Synthesis and Characterisation of the Heptanuclear Trimetallic Cluster $[\{Fe_2(CO)_6\}(\mu_4\text{-}Te)(\mu_3\text{-}Te)\{Ru_3(CO)_{11}\}]$

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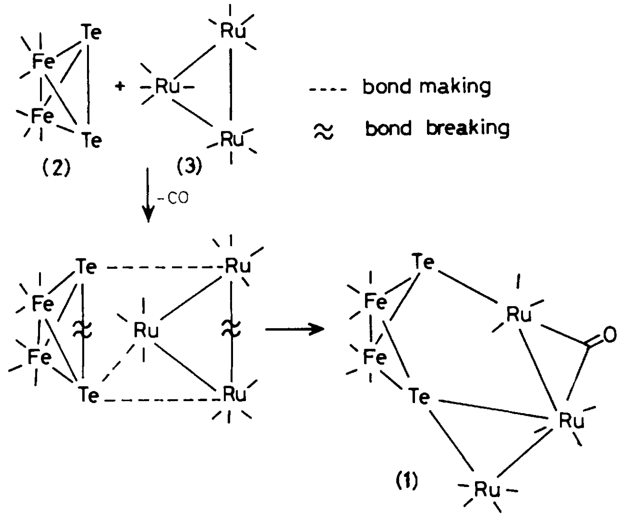
The trimetallic cluster $[\{Fe_2(CO)_6\}(\mu_4\text{-}Te)(\mu_3\text{-}Te)\{Ru_3(CO)_{11}\}]$ (**1**) has been prepared from the room temperature reaction of $Fe_2Te_2(CO)_6$ (**2**) and $Ru_3(CO)_{12}$ (**3**) in benzene, and shown by *X*-ray analysis to consist of an '$Fe_2(CO)_6$' fragment connected to a '$Ru_3(CO)_{11}$' fragment by triply and quadruply bridging tellurium atoms.

In recent years the use of single-atom ligands derived from the main groups has been shown to serve as a useful initial point of contact with metal fragments in the systematic synthesis of high nuclearity clusters.[1] This strategy has been extensively used for the synthesis of numerous sulphur-containing clusters.[2] Although the use of selenium-containing complexes as starting materials for cluster growth has also been reported,[3] the utility of tellurium-containing complexes for similar types of reactions has been only slightly explored. The co-ordinatively unsaturated $M(PPh_3)_2$ (M = Ni, Pd, Pt) fragments have been shown to add across the tellurium atoms in $Fe_2Te_2(CO)_6$ to form the mixed metal complexes, $(CO)_6Fe_2(\mu_3\text{-}Te)_2M(PPh_3)_2$.[4] Here, we report the addition of a '$Ru_3(CO)_{11}$' fragment across the Te–Te bond of (**2**) to yield the novel cluster, $[\{Fe_2(CO)_6\}(\mu_4\text{-}Te)(\mu_3\text{-}Te)\{Ru_3(CO)_{11}\}]$ (**1**), which is the first example of a cluster addition across the Te–Te bond of (**2**).

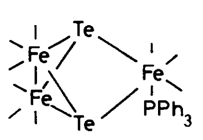
Room temperature stirring of (**2**), (two-fold excess), with $Ru_3(CO)_{12}$ (**3**), in benzene, yielded the novel mixed metal cluster (**1**) in almost quantitative yields. Complex (**1**) was



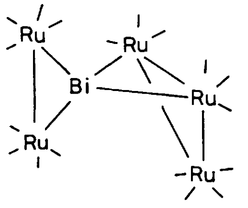
Scheme 1

separated from the unreacted (**2**) on silica gel t.l.c. plates, and was characterised by i.r. spectroscopy and mass spectrometry.[†] The i.r. spectrum exhibits eight bands in the carbonyl stretching region which suggests an asymmetric arrangement of CO ligands. The fast atom bombardment mass spectrum shows a molecular ion peak at 1151, and peaks corresponding to the successive loss of 17 CO groups. Elemental analysis confirms the molecular formula, $Ru_3Fe_2Te_2(CO)_{17}$. The overall mechanism of formation of (**1**) involves the cleavage of the Te–Te bond in (**2**), the loss of a CO group from (**3**) accompanied by the cleavage of a Ru–Ru bond, and the addition of the open '$Ru_3(CO)_{11}$' fragment, so formed, to the tellurium atoms in (**2**), (Scheme 1). The relatively large size of tellurium prevents any bond formation between iron and ruthenium atoms, and an open type of cluster results. This is in marked contrast to the use of the sulphido ligand in cluster growth whereby the initial contact of the adding cluster unit is very often followed by formation of new metal–metal bonds to form clusters with closed types of structures.[5]

Dark red, air stable, brick shaped crystals of (**1**) were obtained from CH_2Cl_2/hexane solution at −4 °C and an *X*-ray analysis was undertaken.[‡] The molecular structure of (**1**) shows that the asymmetric unit contains three independent molecules. An ORTEP diagram of the molecular structure of one molecule is shown in Figure 1, together with selected bond parameters. The three molecules differ primarily in the details of Ru(2)–Ru(3) bridging. Two are clearly μ_2-CO [Ru(3)–C(14)–O(14) angles 148° and 152° respectively] while the third is possibly weakly bridged [Ru(3)–C(14)–O(14) angle 175°].



(**4**)



(**5**)

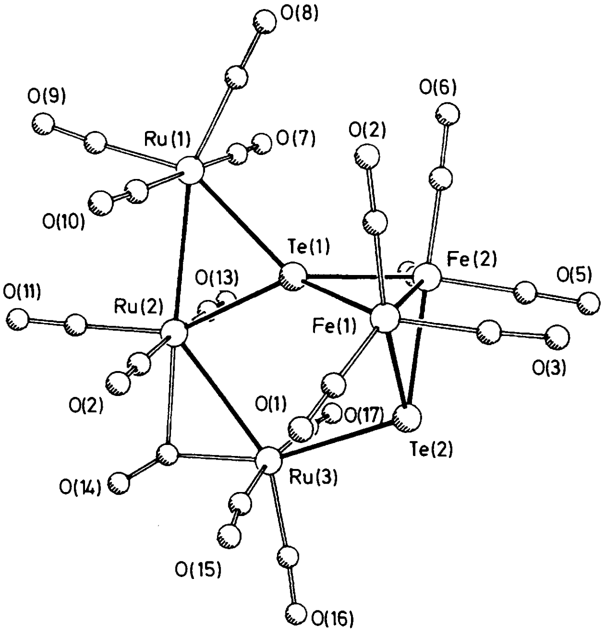


Figure 1. Molecular structure and labelling scheme for $[\{Fe_2(CO)_6\}(\mu_4\text{-}Te)(\mu_3\text{-}Te)\{Ru_3(CO)_{11}\}]$ (**1**). The unit cell contains three crystallographically independent, but chemically similar, molecules; the figure and the following bond distances refer to molecule A. Te(1)–Ru(1), 2.647(1); Te(1)–Ru(2), 2.596(1); Te(1)–Fe(1), 2.485(2); Te(1)–Fe(2), 2.494(2); Te(2)–Ru(3), 2.816(1); Te(2)–Fe(1), 2.592(1); Te(2)–Fe(2), 2.591(2); Ru(1)–Ru(2), 2.971(1); Ru(2)–Ru(3), 2.929(1); Fe(1)–Fe(2), 2.650(2); Ru(2)–C(14), 2.354(10); Ru(3)–C(14), 1.981(10) Å.

The metal core geometry can best be described as an '$Fe_2(CO)_6$' fragment connected to a '$Ru_3(CO)_{11}$' fragment by a pseudo-tetrahedral μ_4-tellurium atom and a μ_3-tellurium atom, and two of the ruthenium atoms are bridged by a μ_2-CO group. The environment of the μ_4-Te atom in (**1**) may be compared with that of the sole bismuth atom in the cluster $Ru_2(CO)_8(\mu_4\text{-}Bi)HRu_3(CO)_{10}$ (**5**), in which the bismuth atom is the link between a Ru_2 and a Ru_3 fragment to give a spiro type of cluster.[6] The two Ru–Ru bond distances in (**1**) are slightly greater than those found in (**3**). Also, the Fe–Fe bond in (**1**) is longer than that observed for the related compound $(CO)_6Fe_2(\mu_3\text{-}Te)_2Fe(CO)_3PPh_3$, (**4**).[7] The average Te–Fe–Te angle of *ca.* 79° observed in (**1**), is slightly more than the average Te–Fe–Te angle of *ca.* 75° in (**4**), indicating a greater opening of the Fe_2Te_2 butterfly tetrahedron to accommodate the larger triruthenium fragment in (**1**).

In terms of the electron counting rules, assuming that the μ_4-Te is a six-electron ligand, and that the μ_3-Te is a four-electron ligand, compound (**1**) is an 84-electron cluster, suggesting the presence of three metal–metal bonds, as

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[†] I.r. spectrum; μ_{CO} (hexane): 2122w, 2093.4s, 2053.5vs, 2040m, 2028w, 2020.7m, 1994m, 1985.5m. M^+; *m/z* 1151

[‡] *Crystal data* for (**1**): $Fe_2Ru_3(CO)_{17}Te_2$, triclinic, a = 10.688(4), b = 17.008(4), c = 24.806(7) Å, α = 80.39(2), β = 77.96(2), γ = 87.73(2)°, U = 4348.6(22) Å^3, Z = 6, $\mu(\text{Mo-}K_\alpha)$ = 46.0 cm^{-1}, D_c = 2.626 g cm^{-3}. Of 14,001 data collected and corrected for absorption (Nicolet R3m, 4° ≤ 2θ ≤ 48°, 293 K), 13,645 were independent, and 9,548 with $F_0 \geq 5\sigma F_0$ were observed. With all atoms anisotropic: R_F = 3.58%, R_{wF} = 4.41%, GOF = 0.993, N_o/N_v = 9548/1106, $\Delta(\rho)_{max}$ = 0.86 e Å^{-3}. SHELXTL (5.1) software, G. Sheldrick, Nicolet XRD, Madison, WI (U.S.A.). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

observed. The metal core geometry of (**1**) can also be described as consisting of a Fe_2Te_2 'butterfly,' with the wing-tip tellurium atoms linked to a bent Ru_3 unit. Although, there are several complexes reported in which the wing tips of (**2**) are bridged by mononuclear co-ordinatively unsaturated species,[8] cluster (**1**) is the first example where a polynuclear metal fragment bridges the wing-tip tellurium atoms of (**2**). In addition, compound (**1**) represents a unique example of a cluster consisting of M_2 and M'_3 units connected by two tellurium atoms. Further work is currently in progress to determine the factors controlling the addition of different metal fragments across the Te–Te bond of (**2**).

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