Synthesis of Cuboidal $(C_5H_4Me)_4Ru_4E_4$ by Condensation of $(C_5H_4Me)Ru(PPh_3)_2EH$ (E = S, Se)

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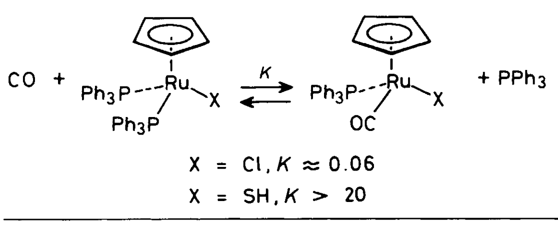
$(C_5H_4R)Ru(PPh_3)_2EH$ (E = S, Se) complexes undergo condensation in hot toluene solutions to give high yields of $[(C_5H_4R)_4Ru_4E_4]$, the first Ru_4E_4 cubanes; a structural study of the Ru_4S_4 species shows two short Ru–Ru distances consistent with a 68e cluster.

Ligand labilization by co-ordinated main group anions is a common phenomenon and often appears to be related to the π-donor abilities of the anion.[1] We report an extraordinary example of such an effect as it applies to the synthesis of the first Ru_4S_4 cubane cluster. Iron–sulphur cubanes, *e.g.* $(C_5H_5)_4Fe_4S_4$[2] and $Fe_4S_4(SR)_4{}^{n-}$,[3] have been studied extensively over the past 15 years but Ru–S clusters have been examined only in the context of carbonyl chemistry.[4]

We have been studying the properties of $(C_5H_5)Ru(PPh_3)_2SH$ in an extension of our recent work on $[(C_5H_5)Ru(PPh_3)_2]_2S_2{}^{2+}$.[5] As will be described in a forthcoming full report,[6] the neutral SH complex can be easily oxidized to the persulphido dication. The RuSH compound is prepared in 65% yield from the reaction of $(C_5H_5)Ru(PPh_3)_2Cl$ and NaSH in refluxing methanol. The yellow–brown, air-sensitive metallothiol is analogous to $(C_5Me_5)Ru(PMe_3)_2SH$ recently described by Bryndza and coworkers.[7] One of the unusual characteristics of $(C_5H_5)Ru(PPh_3)_2SH$ is the lability of the PPh_3 ligands as evidenced by its carbonylation (1 atm, 12 h, toluene soln.) to give $(C_5H_5)Ru(PPh_3)(CO)SH$ (ν_{CO} 1958 cm^{-1} for CH_2Cl_2 solution).† In contrast, the monocarbonylation of $(C_5H_5)Ru(PPh_3)_2Cl$ is thermodynamically unfavourable (equation 1).[8]

In the light of these results we investigated the possibility of condensation of $(C_5H_5)Ru(PPh_3)_2SH$ by thermal elimination of PPh_3 ligands. Refluxing a toluene solution of the SH complex for 18 h indeed gave free PPh_3 together with a poorly soluble red–brown solid. The analogous reaction of the more soluble $(C_5H_4Me)Ru(PPh_3)_2SH$ gave a 65% yield of brown $[(C_5H_4Me)RuS]_n$ (**1**). Cluster (**1**) is highly soluble in polar



(1)

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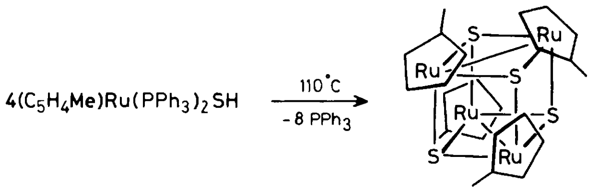
† All new compounds gave satisfactory elemental analyses.



(2)

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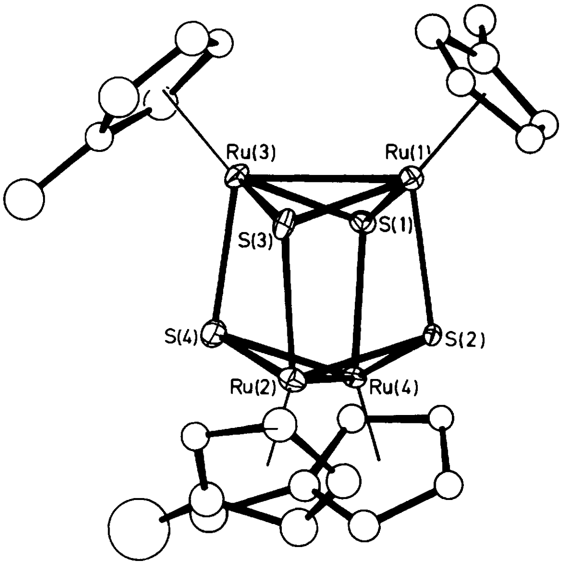

Figure 1. ORTEP drawing of the non-hydrogen atoms of one of two crystallographically independent molecules of [$(C_5H_4Me)_4Ru_4S_4$] (**1**). Important bond distances (Å) and angles (°): Ru(1)–S(1) 2.300(7), Ru(3)–S(1) 2.312(7), Ru(3)–S(3) 2.307(7), Ru(1)–S(3) 2.318(7), Ru(1)–S(2) 2.366(7), Ru(2)–S(3) 2.379(7), Ru(4)–S(1) 2.354(7), Ru(3)–S(4) 2.373(7), Ru(1)–Ru(3) 2.768(3), Ru(2)–Ru(4) 2.766(3); Ru(1)–S(1)–Ru(3) 73.8(2), Ru(1)–S(1)–Ru(4) 101.2(2), Ru(1)–S(2)–Ru(2) 99.8(2), Ru(1)–S(2)–Ru(4) 100.8(3), Ru(3)–Ru(1)–S(1) 53.3(2), Ru(3)–Ru(1)–S(2) 98.7(2), Ru(3)–Ru(1)–S(3) 53.1(2), Ru(3)–Ru(1)–Cp(1) 132.1(5), S(1)–Ru(1)–S(3) 96.3(2), S(1)–Ru(1)–Cp(1) 128.2(6), S(2)–Ru(1)–Cp(1) 129.2(5).

organic solvents and may be crystallized from toluene/hexanes. The electron impact mass spectrum of (**1**) showed a strong envelope of peaks centred at $m/z = 850$ corresponding to a tetramer. The 300 MHz ^1H n.m.r. spectrum of $CDCl_3$ solutions of (**1**) indicate high symmetry suggesting a cubane: only one methyl singlet and two C_5H_4Me multiplets (δ 4.57 and 4.40) are observed. Hydrogen in the SH group of the precursor metallothiol is presumed to be lost as H_2 (equation 2).[9]

Crystals of [$(C_5H_4Me)_4Ru_4S_4$]·0.5 C_6H_6 were grown by slow evaporation of a benzene solution and were examined by single crystal *X*-ray diffraction.‡ There are two very similar clusters in the asymmetric unit. As shown in Figure 1, the cubane is highly distorted. For each cluster two metal–metal distances are bonding [range 2.746(3)—2.768(3) Å] while the other four intermetallic contacts are non-bonding at >3.5 Å. The Ru–S distances invite the view of the cluster as a dimer of $(C_5H_4Me)_2Ru_2S_2$ subunits. The eight 'intradimer' Ru–S distances range from 2.299(7) to 2.324(7) Å while the 'interdimer' Ru–S distances are significantly longer at 2.354(7)—2.379(7) Å.

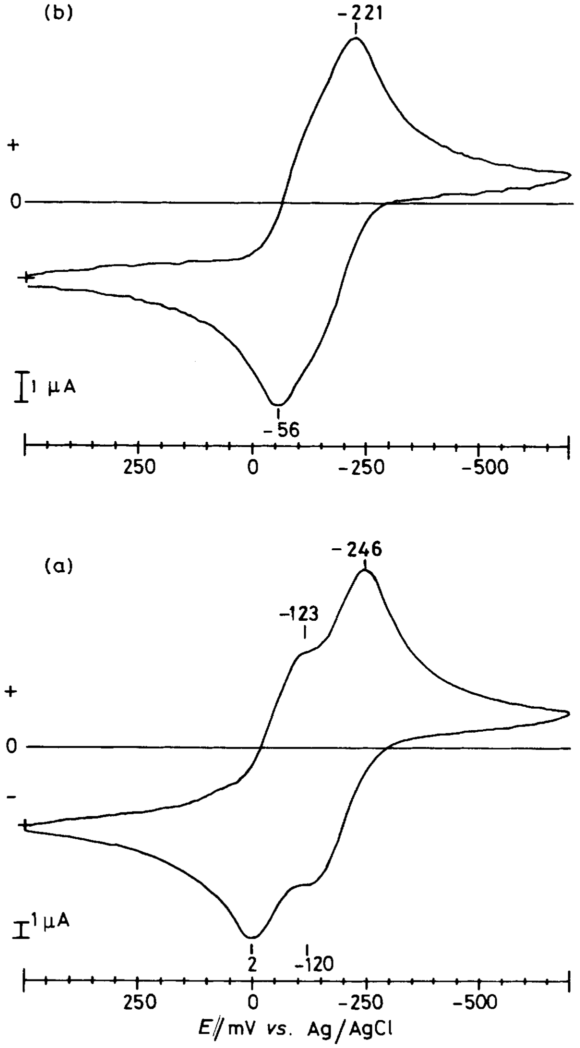

Figure 2. Cyclic voltammograms for 10^{-3} M methylene chloride solutions (0.1 M $Bu^n_4NPF_6$) of (a) [$(C_5H_4Me)_4Ru_4S_4$] and (b) [$(C_5H_4Me)_4Ru_4Se_4$] on a Pt electrode with a scan rate of 200 mV/s.

Cyclic voltammetry studies show that (**1**) undergoes one-electron oxidations at −183 and −62 mV *vs.* Ag/AgCl. A coulommetric measurement at 500 mV confirms that this pair of waves is associated with a two-electron change [Figure 2(a)]. No further oxidations are observed out to 850 mV where a quasireversible oxidation is observed. In view of the recent interest in chrage-transfer salts of metal chalcogenide clusters,[10] the tetracyanoquinodimethane (TCNQ) derivatives of (**1**) were briefly examined. When dichloromethane solutions of (**1**) and TCNQ (2 equiv.) are combined one obtains purple microcrystals analysing as [$(C_5H_4Me)_4Ru_4S_4$]-$(TCNQ)_2$·CH_2Cl_2. When only one equivalent of TCNQ is

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‡ *Crystal data* for (**1**): $C_{24}H_{28}Ru_4S_4$, $M = 1776.13$, monoclinic, $P2_1/n$ (no. 14), $a = 12.177(5)$, $b = 23.904(6)$, $c = 18.922(7)$ Å, $\beta = 90.92(3)°$, $U = 5507(6)$ Å^3, $Z = 8$, (Ru_4S_4 units), $D_c = 2.142$ g cm^{-3}, Mo-K_α radiation; 4969 unique reflections measured with an Enraf-Nonius CAD-4 diffractometer over the range $2.0 \leqslant 2\theta \leqslant 38.0°$ (ω/θ scan mode). The data were corrected for Lorentz, polarization, absorption, and anomalous dispersion effects. The structure was solved by direct methods and refined (difference Fourier synthesis; full matrix least squares) using 2314 reflections with $I > 2.58\sigma(I)$. The final residuals were $R = 0.046$, $R_w = 0.048$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

added to solutions of (**1**) a mixture of unreacted (**1**) and the 1:2 TCNQ salt was obtained.

Starting with $(C_5H_4Me)Ru(PPh_3)_2SeH$ we also prepared $[(C_5H_4Me)RuSe]_4$ as highly soluble brown crystals. The spectroscopy and solubility of the Ru_4Se_4 and Ru_4S_4 clusters are very similar.[11] Cyclic voltammetry indicates that the Ru_4Se_4 species undergoes a near simultaneous two-electron oxidation [Figure 2(b)]. We are currently testing the generality of this condensation method for the synthesis of other cluster compounds.

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