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Preliminary Communication

Complete desulfurization of diethyldithiocarbamato ligands to give a pentaruthenium cluster containing diethylaminomethylidyne ligands

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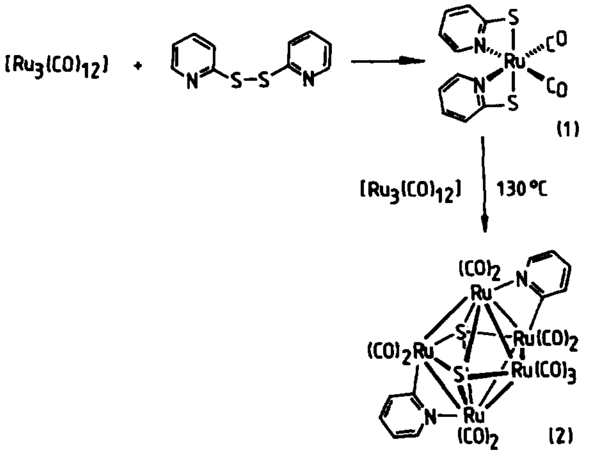
Abstract

Oxidative addition of the disulfide $Et_2NC(S)SSC(S)NEt_2$ to the cluster $[Ru_3(CO)_{12}]$ leads to the diethyldithiocarbamato complex, $[Ru(Et_2NCS_2)_2(CO)_2]$ **3**, which reacts with more $[Ru_3(CO)_{12}]$ to give mainly the pentanuclear cluster, $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}CNEt_2)_2(CO)_{11}]$ **4**, containing bridging diethylaminomethylidyne ligands derived by cleavage of *both* C–S bonds of *both* dithiocarbamato ligands.

The diethyldithiocarbamato ligand (Et_2NCS_2) has been much studied as a generally robust bidentate ligand [1], but in a few cases it has been shown to undergo fragmentation to give complexes containing the diethylthiocarbamyl ligand, Et_2NCS, for example at Mo, Nb and Ta centres [2–5]. In one case, a double desulfurization of the Et_2NCS_2 ligand was proposed to account for the formation of the S_2 complex $[Mo(NPh)(\eta^2\text{-}S_2)(Et_2NCS_2)_2]$ on reaction of PhNCO with $[MoO_2(Et_2NCS_2)_2]$ [6]. In this case the residue of Et_2NCS_2 after abstraction of S_2 was not recovered. However, in some of our recent work in which we were trying to relate the chemistry of pyridine-2-thionato to that of diethyldithiocarbamato ligands, we discovered a reaction leading to complete removal of two S-atoms from the Et_2NCS_2 ligand to form a cluster contain the diethylaminomethylidyne ligand, $CNEt_2$.

The cluster $[Ru_3(CO)_{12}]$ reacts cleanly with the 2,2′-dipyridyl disulfide (pySSpy) to give the pyridine-2-thionato ruthenium(II) complex, $[Ru(pyS)_2(CO)_2]$ **1**, which can also be prepared in other ways [7,8]. We have shown that this ruthenium complex reacts with $[Ru_3(CO)_{12}]$ in refluxing xylene in an open vessel from which CO can escape to give the pentanuclear cluster $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{11}]$, **2**, both pyS ligands having been cleaved into 2-pyridyl and sulfido ligands [9]. Reaction in a sealed glass tube gives additional complexes with higher CO content *viz.* $[Ru_4(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)_2(CO)_{12}]$ and $[Ru_6(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{18}]$. The Ru_5 cluster contains a pentagonal bipyramidal arrangement of the Ru_5S_2 atoms, and the separated sulfido and 2-pyridyl groups are incorporated as ligands (Scheme 1) [9]. This prompted us to use the same procedure in an attempt to synthesise the new diethylthiocarbamyl cluster, $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}Et_2NCS)_2(CO)_{11}]$, by C–S bond cleavage.



Scheme 1.

The disulfide, $Et_2NC(S)SSC(S)NEt_2$, reacts with $[Ru_3(CO)_{12}]$ in refluxing heptane for 8 h to give the diethyldithiocarbamato complex, *cis*-$[Ru(Et_2NCS_2)_2(CO)_2]$ **3**, pale yellow crystals in good yield, by oxidative addition. The formula and structure were confirmed by IR, NMR, and mass spectroscopy [10*]. Reaction between **3** and $[Ru_3(CO)_{12}]$ (mol ratio, 1:1) in refluxing xylene under nitrogen for 30 min gave a mixture from which we separated and characterised a minor uncharacterised green product and deep red crystals of **4** as the main product [11*]. The ^1H NMR spectrum of **4** showed two A_2X_3 patterns and one ABX_3 pattern in intensity ratio 1:1:2, whereas a structure directly analogous to that of **2** would have exhibited four equal intensity ABX_3 patterns. The

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* Reference number with asterisk indicates a note in the list of references.

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mass spectrum indicated that the diethylthiocarbamyl formulation $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}Et_2NCS)_2(CO)_{11}]$ was incorrect, and that **4** actually contains two fewer S atoms than required by this formula.

A single-crystal X-ray structure determination established the molecular structure shown in Fig. 1 [12*]. The Ru_5S_2 core is pentagonal bipyramidal, very similar to that in cluster **2**. There is a Ru_4 butterfly arrangement with the fifth Ru atom bridging the wing-tip Ru atoms and the μ_4-S atoms are pyramidal and thereby behave as 4-electron donors. The organic bridges are diethylaminomethylidyne ($CNEt_2$) rather than diethylthiocarbamyl ligands (Et_2NCS), and this is the first report of this ligand being formed from diethyldithiocarbamate. All four S atoms have been abstracted from the two original Et_2NCS_2 ligands of **3**, but only two remain in the cluster. We do not know the fate of the other two, but they are likely to be incorporated into ruthenium-sulfido by-product. Unlike in cluster **2**, in **4** there is a molecular plane of symmetry, and the organic bridges are differently positioned (compare **2** in Scheme 1 with **4** in Scheme 2) so that the ^{1}H NMR spectrum can be rationalised. One $CNEt_2$ ligand has equivalent Et groups with diastereotopic CH_2 protons giving an ABX_3 ^{1}H NMR pattern and the Et groups in the other ligand are non-equivalent but there is a molecular mirror plane through the ligand so that two A_2X_3 patterns are observed.

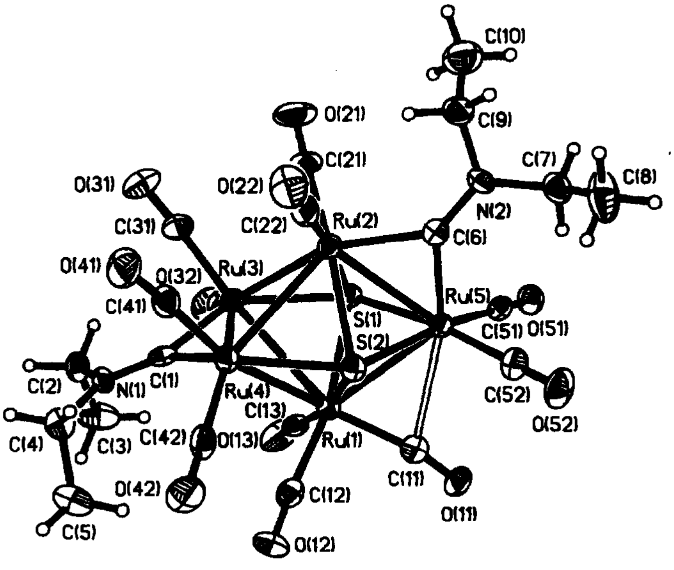
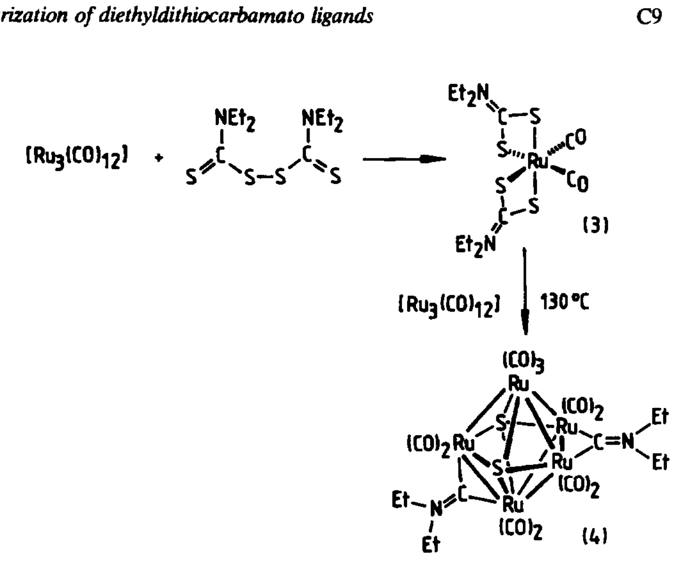


Fig. 1. Molecular structure of the cluster $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}CNEt_2)_2(CO)_{11}]$, **4**. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(3) 2.909(2), Ru(1)–Ru(4) 2.893(2), Ru(1)–Ru(5) 2.829(2), Ru(2)–Ru(3) 2.885(2), Ru(2)–Ru(4) 2.906(2), Ru(2)–Ru(5) 2.719(2), Ru(3)–Ru(4) 2.631(2), Ru(1)–S(1) 2.435(3), Ru(2)–S(1) 2.463(3), Ru(3)–S(1) 2.367(3), Ru(5)–S(1), 2.400(3), Ru(1)–S(2) 2.441(3), Ru(2)–S(2) 2.473(3), Ru(4)–S(2) 2.366(3), Ru(5)–S(2) 2.400(3), Ru(3)–C(1) 1.957(9), Ru(4)–C(1) 1.949(9), Ru(2)–C(6) 2.009(9), Ru(5)–C(6) 1.936(9), C(1)–N(1) 1.29(1), C(6)–N(2) 1.29(1), Ru(3)–C(1)–Ru(4) 84.7(4), Ru(3)–C(1)–N(1) 137.4(6), Ru(4)–C(1)–N(1) 137.9(6), Ru(2)–C(6)–Ru(5) 87.1(3), Ru(2)–C(6)–N(2) 137.3(7), Ru(5)–C(6)–N(2) 135.5(7).



Scheme 2.

The structure of cluster **4** is electron-precise with seven Ru–Ru bonds, the shortest of which are those bridged by the alkylidyne ligands [Ru(2)–Ru(5) 2.719(2) and Ru(3)–Ru(4) 2.631(2) Å with the others in the range 2.829(2) to 2.909(2) Å]. The carbonyl ligand C(11)O(11) is bonded to Ru(1), but could be considered to be semi-bridging to Ru(5).

Note added in proof

Recently an analogue of compound **4** has been reported to be derived from $[Ru_3(CO)_{12}]$ and the thiourea, $(Me_2N)_2CS$. The overall structure of the product $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}CNMe_2)_2(CO)_{11}]$ is similar to that we report for the $CNEt_2$ compound. [U. Bodensieck, H. Stoeckli-Evans, G. Rheinwald and G. Süss-Fink, *J. Organomet. Chem.*, *433* (1992) 167.]

Acknowledgements

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10 Selected spectroscopic data for **3**: $\nu(CO)/cm^{-1}$ (cyclohexane): 2036s and 1974s; ^1H NMR ($CDCl_3$, 400 MHz, J in Hz): δ 3.78, 3.63 (AB q of 1:3:3:1 q, J_{AB} 14.0), 3.67 (1:3:3:1 q), 1.25 (t, J 7.2), 1.23 (t, J 7.2); CHN analysis satisfactory; parent ion observed in MS.

11 Selected spectroscopic data for **4**: $\nu(CO)/cm^{-1}$ (cyclohexane): 2059w, 2029s, 2015vs, 1999m, 1990m, 1983m, 1939w, 1932w, ^1H NMR ($CDCl_3$, 400 MHz, J in Hz): δ 4.92, 4.76 (AB q of 1:3:3:1 q, J_{AB} 13.5); 4.60 (1:3:3:1 q), 3.82 (1:3:3:1 q), 1.86 (t, J 7.2, Me_2), 1.70 (t, J 7.3, Me), 1.26 (t, J 7.3, Me); parent ion observed in MS.

12 Structure of **4**. Deep red platelet, $C_{21}H_{20}N_2O_{11}Ru_5S_2$, $M =$ 1045.90 g mol^{-1}, size $= 0.60 \times 0.40 \times 0.07$ mm^3, monoclinic, $P2_1/n$, $a = 8.536(5)$, $b = 28.76(2)$, $c = 12.453(6)$ Å, $\beta = 105.85(4)°$, $V = 2941(3)$ $Å^3$, $Z = 4$, $D_{calc} = 2.36$ g cm^{-3}, μ(Mo-Kα) $= 26.6$ cm^{-1}, $F(000) = 2000$, Nicolet R3v/m diffractometer, Mo-radiation ($\lambda = 0.71073$ Å), room temperature data corrected empirically for absorption. Direct methods, $R = 0.0493$, $R' = 0.0584$, where $R' = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$ and $w = 1/[\sigma^2(F_o) + 0.00718F_o^2]$, 370 parameters and 4035 data with $I_o > 2\sigma(I_9)$ in the range $5 \geq 2\theta \leq 50°$. All non-H atoms anisotropic, H-atoms included in idealised positions (C–H 0.96 Å, $U = 0.08$ $Å^2$). Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.