

The Systematic Synthesis of Complexes containing μ_3 -CS Ligands as Two-electron Donors. The Preparation and Structure of $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2\{\text{Fe}(\text{PPh}_3)(\text{CO})_2\}(\mu_3\text{-S})(\mu_3\text{-CS})]$

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The η^2 -(CS)-CS₂ ligand in $[\text{Fe}\{\text{PPh}_3\}_2(\text{CO})_2(\eta^2\text{-CS}_2)]$ is cleaved by $[\text{Co}(\eta\text{-C}_5\text{H}_5)\{\text{PPh}_3\}_2]$ at room temperature with formation of $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2\{\text{Fe}(\text{PPh}_3)(\text{CO})_2\}(\mu_3\text{-S})]$ in which the CS ligand acts as a μ_3 two-electron donor to the Co₂Fe triangle.

Both $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\eta^2\text{-CS}_2)]$ and $[\text{Co}(\eta\text{-C}_5\text{H}_5)\{\text{PPh}_3\}(\eta^2\text{-SCNR})]$ have been proposed as intermediates in the formation of $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\mu_3\text{-S})(\mu_3\text{-CX})]$ clusters (X = S,^{1,2} or NR³). The η^2 -(C-S) bond in these SCX ligands can be cleaved by sources of the $\text{Co}(\eta\text{-C}_5\text{H}_5)$ fragment. Therefore, it is reasonable to suggest that such fragments could similarly cleave the SCX ligands when they are coordinated to metal atoms other than cobalt. This would allow the preparation for the first time of heterometallic clusters of the general formula $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2(\text{ML}_n)(\mu_3\text{-S})(\eta_3\text{-CX})]$ in which the CX ligand acts as a triply-bridging two-electron donor through carbon to a Co₂M triangle.

We now report that this has been achieved in the reaction of $[\text{Fe}(\text{PPh}_3)_2(\text{CO})_2(\eta^2\text{-CS}_2)]$ with a benzene solution of $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ at room temperature. After 24 h the mixture was chromatographed to give only one significant fraction. From this was obtained, after recrystallization from ethanol-diethyl ether mixtures, a 72% yield of green crystals of analytically pure $[\{\text{Co}(\eta\text{-C}_5\text{H}_5)\}_2\{\text{Fe}(\text{PPh}_3)(\text{CO})_2\}(\text{S})(\text{CS})]$.[†] Their infrared spectrum (KBr disc) showed two intense $\nu(\text{CO})$ bands at 1917 and 1963 cm⁻¹ and another band at 1020 cm⁻¹ which may be due to the $\nu(\text{CS})$ mode (*cf.* refs. 1 and 2). Their

¹H NMR spectrum (CDCl₃ solution) showed a singlet resonance at δ 4.52 downfield from SiMe₄ due to cyclopentadienyl protons and a multiplet at *ca.* δ 7.4 due to the PPh₃ ligand.

The details of the structure have been confirmed by X-ray diffraction[‡] (Fig. 1). The CS group acts as a triply-bridging two-electron donor ligand through carbon to the Co₂Fe triangle and bonds more or less equally to all three metal atoms. The bond lengths within the CCo₂FeS distorted trigonal bipyramid are normal and compare with those in the related $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\mu_3\text{-S})(\mu_3\text{-CS})]$ complex.⁴ The bond lengths to Fe are always larger than those to Co.

[‡] Crystal data: C₃₂H₂₅Co₂FeO₂PS₂, *M* = 710.36, monoclinic, space group *P*2₁/*n* (non-standard No. 14), *a* = 9.455(1), *b* = 23.161(2), *c* = 13.119(2) Å, β = 95.24(2)°, *U* = 2861(3) Å³, *Z* = 4, *D_c* = 1.65 g cm⁻³, μ = 26.95 cm⁻¹, *F*(000) = 1416. Diffraction data were collected with a CAD4F diffractometer (Radiation Mo-K α , ω -2 θ scan, 2θ = 2-60°). The structure was solved by direct methods⁵ and refined by full-matrix least-squares analysis⁶ using 6229 measured reflections and 4788 observed intensities [*I* > 3 σ *I*] for 311 parameters, *R* = 3.74%, *R_w* = 4.89%. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[†] Satisfactory elemental analyses were obtained.

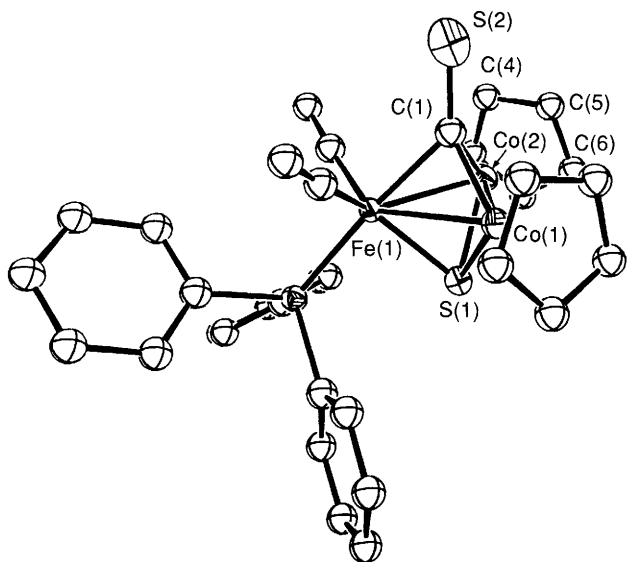


Fig. 1 The molecular structure and atom labelling for $[\{Co(\eta-C_5H_5)\}_2\{Fe(PPh_3)(CO)_2\}(\mu_3-S)]$. Selected bond lengths (Å) and angles (°) are as follows: Co(1)–Co(2) 2.438(1), Co(1)–Fe(1) 2.506(1), Co(2)–Fe(1) 2.509(1), Co(1)–S(1) 2.139(1), Co(2)–S(1) 2.128(1), Fe(1)–S(1) 2.194(1), Co(1)–C(1) 1.913(4), Co(2)–C(1) 1.913(4), Fe(1)–2.078(3), C(1)–S(2) 1.646(3), Co(1)–Co(2)–Fe(1) 60.8(1), Co(2)–Co(1)–Fe(1) 61.0(1), Co(1)–Fe(1)–Co(2) 58.2(1). The C(4)–C(8) cyclopentadienyl ring is disordered.

It is quite clear that this basic reaction is, in principle, capable of extension by varying (i) the heteroallene, (ii) the metal-ligand system to which it is coordinated, and (iii) the nature of the cleaving group. These possibilities are currently under investigation, although not all will be successful (*cf.* ref. 4).

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