Synthesis and Structural Characterisation of Some New Triosmium Alkylidyne Clusters containing Sulfur-donor Ligands. The Formation of C–S and C–C Bonds†

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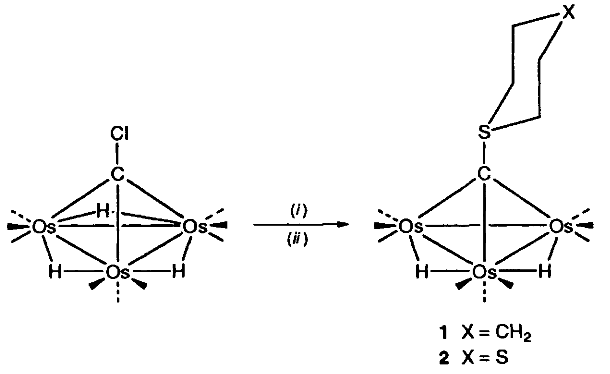
The neutral clusters $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}CS(CH_2)_4CH_2\}]$ **1** and $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}CS(CH_2)_2SCH_2CH_2\}]$ **2** were synthesised in good to moderate yields respectively by the reaction of $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ with 1 equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene, in the presence of a 10-fold excess of thiane or 1,4-dithiane. Under ambient conditions, complex **2** in solution slowly rearranges to a novel ketenylidene-bridged cluster $[Os_3(\mu\text{-}H)_2(CO)_8\{S(CH_2)_2SCH_2CH_2\}(\mu_3\text{-}CCO)]$ **3**, which is formed by exchange of $S(CH_2)_2SCH_2CH_2$ and CO at the μ_3-carbon. All complexes were fully characterised by spectroscopic methods and their molecular structures established by single-crystal X-ray analyses.

We have previously reported the synthesis of some dihydridotriosmium alkylidyne clusters $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CY)]$ (Y = Lewis base) bearing nitrogen-[1] or phosphorus-donor ligands[2] on the apical carbon atom. However, to our knowledge, there is no structurally characterised example of such a complex of the iron triad with neutral sulfur-donor ligands. In addition, few clusters containing the CSR (R = alkyl) ligand have been prepared.[3] Further to investigate the influence of sulfur substituents upon the reactivity of dihydrido alkylidyne clusters, we have prepared the new clusters $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}CS(CH_2)_4CH_2\}]$ **1** and $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}CS(CH_2)_2SCH_2CH_2\}]$ **2** and report here the facile rearrangement of **2** to the corresponding isomer $[Os_3(\mu\text{-}H)_2(CO)_8\{S(CH_2)_2SCH_2CH_2\}(\mu_3\text{-}CCO)]$ **3** under ambient conditions.



Scheme 1 (*i*) $S(CH_2)_4CH_2$ or $S(CH_2)_2SCH_2CH_2$; (*ii*) dbu

Results and Discussion

Our syntheses of compounds **1** and **2** were developed by analogy to the deprotonation method used to prepare $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CY)]$ (Y = Lewis base).[2] That is, the reaction of $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ with 1 equivalent of a deprotonating agent 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu), in the presence of a 10-fold excess of thiane or 1,4-dithiane gives respectively the products **1** and **2** in 50 and 40% yields (Scheme 1). However, no sulfur-containing alkylidyne cluster was isolated when the reaction was carried out using thiophene as the nucleophile.

The spectroscopic data (IR, ^1H NMR and mass) for the new clusters **1** and **2** are summarised in Table 1. They have very similar solution IR spectral patterns in the carbonyl-stretching absorption region. The ^1H NMR spectra of both compounds consist of a singlet in the region δ −19 to −20 due to the two bridging hydride ligands and resonances due to the CH_2 groups of the ligands, which are fully consistent with the solid-state structures. Attempts to assign the CH_2 signals for **1** were made with the aid of ^1H–^1H correlation spectroscopy (COSY).

The molecular structures of both complexes **1** and **2** have been established by X-ray structural analyses. Single crystals of **1** and **2** suitable for diffraction experiments were grown by slow evaporation of hexane–CH_2Cl_2 solutions at room temperature for 2 d. Perspective views of the complexes, together with the atomic labelling schemes, are shown in Figs. 1 and 2 respectively, selected bond distances and angles in Tables 2 and 3. The structures of both complexes consist of a triosmium alkylidyne metal core with the sulfur atom bonded to the μ_3-bridging alkylidyne carbon atom. They both possess nine terminal carbonyl ligands. The two hydride atoms which show up in the ^1H NMR spectra could not be located directly. However, potential-energy calculations[4] suggested that one hydride atom bridges the Os(1)–Os(2) edge and the other Os(2)–Os(3) (for **1**) and Os(1)–Os(3) (for **2**). The metal–alkylidyne carbon bond distances are essentially equivalent and are typical of those in triosmium alkylidyne clusters previously structurally characterised.[1,5] The C–S bond distances are respectively 1.71(4) and 1.68(2) Å for **1** and **2**. The sulfur-donor ligands of both **1** and **2** have been shown to have the chair form as their stable conformations with all the C–C bonds being staggered in their solid states. The only observed structural difference between the two complexes lies in the presence of a pendant sulfur atom at the periphery of complex **2**, which is crucial to the subsequent formation of **3** described below.

When a solution of complex **2** in CH_2Cl_2 was allowed to stand for several days at room temperature, a new compound **3**

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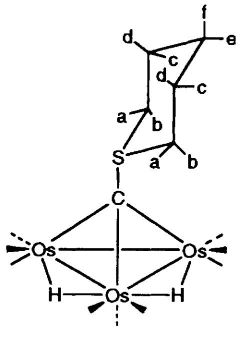
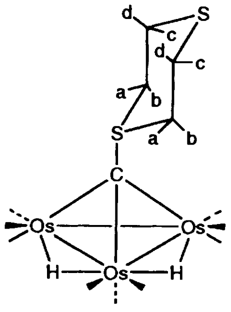
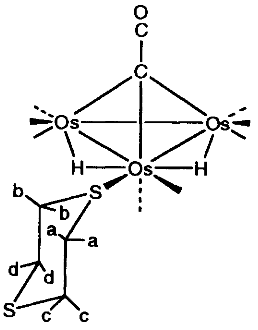
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Spectroscopic data for complexes **1**–**3**

Complex	IR,[a] $\tilde{\nu}$(CO)/cm^{-1}	^{1}H NMR, δ[b]	Mass,[c] *m/z*
 **1**	2094s, 2055vs, 2026vs, 2002m, 1979vs, 1957m, 1940m	2.96 (m, 2 H, H_a or H_b) 2.09 (m, 2 H, H_a or H_b) 1.23 (m, 1 H, H_e or H_f) 0.89 (m, 2 H, H_c or H_d) 0.73 (m, 2 H, H_c or H_d) 0.25 (m, 1 H, H_e or H_f) −19.89 (s, 2 H, OsH)	940 (940)
 **2**	2095s, 2057vs, 2028vs, 2002m, 1981vs, 1959m, 1942m	3.09 (m, 2 H, H_a or H_b) 2.45 (m, 2 H, H_a or H_b) 1.88 (m, 2 H, H_c or H_d) 1.48 (m, 2 H, H_c or H_d) −19.95 (s, 2 H, OsH)	958 (958)
 **3**	2090m, 2047vs, 2036(sh), 1993m, 1982m	2.37 (m, 2 H, H_a or H_b) 2.23 (m, 2 H, H_a or H_b) 2.03 (m, 2 H, H_c or H_d) 1.72 (m, 2 H, H_c or H_d) −18.96 (s, 1 H, OsH) −20.10 (s, 1 H, OsH)	958 (958)

[a] In CH_2Cl_2. [b] In C_6D_6. [c] Simulated values given in parentheses.

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

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Os(1)–Os(2)	2.876(3)	2.880(3)	Os(1)–Os(3)	2.760(3)	2.778(3)
Os(2)–Os(3)	2.878(3)	2.882(3)	Os(1)–C(19)	2.11(4)	2.13(4)
Os(2)–C(19)	2.08(4)	2.13(4)	Os(3)–C(19)	2.13(4)	2.09(4)
S(1)–C(19)	1.71(4)	1.68(4)	S(1)–C(20)	1.76(5)	1.68(6)
C(20)–C(21)	1.57(8)	1.52(8)	C(21)–C(22)	1.64(9)	1.59(9)
C(22)–C(23)	1.44(7)	1.41(8)	C(23)–C(24)	1.61(8)	1.59(8)
S(1)–C(24)	1.69(5)	1.82(5)			
Os(2)–Os(1)–Os(3)	61.4(1)	61.2(1)	Os(1)–Os(2)–Os(3)	57.3(1)	57.6(1)
Os(1)–Os(3)–Os(2)	61.3(1)	61.1(1)	Os(1)–C(19)–S(1)	125(2)	124(2)
Os(2)–C(19)–S(1)	126(2)	123(2)	Os(3)–C(19)–S(1)	135(2)	138(2)
C(19)–S(1)–C(20)	107(2)	108(2)	C(19)–S(1)–C(24)	107(2)	106(2)
S(1)–C(20)–C(21)	114(4)	109(4)	C(20)–C(21)–C(22)	105(5)	110(5)
S(1)–C(24)–C(23)	108(3)	103(3)	C(22)–C(23)–C(24)	116(5)	119(5)

was isolated from a yellow band after chromatography on silica (TLC) with hexane–CH_2Cl_2 (70:30, v/v) as eluent. The conversion is 50% complete after 24 h. Complex **3** shows a completely different IR spectral pattern in the carbonyl region

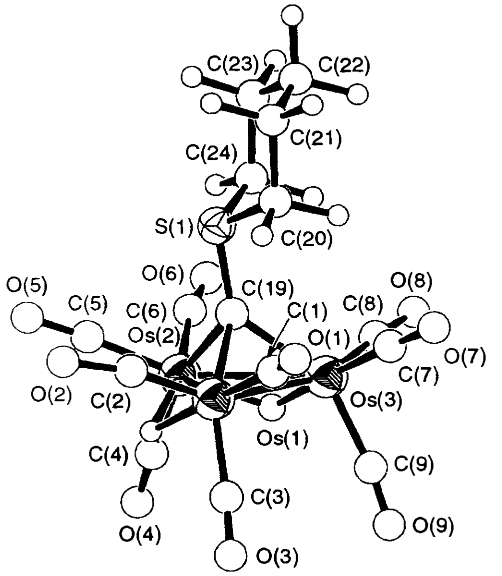


Fig. 1 Molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}\overline{CS(CH_2)_4C}H_2\}]$ **1**

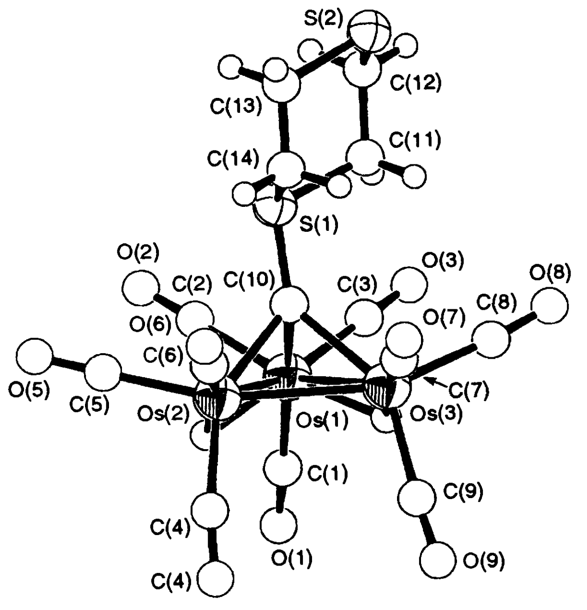


Fig. 2 Molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}\overline{CS(CH_2)_2SCH_2C}H_2\}]$ **2**

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

Os(1)–Os(2)	2.874(1)	Os(1)–Os(3)	2.897(1)
Os(2)–Os(3)	2.762(1)	Os(1)–C(10)	2.12(3)
Os(2)–C(10)	2.12(3)	Os(3)–C(10)	2.18(2)
S(1)–C(10)	1.68(2)	S(1)–C(11)	1.80(2)
C(11)–C(12)	1.47(3)	S(2)–C(12)	1.79(3)
S(2)–C(13)	1.81(3)	C(13)–C(14)	1.42(3)
S(1)–C(14)	1.84(3)		
Os(2)–Os(1)–Os(3)	57.2(1)	Os(1)–Os(2)–Os(3)	61.8(1)
Os(1)–Os(3)–Os(2)	61.0(1)	Os(1)–C(10)–S(1)	125(1)
Os(2)–C(10)–S(1)	129(1)	Os(3)–C(10)–S(1)	135(1)
C(10)–S(1)–C(11)	108(1)	C(10)–S(1)–C(14)	109(1)
S(1)–C(11)–C(12)	112(1)	S(2)–C(12)–C(11)	114(1)
S(1)–C(14)–C(13)	113(1)	S(2)–C(13)–C(14)	113(2)

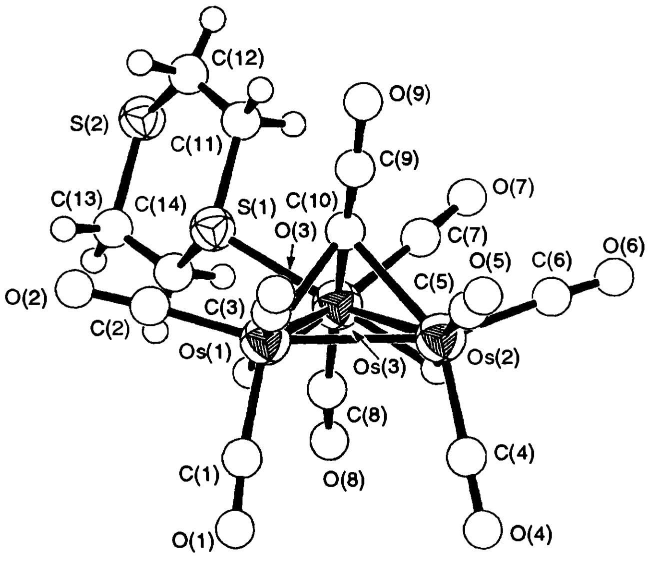
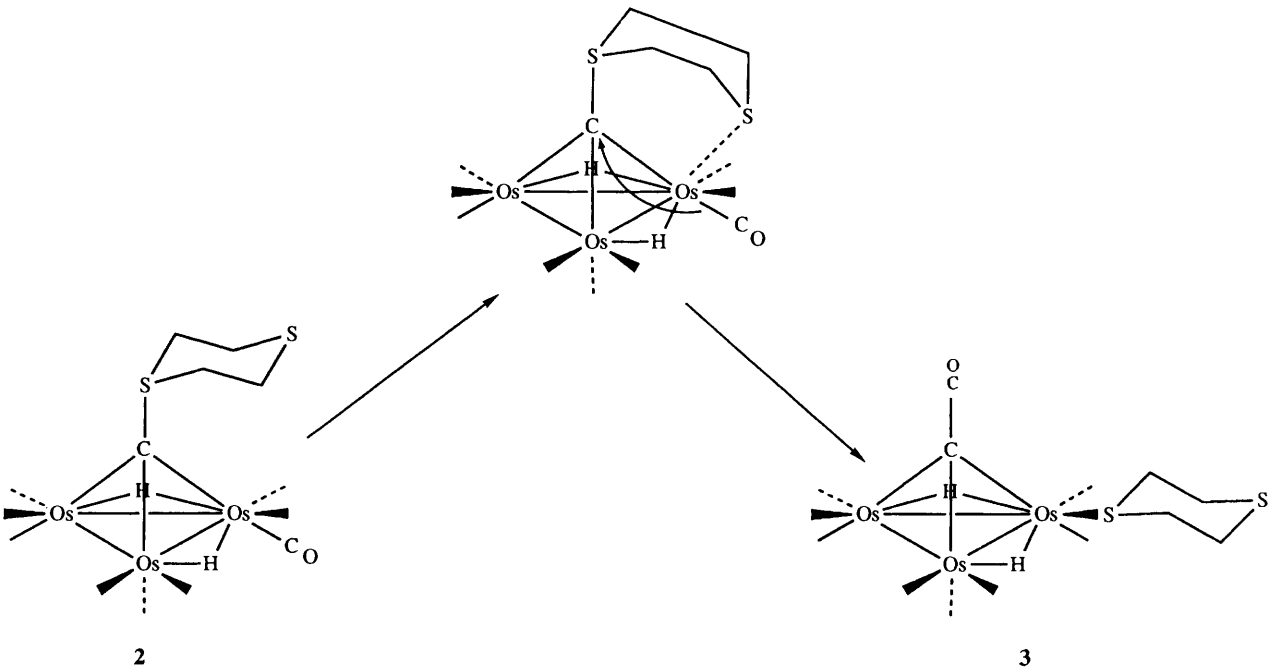


Fig. 3 Molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_8\{\overline{S(CH_2)_2SCH_2C}H_2\}(\mu_3\text{-}CCO)]$ **3**

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

Os(1)–Os(2)	2.750(2)	Os(1)–Os(3)	2.887(1)
Os(2)–Os(3)	2.850(2)	Os(3)–S(1)	2.379(8)
Os(1)–C(10)	2.38(3)	Os(2)–C(10)	2.37(2)
Os(3)–C(10)	1.94(2)	S(1)–C(11)	1.87(3)
C(11)–C(12)	1.30(5)	S(2)–C(12)	1.80(4)
S(2)–C(13)	1.89(4)	C(13)–C(14)	1.32(5)
S(1)–C(14)	1.85(3)	C(9)–C(10)	1.27(3)
C(9)–O(9)	1.18(3)		
Os(2)–Os(1)–Os(3)	60.7(1)	Os(1)–Os(2)–Os(3)	62.0(1)
Os(1)–Os(3)–Os(2)	57.3(1)	Os(1)–C(10)–C(9)	111(2)
Os(2)–C(10)–C(9)	107(2)	Os(3)–C(10)–C(9)	164(2)
O(9)–C(9)–C(10)	166(3)	Os(3)–S(1)–C(11)	110(1)
Os(3)–S(1)–C(14)	108(1)	S(1)–C(11)–C(12)	121(3)
S(2)–C(12)–C(11)	119(3)	S(1)–C(14)–C(13)	115(2)
S(2)–C(13)–C(14)	116(3)		

as compared to the parent cluster **2** but their positive FAB mass spectra exhibit identical molecular ion peaks. The ^1H NMR spectrum of **3** also shows the CH_2 resonances due to the 1,4-dithiane moiety (Table 1). In order structurally to characterise this complex, an X-ray structural analysis was carried out on a single crystal obtained from slow evaporation of a hexane–CH_2Cl_2 solution at room temperature for 3 d. The molecular structure of **3** is depicted in Fig. 3, together with the atomic labelling scheme. Relevant bond distances and angles are shown in Table 4. The solid-state structure of **3** reveals a distorted triosmium alkylidyne metal core with non-equivalent Os–C(10) distances, C(10) being closest to the osmium atom Os(3) by *ca.* 0.44 Å. The two hydrides bridge the Os(1)–Os(3) and Os(2)–Os(3) edges. There are eight terminal carbonyl ligands on the three osmium atoms. The 1,4-dithiane ligand, which acts as a two-electron donor, is σ bonded to Os(3) with Os(3)–S(1) 2.379(8) Å in a pseudo-equatorial position and retains its normal chair conformation. The formation of **3** involves a ligand rearrangement in the precursor complex **2** and the exchange of 1,4-dithiane and CO at the μ_3-carbon occurs to give a neutral triosmium ketenylidene compound. A similar isomerisation process has previously been observed for the thermal conversion of $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CPPh_3)]$ into $[Ru_3(\mu\text{-}H)_2(CO)_8(PPh_3)(\mu_3\text{-}CCO)]$.[6] The ketenylidene is co-ordinated by C(10) on top of the $Os_3(CO)_8(SCH_2CH_2SCH_2CH_2)$ base.



Scheme 2

Table 5 Crystal data and data-collection parameters for complexes 1–3

Compound	1	2	3
Formula	$C_{15}H_{12}O_9Os_3S$	$C_{14}H_{10}O_9Os_3S_2$	$C_{14}H_{10}O_9Os_3S_2$
M	938.92	956.95	956.95
Colour, habit	Colourless plate	Pale yellow block	Yellow plate
Crystal dimensions/mm	0.20 × 0.24 × 0.33	0.32 × 0.32 × 0.38	0.12 × 0.18 × 0.34
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no.2)	$C2/c$ (no.15)	$P\bar{1}$ (no.2)
a/Å	11.080(5)	13.297(3)	11.886(2)
b/Å	23.579(7)	11.487(4)	11.910(2)
c/Å	8.529(4)	28.489(2)	8.609(1)
α/°	98.73(3)	90.0	100.91(2)
β/°	103.16(4)	98.935(8)	96.40(1)
γ/°	89.65(3)	90.0	64.37(1)
U/Å^3	2143(1)	4298(1)	1078.4(3)
Z	4	8	2
D_c/g cm^{-3}	2.909	2.957	2.947
μ(Mo-Kα)/cm^{-1}	178.66	179.15	178.54
F(000)	1672	3408	852
Scan type	ω–2θ	ω–2θ	ω–2θ
Scan rate in ω/° min^{-1}	16.0	16.0	16.0
Scan range/°	0.94 + 0.35 tan θ	0.73 + 0.35 tan θ	1.21 + 0.35 tan θ
Reflections collected	5942	3154	2987
Unique reflections	5597	2996	2821
Observed reflections [$I > 3\sigma(I)$]	2818	2321	1936
No. of refined parameters	265	163	173
Transmission factor range	0.7029–1.0000	0.5090–1.0000	0.5671–1.0000
Weighting scheme, g in $w = 4F_o^2/[\sigma^2(F_o^2) + gF_o^2]^2$	0.010	0.002	0.002
R	0.059	0.049	0.039
R'	0.075	0.056	0.049
Residual electron density/e Å^{-3} (close to Os)	2.53 to −1.83	1.67 to −2.43	1.22 to −1.01

The bond distances within the CCO system C(9)–C(10) 1.27(3) and C(9)–O(9) 1.18(3) Å are comparable to the analogous distances in $[Fe_3(CO)_9(\mu_3\text{-}CCO)]^{2-}$ [1.28(3) and 1.18(3) Å],[7] $[Ru_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}CCO)]^{2-}$ [1.300(10) and 1.171(8) Å][8] and $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CCO)]$ [1.264(37) and 1.154(34) Å].[9] The ketenylidene ligand deviates from a linear geometry by 14° [C(10)–C(9)–O(9) 166(3)°] and is tilted over osmium atom centre Os(2) by an angle of 22.8° between the least-squares line through C(10)–C(9)–O(9) and the perpendicular to the plane of the osmium triangle. It is also worth noting that attempts to prepare the ketenylidene $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CCO)]$ by the reaction of $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ with CO in the presence of dbu failed and only the previously synthesised species $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CN_2C_9H_{16})]$[2] was isolated. Hence, complex **2** provides a facile route for activation of the apical carbon atom by CO and substitution of one of the terminal carbonyls of the parent alkylidyne cluster core by a sulfur-donor ligand.

To explain this phenomenon, we suggest that the more stable chair conformations of the cyclic thioether ligands in both complexes **1** and **2** slowly equilibrate to their less-stable boat

Table 6 Final atomic coordinates for complex **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Os(1)	0.336 4(2)	0.348 25(9)	0.505 6(3)
Os(2)	0.230 9(2)	0.314 30(9)	0.756 9(3)
Os(3)	0.090 8(2)	0.370 65(9)	0.499 9(2)
Os(4)	0.731 3(2)	0.195 66(9)	0.502 2(3)
Os(5)	0.797 5(2)	0.084 73(9)	0.550 7(3)
Os(6)	0.876 2(2)	0.132 40(9)	0.297 4(3)
S(1)	0.314(1)	0.455 1(5)	0.812(2)
S(2)	0.579(1)	0.083 5(6)	0.201(2)
O(1)	0.376(4)	0.436(2)	0.302(5)
O(2)	0.610(4)	0.347(2)	0.685(5)
O(3)	0.321(4)	0.255(2)	0.212(5)
O(4)	0.160(4)	0.188(2)	0.740(5)
O(5)	0.477(5)	0.318(2)	1.005(6)
O(6)	0.084(3)	0.355(1)	1.007(4)
O(7)	0.082(4)	0.469(2)	0.291(5)
O(8)	−0.141(4)	0.408(2)	0.619(5)
O(9)	−0.036(4)	0.284(2)	0.216(6)
O(10)	0.509(4)	0.197(2)	0.662(5)
O(11)	0.647(4)	0.291(2)	0.304(5)
O(12)	0.899(3)	0.267(2)	0.799(4)
O(13)	0.812(4)	−0.043(2)	0.457(5)
O(14)	0.587(3)	0.065(1)	0.711(4)
O(15)	0.984(4)	0.112(2)	0.877(5)
O(16)	1.148(4)	0.165(2)	0.347(5)
O(17)	0.781(3)	0.196(1)	0.013(4)
O(18)	0.901(4)	0.020(2)	0.094(5)
C(1)	0.348(5)	0.407(2)	0.372(6)
C(2)	0.495(6)	0.354(2)	0.608(7)
C(3)	0.317(5)	0.289(2)	0.326(7)
C(4)	0.192(5)	0.236(2)	0.746(6)
C(5)	0.376(5)	0.317(2)	0.916(7)
C(6)	0.148(5)	0.341(2)	0.928(7)
C(7)	0.091(4)	0.432(2)	0.372(6)
C(8)	−0.041(7)	0.394(3)	0.574(8)
C(9)	0.005(5)	0.319(2)	0.318(6)
C(10)	0.593(5)	0.197(2)	0.599(6)
C(11)	0.668(6)	0.254(3)	0.381(7)
C(12)	0.835(5)	0.240(2)	0.695(7)
C(13)	0.804(6)	0.008(3)	0.477(7)
C(14)	0.672(4)	0.071(2)	0.649(6)
C(15)	0.910(5)	0.101(2)	0.756(7)
C(16)	1.048(7)	0.159(3)	0.332(8)
C(17)	0.821(4)	0.170(2)	0.113(6)
C(18)	0.882(5)	0.059(2)	0.180(7)
C(19)	0.255(4)	0.393(2)	0.687(5)
C(20)	0.314(5)	0.509(2)	0.689(6)
C(21)	0.357(7)	0.570(3)	0.788(9)
C(22)	0.258(5)	0.586(2)	0.903(6)
C(23)	0.247(6)	0.544(3)	1.006(8)
C(24)	0.206(5)	0.480(2)	0.915(6)
C(25)	0.698(4)	0.118(2)	0.342(5)
C(26)	0.524(5)	0.132(2)	0.057(6)
C(27)	0.393(6)	0.105(3)	−0.044(8)
C(28)	0.295(5)	0.103(2)	0.037(7)
C(29)	0.343(7)	0.057(3)	0.153(10)
C(30)	0.456(5)	0.081(2)	0.285(7)

Table 7 Final atomic coordinates for complex **2** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Os(1)	0.755 69(8)	−0.049 38(9)	0.704 87(3)
Os(2)	0.595 00(8)	0.072 54(8)	0.645 56(3)
Os(3)	0.778 02(7)	0.043 68(9)	0.612 54(3)
S(1)	0.629 2(5)	−0.213 6(5)	0.616 2(2)
S(2)	0.638 2(6)	−0.407 3(6)	0.524 7(2)
O(1)	0.856(2)	0.078(2)	0.795 9(8)
O(2)	0.620(1)	−0.206(2)	0.756 7(7)
O(3)	0.921(2)	−0.240(2)	0.713 9(8)
O(4)	0.624(2)	0.331(2)	0.665 9(7)
O(5)	0.407(2)	0.010(2)	0.689 9(7)
O(6)	0.464(1)	0.108(2)	0.549 0(7)
O(7)	0.680(1)	0.085(2)	0.510 2(7)
O(8)	0.959(2)	−0.101(2)	0.587 7(7)
O(9)	0.857(2)	0.294(2)	0.617 2(8)
C(1)	0.819(2)	0.027(2)	0.761 9(9)
C(2)	0.674(2)	−0.154(3)	0.741(1)
C(3)	0.861(3)	−0.172(3)	0.712(1)
C(4)	0.604(2)	0.236(2)	0.657 9(9)
C(5)	0.480(2)	0.032(2)	0.675 4(9)
C(6)	0.515(2)	0.094(2)	0.586 1(9)
C(7)	0.719(2)	0.072(2)	0.548 4(9)
C(8)	0.896(2)	−0.043(3)	0.597 7(10)
C(9)	0.824(2)	0.207(3)	0.614(1)
C(10)	0.675(2)	−0.083(2)	0.636 0(8)
C(11)	0.734(2)	−0.306(2)	0.607(1)
C(12)	0.701(2)	−0.418(2)	0.585 0(9)
C(13)	0.536(2)	−0.309(2)	0.532 9(9)
C(14)	0.570(2)	−0.201(2)	0.553 8(9)

Table 8 Final atomic coordinates for complex **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Os(1)	0.870 5(1)	0.296 67(10)	0.910 9(1)
Os(2)	0.825 5(1)	0.405 12(10)	0.642 2(1)
Os(3)	0.745 2(1)	0.211 26(10)	0.639 7(1)
S(1)	0.646 4(7)	0.142 1(7)	0.802 2(9)
S(2)	0.437 6(9)	0.009 7(9)	0.757(1)
O(1)	1.152(2)	0.155(2)	0.910(2)
O(2)	0.828(2)	0.184(2)	1.181(3)
O(3)	0.872(2)	0.531(2)	1.125(2)
O(4)	1.095(2)	0.307(2)	0.532(3)
O(5)	0.825(2)	0.656(2)	0.807(2)
O(6)	0.680(2)	0.513(2)	0.349(3)
O(7)	0.530(2)	0.292(2)	0.392(2)
O(8)	0.887(2)	−0.043(2)	0.440(2)
O(9)	0.515(2)	0.576(2)	0.888(3)
C(1)	1.047(3)	0.204(3)	0.915(3)
C(2)	0.841(3)	0.232(3)	1.078(4)
C(3)	0.872(3)	0.441(3)	1.044(4)
C(4)	0.992(3)	0.342(3)	0.572(3)
C(5)	0.822(3)	0.564(3)	0.743(3)
C(6)	0.730(3)	0.479(3)	0.457(4)
C(7)	0.610(3)	0.264(3)	0.481(3)
C(8)	0.834(3)	0.045(3)	0.518(4)
C(9)	0.601(3)	0.484(3)	0.837(3)
C(10)	0.675(2)	0.376(2)	0.769(2)
C(11)	0.473(3)	0.220(3)	0.773(5)
C(12)	0.402(4)	0.175(3)	0.817(7)
C(13)	0.613(4)	−0.071(3)	0.785(6)
C(14)	0.678(3)	−0.025(3)	0.725(5)

forms in the solution state. Assuming no significant change of the alkylidyne carbon–sulfur bond length, flipping of the 1,4-dithiane from the chair conformation to the boat form will bring the pendant sulfur atom S(2) into the co-ordination sphere of atom Os(1) in complex **2**. Intramolecular ligand scrambling for the boat form of the precursor complex **2** is then favoured by formation of the Os–S bond (Scheme 2). However, the absence of an unco-ordinated sulfur atom in the boat form of **1** and the unfavourable steric interactions between the thiane and the pseudo-equatorial carbonyl ligands preclude any rearrangement and only the chair conformation occurs.

As far as the bonding description is concerned, both structural features and spectroscopic data (IR) for complexes **1**–**3** are consistent with a charge-separated zwitterionic formulation.[1b,2] For **3**, the ketenylidene ligand can be represented by either $[\mathrm{Os}_3{}^-]{\equiv}\mathrm{C{-}C{\equiv}O}^+$ or $[\mathrm{Os}_3]{=}\mathrm{C{=}C{=}O}$.

Experimental

None of the compounds reported is particularly air-sensitive, however all reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (CO stretching region). Dichloromethane was dried over CaH_2 and hexane distilled from sodium–benzophenone. The starting cluster $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ was prepared as described previously.[5a] The ligands were obtained from Lancaster Synthesis and used as received. Infrared spectra were recorded on a Bio-Rad FTS-7 IR spectrometer using 0.5 mm solution cells, ^1H NMR and ^1H–^1H COSY spectra on a JEOL GSX 270FT-NMR spectrometer [reference $SiMe_4$ (δ 0)] and mass spectra on a Finnigan MAT 95 instrument with the fast atom bombardment (FAB) technique. Routine separation of products were performed in the air by thin-layer chromatography using plates coated with Merck Kieselgel 60 GF_{254}.

Preparations.—$[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CY)]$ [Y = $\overline{S(CH_2)_4C}H_2$ **1** *or* $\overline{S(CH_2)_2SCH_2C}H_2$ **2**]. The complex $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ (87.3 mg, 0.10 mmol) and thiane (0.10 g, 1.0 mmol) or 1,4-dithiane (0.12 g, 1.0 mmol) were dissolved in CH_2Cl_2. Dropwise addition of a dbu–CH_2Cl_2 solution (0.10 mmol) gave a yellow solution. The mixture was stirred at room temperature for 15 min and subsequently evaporated to dryness under vacuum. The residue was purified by TLC using hexane–CH_2Cl_2(80 : 20, v/v) as eluent. Complex **1** was isolated as an off-white solid in 50% yield (47 mg) whereas pale yellow compound **2** was obtained in 40% yield (38 mg) (Found: C, 19.35; H, 1.30. Calc. for $C_{15}H_{12}O_9Os_3S$ **1**: C, 19.20; H, 1.30. Found: C, 17.40; H, 0.95. Calc. for $C_{14}H_{10}O_9Os_3S_2$ **2**: C, 17.55; H, 1.05%).

$[Os_3(\mu\text{-}H)_2(CO)_8\{\overline{S(CH_2)_2SCH_2C}H_2\}(\mu_3\text{-}CCO)]$ **3**. Compound **2** (40 mg, 0.04 mmol) was dissolved in CH_2Cl_2 (20 cm^3) under nitrogen to give a pale yellow solution. The mixture was allowed to stir for 24 h, resulting in a deep yellow solution. Following evaporation of most of the solvent, the mixture was subjected to preparative TLC using hexane–CH_2Cl_2(70 : 30, v/v) as eluent to afford crude yellow crystals of $[Os_3(\mu\text{-}H)_2(CO)_8\{\overline{S(CH_2)_2SCH_2C}H_2\}(\mu_3\text{-}CCO)]$ **3** (20 mg, 0.02 mmol) in 50% yield (Found: C, 17.30; H, 1.15. Calc. for $C_{14}H_{10}O_9Os_3S_2$: C, 17.55; H, 1.05%).

X-Ray Data Collection, Solution and Refinement.—Crystals of complexes **1**–**3** suitable for X-ray analysis were mounted on glass fibres with epoxy resin. Intensity data were collected at 298 K on a Rigaku AFC7R diffractometer using graphite-monochromatised Mo-Kα radiation (λ = 0.710 73 Å). Details of the intensity-data collection and processing parameters are summarised in Table 5. The intensity data were corrected for Lorentz-polarisation effects and semiempirical absorption corrections were made based on the ψ-scan method.[10] For **1**, decay (12.6%) of the crystal in the X-ray beam was observed. A linear decay correction was applied. The structures were solved by a combination of direct methods (SIR 88)[11] and Fourier-difference techniques and refined by full-matrix least-squares analysis. The Os and S atoms in **1**; Os, S and C in the 1,4-dithiane in **2** and Os, S, C in the 1,4-dithiane and ketenylidene ligand in **3** were refined anisotropically. The hydrogen atoms of the organic moieties were placed in their idealised positions (C–H 0.95 Å) while the metal hydride atom positions were estimated by potential-energy calculations.[4] All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.[12] Final atomic coordinates for **1**, **2** and **3** are listed in Tables 6, 7 and 8 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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