

# The activation of carbon disulfide by a cluster. The reaction of the $\mu_3$ -CS complex $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2\{\text{Fe}(\text{CO})_2\text{PPh}_3\}(\mu_3\text{-S})(\mu_3\text{-CS})]$ with $\text{CS}_2$

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When  $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2\{\text{Fe}(\text{CO})_2\text{PPh}_3\}(\mu_3\text{-S})(\mu_3\text{-CS})]$  is refluxed in  $\text{CS}_2$  solution, it is converted to  $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2\{\text{Fe}(\text{CO})\text{PPh}_3\}(\mu_3\text{-S})(\mu_3\text{-CSC}(\text{S})\text{S})]$  which contains an unusual  $\text{C}_2\text{S}_3$  bridging ligand.

$[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2\{\text{Fe}(\text{CO})_2\text{PPh}_3\}(\mu_3\text{-S})(\mu_3\text{-CS})]$  **I** is formed when the  $\eta^2\text{-CS}_2$  ligand in  $[\text{Fe}(\text{PPh}_3)_2(\text{CO})_2(\eta^2\text{-CS}_2)]$  is cleaved by  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ .<sup>1,2</sup> When a solution of this compound in carbon disulfide is heated to reflux for 12 hours, a further molecule of  $\text{CS}_2$  is taken up and CO is lost. The product, **II**, is obtained in 75% yield. It is a brown crystalline solid which, when crystallized from carbon disulfide solution, analyses as  $\text{Co}_2(\eta\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})(\text{PPh}_3)(\text{S})(\text{CS})\cdot 2\text{CS}_2$ . This is consistent with NMR and IR spectroscopic data,<sup>‡</sup> but does not define the actual structure of **II** which was determined by X-ray crystallography on a crystal grown from benzene solution which analyzed as  $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2\{\text{Fe}(\text{CO})\text{PPh}_3\}(\mu_3\text{-S})(\mu_3\text{-CSC}(\text{S})\text{S})]\cdot 2\text{C}_6\text{H}_6$ .<sup>§</sup> It is illustrated in Fig. 1.

The molecular structure of **II** is closely related to that of **I**.<sup>2</sup> and is based on an  $\text{FeCo}_2$  triangle capped on one face by a  $\mu_3\text{-S}$  ligand and on the other by a  $\mu_3\text{-C}$  atom. The coordination about each of the two Co atoms is completed by a  $\eta^5\text{-C}_5\text{H}_5$  group whilst that about Fe is completed by a CO and a  $\text{PPh}_3$  ligand and the  $\text{S}^*$  atom of a  $\text{S}^*\text{C}(\text{S})\text{S}$  moiety which is also bonded to the  $\mu_3\text{-C}$  atom. The coordination about Fe is severely distorted from that found in **I** where the  $\text{Fe}(\text{L})_3$  fragment is more or less symmetrical with respect to an axis from Fe to the midpoint of the Co–Co bond. Furthermore the  $\text{FeCo}_2$  triangle is no longer an isosceles triangle as it is in **I** [ $\text{Fe–Co} = 2.5099(6), 2.5061(6)$  Å] as  $\text{Fe}(1)\text{–Co}(1)$  at  $2.642(3)$  Å is very much longer than  $\text{Fe}(1)\text{–Co}(2)$  at  $2.502(4)$  Å.

The  $\text{C}_2\text{S}_3$  ligand has no precedent. The various C–S bond lengths lie between those for a  $\text{C}=\text{S}$  (*ca.* 1.62 Å in thioketones)<sup>3</sup>

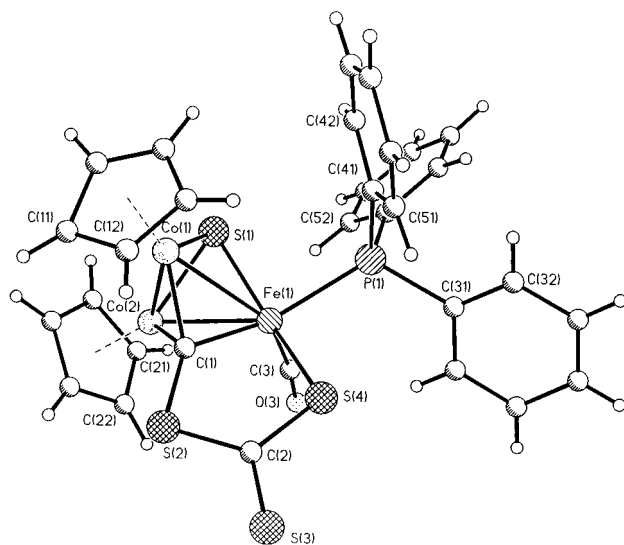
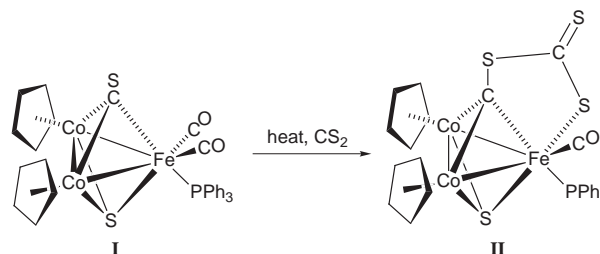


Fig. 1 Structure of  $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2\{\text{Fe}(\text{CO})(\text{CS}_2)\text{PPh}_3\}(\mu_3\text{-S})(\mu_3\text{-CS})]$



Scheme 1

and a C–S (*ca.* 1.82 Å in thioethers)<sup>3</sup> which is indicative of delocalised bonding. In particular the  $\mu_3\text{-C–S}$  distance in **II** [1.774(11) Å] is very long compared with that in **I** [1.638(3) Å] or its S-methylated derivative,  $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2\{\text{Fe}(\text{CO})_2\text{PPh}_3\}(\mu_3\text{-S})(\mu_3\text{-CSMe})]$ , **I**, **[III]**,<sup>2</sup> [1.728(7) Å]. The C–S distances are all longer than the comparable ones in  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CNBu}^t)(\text{S}_2\text{C}=\text{S})]$ .<sup>4</sup> The overall reaction which gives rise to **II** is shown in Scheme 1. It is reminiscent of that of a thiolate anion,  $\text{RS}^-$ , which with  $\text{CS}_2$  forms a thioxanthate anion  $[\text{RSCS}_2]^-$ <sup>5</sup> and is a reflection of the nucleophilicity of the  $\mu_3\text{-CS}$  ligand which has been illustrated by the ease with which **I** is alkylated to **III**<sup>+</sup> salts. The related complex  $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_3(\mu_3\text{-S})(\mu_3\text{-CS})]$  is also readily alkylated at S to give  $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_3(\mu_3\text{-S})(\mu_3\text{-CSMe})]$ , but it does not react with  $\text{CS}_2$ . This implies that the conversion of **I** to **II** takes place because the first-formed  $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2\{\text{Fe}(\text{CO})_2\text{PPh}_3\}(\mu_3\text{-S})(\mu_3\text{-CS}\rightarrow\text{CS}_2)]$  intermediate can undergo CO loss with the formation of an Fe–S bond which stabilizes the  $\text{C}_2\text{S}_3$  ligand.

Analogues of **II** are obtained when  $\text{PPh}_3$  in **I** is replaced by  $(\text{PhO})_3\text{P}$  or  $\text{Bu}^n_3\text{P}$ , but not when it is replaced by  $(\text{MeO})_3\text{P}$ . The extent of this reaction is being investigated at present.

The exocyclic S atom in **II** is nucleophilic and with electrophiles E such as  $\text{Me}^+(\text{I}^-)$  or  $\text{HgCl}_2$  gives  $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2\{\text{Fe}(\text{CO})\text{PPh}_3\}(\mu_3\text{-S})(\mu_3\text{-CSC}(\text{S}\rightarrow\text{E})\text{S})]$  adducts. These have been characterized by elemental analysis and spectroscopy.

Attempts to use **I** to activate other cumulenes such as  $\text{CO}_2$ , COS and MeNCS have not, as yet, been successful. The only isolable product has been  $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_3(\mu_3\text{-S})(\mu_3\text{-CS})]$ ,<sup>6</sup> which is a thermal decomposition product of **I**.

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## Notes and References

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<sup>‡</sup> Spectroscopic data for **II**:  $\nu(\text{CO})$  1922  $\text{cm}^{-1}$  (KBr disc);  $^1\text{H NMR}$  ( $\text{CDCl}_3$  solution)  $\delta$  4.11(s) and 4.90(s) ( $\text{C}_5\text{H}_5$ ); 7.40 (m) ( $\text{PPh}_3$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$  solution)  $\delta$  84.93 and 86.08 ( $\text{C}_5\text{H}_5$ ); 128.3(d), 130.2(s), 133.5(d), 135.0(d) ( $\text{PPh}_3$ ); 218.7 (d,  $J = 22.2$  Hz; CO); 243.4 (d,  $J = 18.7$  Hz; SCS); 346.1 (d,  $J = 15.3$  Hz;  $\mu_3\text{-C}$ ) [all downfield from  $(\text{CH}_3)_4\text{Si}$ ; d = doublet].

<sup>§</sup> Crystal data for **II**:  $\text{C}_{43}\text{H}_{37}\text{Co}_2\text{FeO}_4\text{P}_2\text{S}_4$ ,  $M = 902.65$ , monoclinic, space group  $P2_1/n$ ,  $a = 9.853(13)$ ,  $b = 19.97(2)$ ,  $c = 20.61(2)$  Å,  $\alpha = 90$ ,  $\beta =$

91.79(4),  $\gamma = 90^\circ$ ,  $U = 4055(8) \text{ \AA}^3$ ;  $Z = 4$ ;  $D_c = 1.478 \text{ Mg m}^{-3}$ ; absorption coefficient  $1.440 \text{ mm}^{-1}$ ;  $F(000) 1848$ ; data collection  $2.04 < \theta < 25.01^\circ$ ,  $-11 < h < 0$ ,  $0 < k < 23$ ,  $-24 < l < 24$ , reflections collected 6687, independent reflections collected 6380. Solved by direct methods.<sup>8</sup> Refined by full-matrix least-squares<sup>9</sup> to  $R_1 = 0.0692$  and  $wR_2 = 0.1575$  [ $I = 2\sigma(I)$ ], and  $R_1 = 0.1488$  and  $wR_2 = 0.1823$ ; max. and min. residual electron densities =  $1.482$  and  $-0.620 \text{ e \AA}^{-3}$ , respectively. CCDC 182/907.

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