The activation of carbon disulfide by a cluster. The reaction of the μ_3-CS complex [{Co(η-C_5H_5)}$_2${Fe(CO)$_2$PPh$_3$}(μ_3-S)(μ_3-CS)] with CS_2

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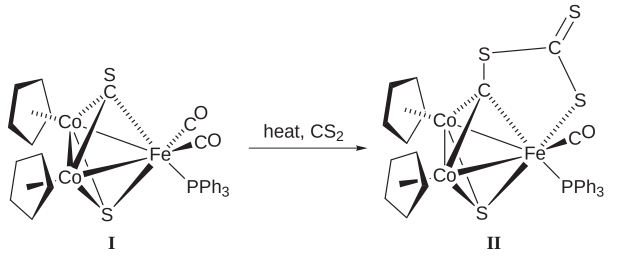
When [{Co(η-C_5H_5)}$_2${Fe(CO)$_2$PPh$_3$}(μ_3-S)(μ_3-CS)] is refluxed in CS_2 solution, it is converted to [{Co(η-C_5H_5)}$_2${Fe(CO)PPh$_3$}(μ_3-S){μ_3-CSC(S)S}] which contains an unusual C_2S_3 bridging ligand.

[{Co(η-C_5H_5)}$_2${Fe(CO)$_2$PPh$_3$}(μ_3-S)(μ_3-CS)] **I** is formed when the η^2-CS_2 ligand in [Fe(PPh$_3$)$_2$(CO)$_2$(η^2-CS_2)] is cleaved by [Co(η-C_5H_5)(PPh$_3$)$_2$].[1,2] When a solution of this compound in carbon disulfide is heated to reflux for 12 hours, a further molecule of 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 Co_2(η-C_5H_5)$_2$Fe(CO)(PPh$_3$)(S)(CS)·2CS_2. This is consistent with NMR and IR spectroscopic data,[‡] 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 [{Co(η-C_5H_5)}$_2${Fe(CO)PPh$_3$}(μ_3-S){μ_3-CSC(S)S}]·2C_6H_6.[§] It is illustrated in Fig. 1.

The molecular structure of **II** is closely related to that of **I**[1,2] and is based on an $FeCo_2$ triangle capped on one face by a μ_3-S ligand and on the other by a μ_3-C atom. The coordination about each of the two Co atoms is completed by a η^5-C_5H_5 group whilst that about Fe is completed by a CO and a Ph_3P ligand and the S^* atom of a S^*C(S)S moiety which is also bonded to the μ_3-C atom. The coordination about Fe is severely distorted from that found in **I** where the Fe(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 $FeCo_2$ triangle is no longer an isosceles triangle as it is in **I** [Fe–Co = 2.5099(6), 2.5061(6) Å] as Fe(1)–Co(1) at 2.642(3) Å is very much longer than Fe(1)–Co(2) at 2.502(4) Å.

The C_2S_3 ligand has no precedent. The various C–S bond lengths lie between those for a C=S (*ca.* 1.62 Å in thioketones)[3] and a C–S (*ca.* 1.82 Å in thioethers)[3] which is indicative of delocalised bonding. In particular the μ_3-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, [{Co(η-C_5H_5)}$_2${Fe(CO)$_2$PPh$_3$}(μ_3-S)(μ_3-CSMe)]I, [**III**]I,[2] [1.728(7) Å]. The C–S distances are all longer than the comparable ones in [Co(η-C_5H_5)(CNBu^t)(S_2C=S)].[4] The overall reaction which gives rise to **II** is shown in Scheme 1. It is reminiscent of that of a thiolate anion, RS^-, which with CS_2 forms a thioxanthate anion [$RSCS_2$]$^{-5}$ and is a reflection of the nucleophilicity of the μ_3-CS ligand which has been illustrated by the ease with which **I** is alkylated to **III**$^+$ salts. The related complex [{Co(η-C_5H_5)}$_3$(μ_3-S)(μ_3-CS)] is also readily alkylated at S to give [{Co(η-C_5H_5)}$_3$(μ_3-S)(μ_3-CSMe)]I, but it does not react with CS_2. This implies that the conversion of **I** to **II** takes place because the first-formed [{Co(η-C_5H_5)}$_2${Fe(CO)$_2$PPh$_3$}(μ_3-S)(μ_3-CS$\rightarrow$$CS_2$] intermediate can undergo CO loss with the formation of an Fe–S bond which stabilizes the C_2S_3 ligand.



Scheme 1

Analogues of **II** are obtained when Ph_3P in **I** is replaced by (PhO)$_3$P or Bu$^n_3$P, but not when it is replaced by (MeO)$_3$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 Me^+(I^-) or $HgCl_2$ gives [{Co(η-C_5H_5)}$_2${Fe(CO)PPh$_3$}(μ_3-S){μ_3-CSC(S$\rightarrow$E)S}] adducts. These have been characterized by elemental analysis and spectroscopy.

Attempts to use **I** to activate other cumulenes such as CO_2, COS and MeNCS have not, as yet, been successful. The only isolable product has been [{Co(η-C_5H_5)}$_3$(μ_3-S)(μ_3-CS)],[6] which is a thermal decomposition product of **I**.

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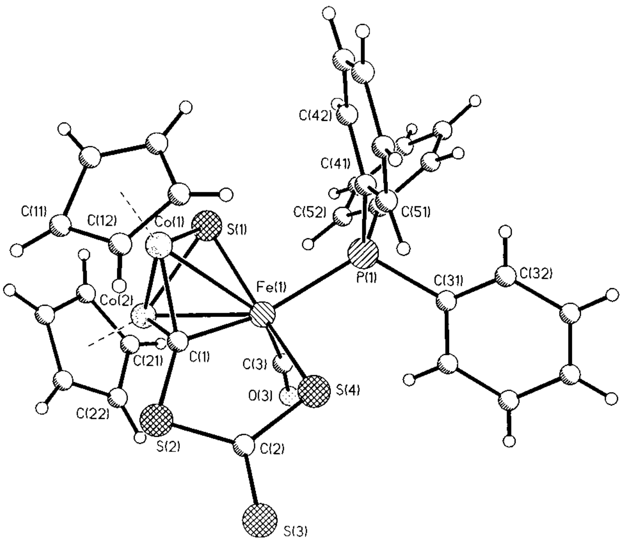

Fig. 1 Structure of {Co(η-C_5H_5)}$_2${Fe(CO)(CS_2)PPh$_3$}(μ_3-S)(μ_3-CS)]

Notes and References

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[‡] *Spectroscopic data* for **II**: υ(CO) 1922 cm^{-1} (KBr disc); ^{1}H NMR ($CDCl_3$ solution) δ 4.11(s) and 4.90(s) (C_5H_5); 7.40 (m) (PPh$_3$); ^{13}C NMR ($CDCl_3$ solution) δ 84.93 and 86.08 (C_5H_5); 128.3(d), 130.2(s), 133.5(d), 135.0(d) (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; μ_3-C) [all downfield from (CH_3)$_4$Si; d = doublet].

[§] *Crystal data* for **II**: $C_{43}H_{37}Co_2FeOPS_4$, M = 902.65, monoclinic, space group $P2_1/n$, a = 9.853(13), b = 19.97(2), c = 20.61(2) Å, α = 90, β =

91.79(4), $\gamma = 90°$, $U = 4055(8)$ Å^3; $Z = 4$; $D_c = 1.478$ Mg m^{-3}; absorption coefficient 1.440 mm^{-1}; $F(000)$ 1848; data collection $2.04 < \theta < 25.01°$, $-11 < h < 0$, $0 < k < 23$, $-24 < l < 24$, reflections collected 6687, independent reflections collected 6380. Solved by direct methods.[8] Refined by full-matrix least-squares[9] 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 e Å^{-3}, respectively. CCDC 182/907.

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