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## Desulfurization of Thiophenes with Ruthenium Clusters

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The cluster  $[\text{Ru}_3(\text{CO})_{12}]$  reacts with 2-methylthiophene in refluxing tetrahydrofuran to give products of oxidative addition by C–H cleavage,  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_2\text{MeS})(\text{CO})_{10}]$  (*exo* and *endo*), as well as two compounds derived by S–C bond cleavage,  $[\text{Ru}_2(\mu\text{-C}_4\text{H}_3\text{Me})(\text{CO})_6]$  and  $[\text{Ru}_4(\mu_3\text{-S})(\mu\text{-C}_4\text{H}_3\text{Me})(\text{CO})_{11}]$  (X-ray structure determined), this being the first example of the fragmentation of a thiophene to leave both the inorganic and the organic fragments, S and  $\text{C}_4\text{H}_3\text{Me}$ , co-ordinated in the same organometallic compound.

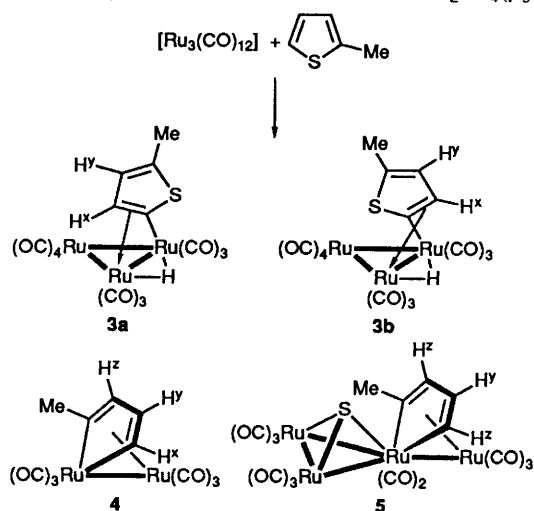
The homogeneous desulfurization of thiophene with transition-metal compounds has provided an important model for the catalytic heterogeneous dehydrosulfurization of thiophenic components of crude oil and understandably the co-ordination and organometallic chemistry of thiophene has been studied with enthusiasm.<sup>1</sup> The cluster  $[\text{Fe}_3(\text{CO})_{12}]$  reacts with thiophene with loss of the sulfur atom to give the ferrole compound  $[\text{Fe}_2(\mu\text{-C}_4\text{H}_4)(\text{CO})_6]$ ,<sup>2</sup> while  $[\text{Fe}_2(\mu\text{-C}_4\text{H}_3\text{MeS})(\text{CO})_6]$  as well as the sulfur-free species  $[\text{Fe}_2(\mu\text{-C}_4\text{H}_3\text{Me})(\text{CO})_6]$  are formed from 2-methylthiophene.<sup>3,4</sup> Insertion of an iron atom into the less-hindered C–S bond occurs to give the ring-opened thiophene derivative. In contrast, we have shown that thiophene does not ring open with  $[\text{Os}_3(\text{CO})_{12}]$  or  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  but gives exclusively C–H bond cleavage to yield the thienyl isomers  $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_3\text{S})(\text{CO})_{10}]$  (*exo* and *endo* isomers in rapid equilibrium), which decarbonylate to the cluster  $[\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-C}_4\text{H}_2\text{S})(\text{CO})_9]$  which contains a triply bridging 'benzyne'-type ligand.<sup>5–8</sup>

To see which type of behaviour  $[\text{Ru}_3(\text{CO})_{12}]$  would adopt it was treated with thiophene and 2-methylthiophene (Scheme 1). Thiophene itself reacts to give the sulfur-free species  $[\text{Ru}_2(\mu\text{-C}_4\text{H}_4)(\text{CO})_6]$  **1** (20%), clearly derived by C–S bond cleavage as in the iron case, as well as a tetranuclear cluster  $[\text{Ru}_4(\mu_3\text{-S})(\mu\text{-C}_4\text{H}_4)(\text{CO})_{11}]$  **2** (7%) which contains separated S and  $\text{C}_4\text{H}_4$  ligands. Most of the material could not be isolated. Better yields were obtained from 2-methylthiophene and, in this case, products of both C–H and C–S bond cleavage were obtained; no evidence for C–H bond cleavage was found for thiophene itself.† Scheme 1 shows the four products obtained; the *exo* and *endo* isomers containing the thienyl ligand, **3a** and **3b**, were obtained as an inseparable mixture. The <sup>1</sup>H NMR spectrum‡ of this mixture at room temperature (27 °C) showed broad resonances for each of the four distinct H atoms, but at –27 °C the rate of *exo*–*endo* interconversion had been reduced sufficiently for the spectrum to contain four strong and four weak resonances for the *exo* and *endo* isomers respectively [defined in terms of the position of the S atom with respect to the  $\text{Ru}(\text{CO})_4$  group]. We believe that the *exo* isomer is the major one as found in the corresponding osmium case.<sup>5,6</sup>

The tetranuclear compound **5** was believed to have the structure shown because of the correspondence of its spectra‡

† The cluster  $[\text{Ru}_3(\text{CO})_{12}]$  (0.200 g, 0.313 mmol) and 2-methylthiophene (0.101 g, 1.03 mmol) (distilled from sodium–benzophenone) were refluxed in tetrahydrofuran (50 cm<sup>3</sup>) for 24 h under N<sub>2</sub>. The yellow-brown solution was taken to dryness under reduced pressure and the residue separated by TLC on silica with light petroleum (b.p. 40–60 °C) as eluent to give three bands which yielded yellow compound **4** (0.030 g, 15%), orange **3** (0.034 g, 17%) and yellow **5** (0.088 g, 44%). A similar reaction with carefully purified thiophene gave **1** (20%) and **2** (8%) as the only isolable compounds.

‡ Selected spectroscopic data for clusters 1–5 (IR/cm<sup>–1</sup> for cyclohexane solutions; <sup>1</sup>H NMR at 300 MHz, *J* in Hz): **1**, ν(CO) 2085m, 2054vs, 2010(sh), 2014vs, 1998m and 1986m; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.17 (m) and 6.17 (m) (AA'BB'); **2**, ν(CO) 2097w, 2076s, 2049vs, 2039w, 2033m, 2010s, 2003m, 1989w, 1938vw and 1902vw; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.17 (m) and 6.17 (m) (AA'BB'); **3**, ν(CO) (*endo* + *exo*) 2089w, 2061vs, 2036s, 2010(sh), 1999s, 1978m and 1975w; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 246 K) δ(3a, *exo*, 67%) 7.08 (m, H<sup>a</sup>), 4.78 (d, H<sup>b</sup>), 2.10 (d, CH<sub>3</sub>) and –17.04 (s, RuH) [*J*(H<sup>a</sup>Me) = 1.0, *J*(H<sup>a</sup>H<sup>b</sup>) = 2.7]; (3b, *endo*, 33%) 6.93 (d, H<sup>a</sup>), 5.31 (d, H<sup>b</sup>), 2.01 (d, CH<sub>3</sub>) and –15.37 (s, RuH) [*J*(H<sup>a</sup>Me) = 1.0, *J*(H<sup>a</sup>H<sup>b</sup>) = 2.7]; (298 K) (*exo* + *endo*) δ 7.06 (s, br, H<sup>a</sup>), 4.90 (s, br, H<sup>b</sup>), 2.07 (s, br, CH<sub>3</sub>) and –16.8 (s, br, RuH); **4**, ν(CO) 2082m, 2050s, 2011vs, 1994m and 1982m; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.07 (dd, H<sup>a</sup>), 6.50 (dd, H<sup>b</sup>), 6.23 (m, H<sup>c</sup>) and 2.47 (d, CH<sub>3</sub>) [*J*(H<sup>a</sup>H<sup>b</sup>) = 6.2, *J*(H<sup>b</sup>H<sup>c</sup>) = 2.3, *J*(H<sup>a</sup>Me) = 2.4, *J*(H<sup>b</sup>Me) = 0.5]; **5**, ν(CO) 2094w, 2076s, 2047vs, 2030m, 2011s, 1999m, 1987w, 1933vw and 1901vw; <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ 7.17 (dd, H<sup>a</sup>), 6.26 (m, H<sup>b</sup>), 6.47 (dd, H<sup>c</sup>) and 2.35 (d, CH<sub>3</sub>) [*J*(H<sup>a</sup>H<sup>b</sup>) = 5.8, *J*(H<sup>b</sup>H<sup>c</sup>) = 2.3, *J*(H<sup>a</sup>H<sup>c</sup>) = 2.4, *J*(H<sup>a</sup>Me) = 0.5].



Scheme 1

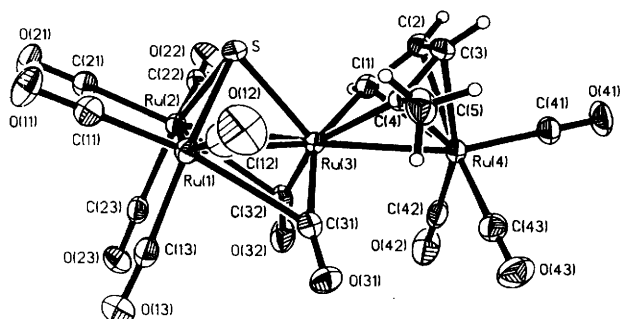
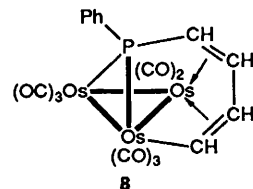
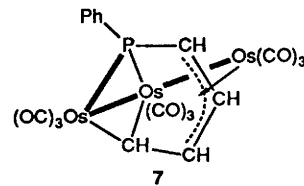
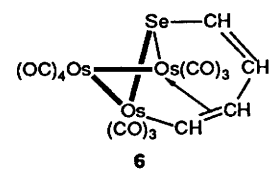


Fig. 1 Molecular structure of the cluster  $[\text{Ru}_4(\mu_3\text{-S})(\mu\text{-C}_4\text{H}_3\text{Me})(\text{CO})_{11}]$  **5**. Selected bond lengths ( $\text{\AA}$ ): Ru(1)–Ru(2) 2.727(1), Ru(1)–Ru(3) 2.840(1), Ru(2)–Ru(3) 2.815(1), Ru(3)–Ru(4) 2.745(1), Ru(1)–S 2.348(2), Ru(2)–S 2.345(1), Ru(3)–S 2.332(1), Ru(3)–C(1) 2.066(6), Ru(3)–C(4) 2.070(5), Ru(4)–C(1) 2.251(5), Ru(4)–C(2) 2.226(6), Ru(4)–C(3) 2.218(5), Ru(4)–C(4) 2.292(5), Ru(3)–C(31) 1.943(6), Ru(3)–C(32) 1.935(5), Ru(1)–C(31) 2.572(5) and Ru(2)–C(32) 2.551(5)

to those of the selenophene derivative,  $[\text{Ru}_4(\mu_3\text{-Se})(\mu\text{-C}_4\text{H}_4)(\text{CO})_{11}]$ .<sup>9</sup> An X-ray structure determination has confirmed that the compounds are related (Fig. 1).<sup>\*</sup> The electron-precise cluster contains a sulfur-capped triangle of ruthenium atoms [Ru(1) to Ru(3)] and the bridging  $\text{C}_4\text{H}_3\text{Me}$  ligand links atom Ru(3) of this triangle to a spiked ruthenium atom [Ru(4)]. Three of the metal atoms have three CO ligands, while Ru(3) has two CO ligands which are semibridging to Ru(1) and Ru(2). Atom Ru(3) has substituted the S atom of the 2-methylthiophene ring and remains bonded to both of the fragments, S and  $\text{C}_4\text{H}_3\text{Me}$ , of the heterocycle. This is the first example of a desulfurization of a thiophene ring in which the components remain co-ordinated within the same complex. Based on analogies with selenophene, tellurophene and phenylphosphole chemistry,<sup>5,6,11,12</sup> we suggest that the sulfur-extrusion reaction occurs *via* ring-opened compounds, analogous to  $[\text{Os}_3(\mu\text{-C}_4\text{H}_4\text{Se})(\text{CO})_{10}]$  **6** formed from selenophene and compounds **7** and **8** from phenylphosphole. Compounds **6–8** have the general formula  $[\text{Os}_3(\text{C}_4\text{H}_4\text{X})(\text{CO})_x]$ , where X = Se or PPh and  $x = 8–10$ , and the corresponding compounds  $[\text{Ru}_3(\text{C}_4\text{H}_3\text{MeS})(\text{CO})_x]$  ( $x = 8–10$ ) are likely to be involved as



intermediates, prior to cleavage of the second S–C bond and formation of **4** and **5**.

#### Acknowledgements

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\* Crystal data.  $\text{C}_{16}\text{H}_6\text{O}_{11}\text{Ru}_4\text{S}$  **5**,  $M = 810.56$ , yellow crystal, dimensions  $0.35 \times 0.42 \times 50$  mm, monoclinic, space group  $P2_1/c$ ,  $a = 8.432(2)$ ,  $b = 14.365(4)$ ,  $c = 18.728(4)$   $\text{\AA}$ ,  $\beta = 102.64(2)^\circ$ ,  $U = 2213.2(8)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $\lambda = 0.71073$   $\text{\AA}$ ,  $\mu(\text{Mo-K}\alpha) = 27.72$   $\text{cm}^{-1}$ ,  $F(000) = 1528$ . Direct methods (SHELXTL-PLUS),<sup>10</sup> 5089 unique absorption-corrected data having  $5 \leq 2\theta \leq 55^\circ$  and with  $I_o \geq 2\sigma(I_o)$  used in the refinement, 289 parameters in the model (all non-H atoms anisotropic), final  $R = 0.035$  and  $R' = 0.033 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  with  $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$ . Hydrogen atoms were located in difference maps but were finally included in calculated positions (C–H 0.96  $\text{\AA}$ ,  $U_{\text{iso}} = 0.08$   $\text{\AA}^2$ ). Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

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