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A new two-strand chain cluster: the synthesis and characterisation of $[Os_3(CO)_{11}\{\mu_3\text{-}\eta^4\text{-}(C_4H_3S)C_2C_2(C_4H_3S)\}]$ †

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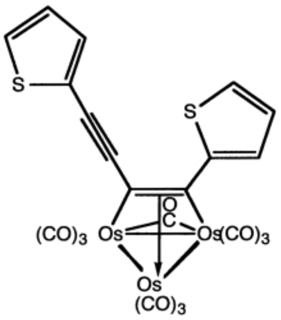
Reaction of the labile triosmium cluster $[Os_3(CO)_{10}(NCMe)_2]$ with the thienyl substituted diyne $[(C_4H_3S)C_2C_2(C_4H_3S)]$ affords $[Os_3(CO)_{10}\{\mu_3\text{-}\eta^2\text{-}(C_4H_3S)C_2C_2(C_4H_3S)\}]$ 1 and the novel co-linear cluster $[Os_3(CO)_{11}\{\mu_3\text{-}\eta^4\text{-}(C_4H_3S)C_2C_2(C_4H_3S)\}]$ 2 in reasonable yield; the X-ray structure of 2 shows that the diyne is coordinated to an 'open' triosmium unit as a 1,2,3-triene-1,4-diyl unit with essentially equal C=C bond distances.

The reaction of alkynes with metal clusters have been extensively studied,[1] and there has been more recent interest in the nature of the interactions between metal cluster compounds and diyne units.[2,3] The presence of the two C–C multiple bonds in the diyne provides a greater opportunity for interactions with several metal centres and leads to the possibility of metal and ligand arrangements that have not been observed for polyalkyne systems. The formation of extended carbon chains generated from carbon–carbon bond formation during a reaction are well established,[4] but there are rather fewer examples of reactions of transition metal clusters with diynes themselves, where the carbon chain is pre–formed. Recent reports in the area include the linking of triosmium and dicobalt carbonyl units through a diyne to form a series of compounds with the formula $[\{Os_3(CO)_{10}\}(\mu_3\text{-}\eta^2{:}\mu\text{-}\eta^2\text{-}RC_2C_2R')\{Co_2(CO)_6\}]$ (R = R′ = Me; R = H, R′ = SiMe$_3$).[5,6] A series of tri- and tetraruthenium clusters that contain diyne ligands derived from 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne have also been reported.[7]

Our interest in organometallic diyene systems stems from the use of polyynes and diyenes in the formation of novel organometallic polymers,[8] and in the formation of redox active, mixed-metal complexes.[9] As part of these investigations we studied the reactions of a variety of metal cluster species with functionalised diynes of the form RC_2C_2R where R = C_4H_3S and C_5H_4N. We now report the reaction of the triosmium cluster, $[Os_3(CO)_{10}(NCMe)_2]$, with 1,4-bis(2-thienyl)butadiyene and the formation of the novel two-stranded, chain cluster $[Os_3(CO)_{11}\{\mu_3\text{-}\eta^4\text{-}(C_4H_3S)C_2C_2(C_4H_3S)\}]$.

The reaction of equimolar quantities of $[Os_3(CO)_{10}(NCMe)_2]$ and 1,4-bis(2-thienyl)butadiyene, $[(C_4H_3S)C_2C_2(C_4H_3S)]$, in dichloromethane, at room temperature, resulted in a darkening of the orange solution.§ Subsequent solvent removal and purification by TLC using a 9:1 ratio of hexane:dichloromethane as eluent afforded an orange and a yellow band as the two major products. The two products were initially characterised by IR, ^{1}H and ^{13}C NMR spectroscopies and negative ion FAB mass spectrometry. The orange product, **1**, isolated in 40% yield, exhibited an IR spectrum in the ν(CO) region showing the presence of both terminal and bridging carbonyls, and a pattern that was closely related to that of the known diyne cluster $[Os_3(CO)_9(\mu\text{-}CO)\{Me_3SiC{\equiv}C\text{–}C{\equiv}CSiMe_3\}]$[3] in which one of the C–C multiple bonds caps the face of the Os_3 triangle in a μ_3-η^2-fashion. The ^{1}H NMR spectrum confirmed the presence of two inequivalent thienyl rings. The ^{13}C NMR spectrum also confirmed the presence of two thienyl rings and displayed signals in the same region as those reported for the diyne carbons in $[Os_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}\eta^2\text{-}Me_3SiC{\equiv}C\text{–}C{\equiv}CSiMe_3\}]$.[3] The highest peak in the mass spectrum, at m/z 1038, corresponded to the formula $[Os_3(CO)_{10}\{\mu_3\text{-}\eta^2\text{-}(C_4H_3S)C_2C_2(C_4H_3S)\}]$ **1** less one CO, and so this complex was identified as a further member[3] of the series $[Os_3(CO)_{10}\{\mu_3\text{-}\eta^2\text{-}RC_2C_2R\}]$ with R = C_4H_3S.



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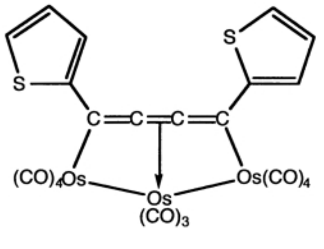

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The IR spectrum in the ν(CO) region of the yellow product, **2**, indicated the presence of terminal carbonyl ligands. The ^{1}H and ^{13}C NMR spectra suggested that the two thienyl rings of the diyne ligand were equivalent; consistent with the free rotation of the rings in solution. The ^{13}C NMR also confirmed the presence of the diyne carbon atoms, exhibiting two signals at δ 85.14 and 84.61. The highest peak in the mass spectrum, at m/z 1038, was consistent with the formulation "$Os_3(CO)_9\{(C_4H_3S)C_2C_2(C_4H_3S)\}$", but as in the case of **1** it was possible that additional carbonyl groups were present, but were not accounted for in this formulation. In order to establish the molecular formulation and the exact nature of the structure of **2** a single crystal X-ray analysis was undertaken.¶

The molecular structure of $[Os_3(CO)_{11}\{\mu_3\text{-}\eta^4\text{-}(C_4H_3S)C_2C_2(C_4H_3S)\}]$ **2** is illustrated in Fig. 1 which includes selected bond parameters. The three osmium atoms form a bent chain [Os(1)–Os(2)–Os(3) 162.91(3)°] that is bridged by a bis(thienyl)butatriene-1,4-diyl ligand. The C_4 chain, that forms the central feature of this ligand, is effectively linear [C(1)–C(2)–C(3) 172(2), C(2)–C(3)–C(4) 175.5(14)°], and lies approximately parallel to the triosmium chain. The whole Os_3C_4 unit is planar with a mean deviation from the plane defined by these seven atoms of only 0.007 Å. The two thienyl rings, one at each end of the C_4 chain, are also planar and make angles of 2.9° [for S(1)–C(8)] and 17.4° [for S(2)–C(12)] with the Os_3C_4 plane. Within experimental error the three C–C bond lengths of the C_4 chain are equal, with an average value of 1.32 Å, consistent with multiple bond character. The bonding interaction between the

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† Dedicated to the memory of Dr Ron Snaith, a close friend and an outstanding chemist.

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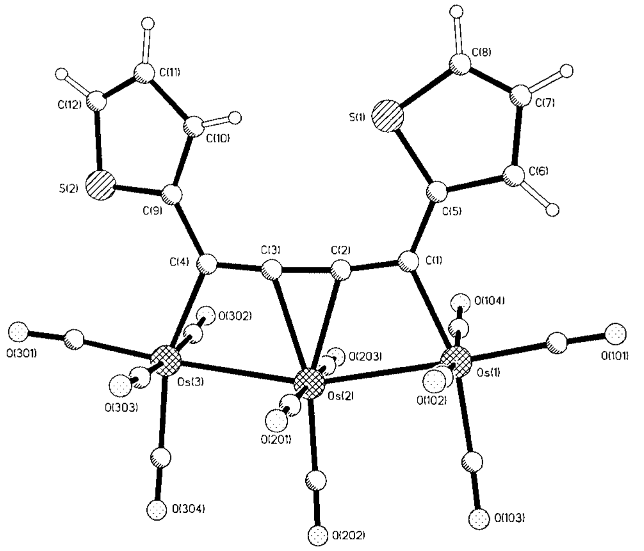
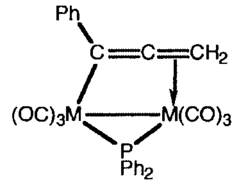


Fig. 1 The molecular structure of **2** with atom numbering scheme, showing the major occupancy of the thiophenyl rings. Selected bond lengths and angles: Os(1)–Os(2) 2.906(2), Os(2)–Os(3) 2.911(2), Os(1)–C(1) 2.121(14), Os(2)–C(2) 2.32(2), Os(2)–C(3) 2.321(13), Os(3)–C(4) 2.136(13), C(1)–C(2) 1.32(2), C(2)–C(3) 1.35(2), C(3)–C(4) 1.30(2), C(1)–C(5) 1.44(2), C(4)–C(9) 1.51(2) Å; Os(1)–Os(2)–Os(3) 162.91(3), Os(3)–C(4)–C(3) 111.0(10), Os(3)–C(4)–C(9) 127.4(9), Os(1)–C(1)–C(2) 106.8(10), Os(1)–C(1)–C(5) 132.0(10), C(3)–C(2)–C(1) 172(2), C(4)–C(3)–C(2) 175.5(14), C(2)–C(1)–C(5) 121.2(13), C(3)–C(4)–C(9) 121.4(12)°.

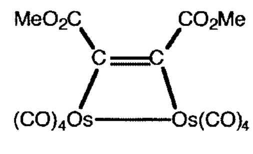
Os_3 and the C_4 chain can most simply be described as a σ-interaction between C(1) and Os(1) and C(4) and Os(3), and a π-interaction between Os(2) and C(2)/C(3). The ligand thus provides four electrons for ligand–metal bonding, and the total count for the cluster is 50 electrons, consistent with the near linear arrangement of the metal atoms. The eleven carbonyls are all essentially linear, with four bound to each of Os(1) and Os(3) and three bound to Os(2), so that each metal atom adopts a distorted octahedral geometry. The carbonyls on adjacent metal atoms are eclipsed, a configuration enforced by the presence of the diyne ligand. This is in contrast to the configuration in the linear cluster $\{Cl[Os(CO)_4]_3Cl\}$ where they are staggered, presumably to reduce ligand–ligand repulsions.[10]

In the crystal structure the two thienyl rings in each cluster are disordered over two orientations generated by rotation about the C(1)–C(5) and C(4)–C(9) bonds. The occupancies for the major and minor components are 0.78 : 0.22, and the rings are inequivalent, the S-atoms on one ring are directed inwards towards a H-atom on the other ring, *i.e. cis* to the diyne, the S-atom of the second ring being *trans* to the diyne. Despite this disorder a number of intermolecular contacts involving the thienyl S-atoms are apparent. There are two S···S contacts at *ca.* 3.62 Å involving S(1) and a second S(1) atom related by a centre of symmetry, and S(1A) and S(2) related by $0.5 - x$, $0.5 + y$, $0.5 - z$. There are several S···O contacts involving carbonyl ligands in the range 3.2–3.3 Å.

While the structure of cluster **2** is novel, it is related to that of the dinuclear allenyl clusters $[M_2(CO)_6(\mu\text{-}\eta^1:\eta^2\text{-}PhCCCH_2)(\mu\text{-}PPh_2)]$ (M = Ru **3a**, Os **3b**)[11] by the extension of the C and Os chains by one atom each. As such, these dinuclear clusters and **2** could be considered as members of the series of chain clusters $M_n(RC_{2n-1}R_2)$ and $M_n(RC_{2n-2}R)$ respectively, the $n = 2$ members of the second series being exemplified by the μ-η₂-|| alkyne cluster $[Os_2(CO)_8\{C_2(CO_2Me)_2\}]$ **4**.[12] However, there is a mismatch in the Os–Os and C=C bond lengths, as evidenced by the deviation of the Os–Os–Os angle in **2** from linearity. A related pattern of a four carbon chain spanning a triruthenium unit has also been observed in the mixed metal cluster $[Ru_3Co_2(\mu_5\text{-}\eta^2:\eta^2\text{-}PhC_2C_2Ph)(CO)_{14}]$, but in this case the carbon chain is stabilized by additional π-bonding to two "$Co(CO)_3$" units.[13]



M = Ru **3a**, Os **3b**



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The double strand structure of **2** is novel, and there are few reported examples of linear or near linear triosmium clusters.[14] None of the other functionalised diynes with the general formula RC_2C_2R in their reactions with $[Os_3(CO)_{10}(NCMe)_2]$ have so far been observed to give a product analogous to **2**.[6] An analogous reaction of the same thienyl functionalised ligand with $[Os_3(CO)_{11}(NCMe)]$ does not produce **2**, and thermal decarbonylation of **2** does not yield the μ_3-η^2 bound cluster **1**. This suggests that **2** is generated *via* CO ligand scavenging by an activated intermediate.

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Notes and references

§ Stirring $[Os_3(CO)_{10}(MeCN)_2]$ (0.20 g, 0.214 mmol) and 1,4-bis(thiophenyl)butadiyne (50 mg, 0.0235 mmol) in dichloromethane at 20 °C results in a darkening of the orange solution. Solvent removal followed by TLC on silica plates afforded an orange and yellow product [hexane–CH_2Cl_2 (9 : 1)]. The orange product was isolated from the top of the plate near the solvent front and identified as $[Os_3(\mu\text{-}CO)(CO)_9\{\mu_3\text{-}\eta_2\text{-}(SC_4H_3)C_2C_2(C_3H_4S)\}]$ **1** and isolated in 40% yield (Found: C, 26.02; H, 0.78%. Calc. for $C_{22}H_6O_{10}Os_3S_2$: C, 24.76; H, 0.56%). The yellow product was recovered from close to the first band and spectroscopically and crystallographically identified as $[Os_3(CO)_{11}\{\mu_3\text{-}\eta_1:\eta_2:\eta_1\text{-}(SC_4H_3)\text{-}C_2C_2(C_3H_4S)\}]$ **2** in 20% yield (Found: C, 25.90; H, 0.83%. Calc. for $C_{23}H_6O_{11}Os_3S_2$: C, 25.22; H, 0.55%) Spectroscopic data: **1**, IR (CH_2Cl_2) 2128(w), 2101(m), 2067(vs), 2054(s), 2051(ms), 2005(m), 1842(w, br) cm^{-1}; NMR (500 MHz, CD_2Cl_2, ^1H), δ 7.33 (dd, 1H, $^3J = 3.81$, $^4J = 1.10$), 7.29 (dd, 1H, $^3J = 5.13$, $^4J = 1.06$), 7.26 (dd, 1H, $^3J = 3.67$, $^4J = 1.12$), 7.16 (dd, 1H, $^3J = 5.03$, $^4J = 1.06$), 6.98 (dd, 1H, $^3J = 3.80$, $^3J = 3.67$), 6.96 (dd, 1H, $^3J = 5.18$, $^3J = 5.00$ Hz), (400 MHz, CD_2Cl_2, ^{13}C), δ 174–180 (br, 10CO) 155.98, 145.85 (s, 2C, C^{ipso}) 131.94, 128.46, 128.00, 127.49, 127.25, 126.53 (s, 2C, C^H) 112.89, 106.36 (s, 2C, COs), 95.40, 87.94 (s, 2C, C≡C); negative FAB mass spectrum *m*/*z* 1038 (*M* − CO); **2**, IR (CH_2Cl_2) 2101(m), 2067(m), 2046(vs), 2035(sh), 2004(m), 1958(w), NMR (500 MHz, CD_2Cl_2, ^1H), δ 7.43 (dd, 2H, $^3J = 4.60$, $^4J = 1.04$, CH), 7.24 (dd, 2H, $^3J = 3.68$, $^4J = 1.06$, CH), 7.18 (dd, 2H, $^3J = 4.57$, $^3J = 3.72$ Hz, CH), (400 MHz, CD_2Cl_2, ^{13}C) δ 187.30 (s, 2C, CO), 184.69 (s, 1C, CO), 174.49 (s, 4C, CO) 172.91 (s, 2C, CO), 166.27 (s, 2C, CO), 154.74 (s, 2C, C^{ipso}) 128.28, 127.25, 127.00 (s, 6C, CH), 85.14, 84.61 (s, 4C, diynyl chain C); negative FAB mass spectrum *m*/*z* 1038 (*M* − 2CO).

¶ Crystal data for **2**: $C_{23}H_6O_{11}Os_3S_2$, $M = 1201.13$, monoclinic, space group $P2_1/c$ (No. 14), $a = 7.071(4)$, $b = 21.964(12)$, $c = 16.564(10)$ Å, $\beta = 96.15(4)°$, $U = 2558(3)$ Å³, $Z = 4$, $\mu(Mo\text{–}K_\alpha) = 15.090$ mm^{-1}, $T = 195(2)$ K. 6205 reflections collected, 4495 unique absorption corrected data ($R_{int} = 0.0749$; max., min. relative transmission 1.000, 0.155). Structure solved by direct methods (Os atoms) (SIR-92[15]) and refined with Os and O atoms anisotropic by full–matrix least squares based on F^2 (SHELXL–97[16]). The thienyl rings were disordered over two positions and were refined with appropriate constraints to their positional and thermal parameters. Refinement with 243 parameters and 24 restraints converged at $R_1 = 0.0626$, $wR_2 = 0.1665$ for 3972 unique data with $F > 4\sigma(F)$, and $R_1 = 0.0693$ and $wR_2 = 0.1776$ (all data). CCDC reference number 186/2215. See http://www.rsc.org/suppdata/dt/b0/b006696f/ for crystallographic files in .cif format.

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