.7(3)	3079.6(2)	7442.6(2)	C(121)	2992(5)	2274(3)	6228(3)
S	−1789(2)	2680(2)	4942(2)	C(122)	3304(5)	2921(3)	6486(3)
P(1)	2190(2)	1770(1)	6801(1)	C(123)	3909(5)	3320(3)	6083(3)
P(2)	−2246(2)	4014(1)	7481(1)	C(124)	4202(5)	3072(3)	5422(3)
O(1)	2161(6)	3179(4)	8298(4)	C(125)	3890(5)	2426(3)	5164(3)
O(2)	402(7)	1326(4)	8487(4)	C(126)	3285(5)	2027(3)	5567(3)
O(3)	−851(6)	1387(4)	6139(4)	C(131)	1924(5)	994(3)	6231(3)
O(4)	1220(6)	2898(4)	4971(4)	C(132)	2382(4)	373(3)	6460(3)
O(5)	2025(6)	4258(4)	7050(4)	C(133)	2194(5)	−193(2)	5994(3)
O(6)	−796(6)	4706(4)	5378(3)	C(134)	1548(5)	−138(3)	5299(3)
O(7)	204(6)	3538(4)	8922(4)	C(135)	1090(4)	483(3)	5070(3)
O(8)	−1976(6)	1920(4)	8252(4)	C(136)	1278(5)	1049(3)	5536(3)
N	−1817(6)	2745(4)	6338(4)	C(211)	−1585(5)	4663(3)	8132(3)
C(1)	1618(9)	2854(6)	7846(6)	C(212)	−689(5)	4981(3)	7965(3)
C(2)	561(9)	1664(6)	7985(6)	C(213)	−126(4)	5422(3)	8484(4)
C(3)	−283(9)	1732(5)	6507(6)	C(214)	−458(5)	5545(3)	9170(3)
C(4)	830(9)	3094(6)	5454(6)	C(215)	−1353(5)	5227(4)	9338(3)
C(5)	1363(9)	3935(5)	6758(6)	C(216)	−1917(5)	4786(3)	8819(4)
C(6)	−449(9)	4241(6)	5707(5)	C(221)	−3490(4)	3887(4)	7826(4)
C(7)	−261(8)	3351(6)	8361(6)	C(222)	−3645(5)	3338(3)	8284(4)
C(8)	−1641(8)	2384(6)	7943(6)	C(223)	−4598(6)	3260(3)	8539(4)
C(9)	−1227(8)	2930(5)	5831(5)	C(224)	−5396(4)	3730(4)	8337(4)
C(10)	−2753(9)	2393(5)	6061(6)	C(225)	−5241(5)	4279(4)	7879(4)
C(11)	−2845(9)	2315(6)	5295(6)	C(226)	−4288(6)	4357(3)	7624(4)
C(12)	−3452(9)	2178(6)	6529(6)	C(231)	−2655(5)	4477(3)	6593(3)
C(111)	3199(5)	1508(3)	7594(3)	C(232)	−2504(5)	5172(3)	6513(3)
C(112)	2908(4)	1051(3)	8114(3)	C(233)	−2857(6)	5489(2)	5828(4)
C(113)	3653(5)	806(3)	8697(3)	C(234)	−3361(5)	5111(3)	5222(3)
C(114)	4689(5)	1019(3)	8760(3)	C(235)	−3513(5)	4416(3)	5302(3)
				C(236)	−3160(5)	4099(2)	5988(3)

η^2-C=NCMe=CHS)$(PPh_3)_2$] **3** as orange crystals (0.035 g, 40%) after recrystallization from hexane–CH_2Cl_2 at −20 °C.

Compound **2** (Found: C, 31.40; H, 1.80; N, 1.20. Calc. for $C_{31}H_{20}NO_9Os_3PS$: C, 31.45; H, 1.70; N, 1.20%). IR [ν(CO), CH_2Cl_2]: 2089s, 2049vs, 2011vs, 1997s, 1978m, 1965w and 1939w cm $^{-1}$. ^{1}H NMR ($CDCl_3$, 400 MHz): major isomer (85%), δ 7.28 (m, 15 H), 6.20 (s, 1 H), 1.52 (s, 3 H) and −14.24 (d, 1 H, J_{PH} = 11.6); minor isomer (15%), δ 7.28 (m, 15 H), 6.26 (s, 1 H), 2.14 (s, 3 H) and −13.95 (d, 1 H, J_{PH} = 11.4 Hz). The phenyl proton resonances of the isomers are overlapped.

Compound **3** (Found: C, 40.75; H, 2.65; N, 1.00. Calc. for $C_{48}H_{35}NO_8Os_3P_2S$: C, 40.65; H, 2.50; N, 1.00%). IR [ν(CO), CH_2Cl_2]: 2064m (sh), 2057m, 2022vs, 1992s, 1982s, 1968m and 1951m cm^{-1}. ^{1}H NMR ($CDCl_3$, −50 °C, 400 MHz): four isomers, isomer **3a** (70%), δ 7.32 (m, 30 H), 6.14 (s, 1 H), 1.42 (s, 3 H) and −14.02 (d, 1 H, J_{PH} = 12.0); isomer **3b** (12%), δ 7.32 (m, 30 H), 6.18 (s, 1 H), 1.37 (s, 3 H) and −14.04 (d, 1 H, $J_{PH} \approx$ 12.0); isomer **3c** (11%), δ 7.32 (m, 30 H), 6.16 (s, 1 H), 2.01 (s, 3 H) and −13.58 (d, 1 H, J_{PH} = 11.6); isomer **3d** (7%), δ 7.32 (m, 30 H), 6.24 (s, 1 H), 2.05 (s, 3 H) and −13.88 (d, 1 H, J_{PH} = 11.6 Hz). The signals due to the phenyl protons of the PPh_3 ligands for the isomers **3a**–**3d** overlap.

Reaction of compound 2 with PPh_3

A solution of compound **2** (0.016 g, 0.014 mmol) and PPh_3 (0.008 g, 0.030 mmol) in toluene (20 cm^3) was refluxed for 12 h. The solvent was removed *in vacuo* and the residue chromatographed by TLC on silica gel. Elution with hexane–CH_2Cl_2 (10:3, v/v) gave two bands. The faster-moving band gave unreacted **2** (0.002 g) while the second band gave **3** (0.015 g, 79%).

Reaction of compound 1 with 4-methylthiazole

A solution of compound **1** (0.074 g, 0.078 mmol) and 4-methylthiazole (35 μl, 0.386 mmol) in toluene (20 cm^3) was refluxed for 24 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane–CH_2Cl_2 (5:1, v/v) gave three bands. The faster-moving band gave $[Os_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}C{=}NCMe{=}CHS)(\mu\text{-}1,5\text{-}\eta^2\text{-}CH{=}NCMe{=}CS)]$ **4** (0.021 g, 27%) as orange crystals after recrystallization from hexane–CH_2Cl_2 at −20 °C. The second band yielded $[Os_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}C{=}NCMe{=}CHS)_2]$ **5** (0.032 g, 42%) as orange crystals from hexane–CH_2Cl_2 at −20 °C. The third band gave a small quantity (≈0.002 g) of an uncharacterized compound.

Compound **4** (Found: C, 19.50; H, 1.85; N, 3.05. Calc. for $C_{16}H_{10}N_2O_8Os_3S_2$: C, 19.35; H, 1.30; N, 2.85%). IR [ν(CO), hexane]: 2084w, 2064m, 2051vs, 2036s, 2024s, 2013m, 2004s and 1982m cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.58 (s, 1 H), 6.48 (q, 1 H, J_{HH} = 1.0), 2.29 (s, 3 H), 2.17 (d, 3 H, J_{HH} 1.0 Hz), −11.08 (s, 1 H) and −12.58 (s, 1 H).

Compound **5** (Found: C, 19.64; H, 1.35; N, 2.95. Calc. for $C_{16}H_{10}N_2O_8Os_3S_2$: C, 19.35; H, 1.00; N, 2.80%). IR [ν(CO), hexane]: 2082m, 2049s, 2036s, 2009 (sh), 2002s, 1990m and 1980m cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): 6.97 (q, 1 H, J_{HH} = 1.1), 6.50 (q, 1 H, J_{HH} = 1.1), 2.45 (d, 3 H, J_{HH} = 1.1), 2.17 (d, 3 H, J_{HH} = 1.1 Hz), −11.37 (s, 1 H) and −12.53 (s, 1 H).

Reaction of $[Ru_3(CO)_{12}]$ with 4-methylthiazole

To a thf solution (40 cm^3) of $[Ru_3(CO)_{12}]$ (0.200 g, 0.313 mmol) and 4-methylthiazole (29 μl, 0.319 mmol) was added five drops of a freshly prepared thf solution of sodium-benzophenone. The resulting solution was heated to reflux for 2 h. The solvent was removed *in vacuo* and the residue chromatographed by TLC on silica gel. Elution with hexane–CH_2Cl_2 (10:3, v/v) gave an orange band which yielded $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}C{=}NCMe{=}CHS)]$ **6** (0.032 g, 15%) as orange crystals from hexane–CH_2Cl_2 at −20 °C (Found: C, 24.90; H, 1.00; N, 2.15. Calc. for $C_{14}H_5NO_{10}Ru_3S$: C, 24.65; H, 0.75; N, 2.05%). IR [ν(CO), hexane]: 2098w, 2061s, 2052s, 2023s, 2019s, 2004s, 1998m and 1987m cm^{-1}. ^1H NMR ($CDCl_3$, 360 MHz): δ 6.76 (q, 1 H, J_{HH} = 0.9), 2.29 (d, 3 H, J_{HH} = 0.9 Hz) and −14.23 (s, 1 H). Mass spectrum: *m/z* 685 (^{102}Ru).

A similar reaction of $[Ru_3(CO)_{12}]$ (0.200 g, 0.313 mmol) and 4-methylthiazole (142 μl, 1.56 mmol) in the presence of ten drops of a freshly prepared thf solution of sodium–benzophenone followed by similar chromatographic work-up gave $[Ru_3(\mu\text{-}H)_2(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}C{=}NCMe{=}CHS)_2]$ **7** (0.041 g, 18%) as orange crystals after recrystallization from pentane–CH_2Cl_2 at −20 °C (Found: C, 26.75; H, 1.55; N, 3.95. Calc. for $C_{16}H_{10}N_2O_8Ru_3S_2$: C, 26.50; H, 1.40; N, 3.85%). IR [ν(CO), hexane]: 2082m, 2048vs, 2010vs, 1992s and 1962w cm^{-1}. ^1H NMR ($CDCl_3$, MHz): δ 6.75 (q, 1 H, J_{HH} = 0.9), 6.66 (q, 1 H, J_{HH} = 0.8), 2.37 (d, 3 H, J_{HH} = 0.8), 2.28 (d, 3 H, J_{HH} = 0.9), −12.04 (d, 1 H, J_{HH} = 0.9) and −12.94 (d, 1 H, J_{HH} = 0.8 Hz).

Reaction of compound 6 with 4-methylthiazole

To a thf solution (20 cm^3) of compound **6** (0.025 g, 0.037 mmol) and 4-methylthiazole (7 μl, 0.077 mmol) were added three drops of a solution of sodium–benzophenone. The reaction mixture was refluxed for 1 h at which time analytical TLC indicated complete consumption of **6**. The solvent and excess of 4-methylthiazole were removed under vacuum. The residue was chromatographed on silica gel TLC plates eluting with hexane–CH_2Cl_2 (10:3, v/v). Only one band was eluted from which the cluster **7** (0.010 g, 37%) was isolated as orange crystals.

Attempted decarbonylation of compound 1

An octane solution (50 cm^3) of cluster **1** (0.032 g, 0.244 mmol) was refluxed for 48 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane–CH_2Cl_2 (5:1) gave only **1** (0.210 g).

In another experiment a solution of compound **1** (0.125 g, 0.132 mmol) in hexane (100 cm^3) was photolysed using a Rayonet photochemical reactor irradiating with 3000 Å lamps for 3 h. Separation (TLC) as above gave only **1** (0.105 g).

X-Ray crystallography

All crystallographic measurements for compounds **1**–**3** were made at 150 K using a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator using Mo-Kα radiation (λ = 0.710 69 Å) by following procedures described elsewhere.[29] The structures were solved by direct methods (SHELXS 86)[30] and standard difference syntheses, and refined on F_o^2 by full-matrix least squares (SHELXL 93)[31] using all unique data above background corrected for Lorentz and polarisation factors and absorption effects (DIFABS).[32] In all cases, the non-hydrogen atoms were refined anisotropically. The bridging hydrogens were located from difference maps; these were included in the calculations of F_c (with U_{iso} fixed at 0.04 $Å^2$) but not refined. Other hydrogens were included in geometric positions (riding model) with U_{iso} set at 1.2 times the U_{eq} of the parent. In both **2** and **3** the phenyl rings were treated as idealized hexagons with C–C 1.390 Å and C–C–C (internal) 120.0°. Sources of atomic scattering factors as in ref. 31. All calculations were done on a 486DX2/66 personal computer. Diagrams were drawn by SNOOPI.[33] The crystal data, details of data collection and structure refinement parameters are presented in Table 4. The fractional atom coordinates are presented in Tables 5–7.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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