Metal-promoted Trimerization of Carbon Disulphide. Synthesis and Structure of the Dinuclear Copper(I) Complex $[(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2]$

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The complex $[(PPh_3)_2Cu(\eta^2\text{-}BH_4)]$ reacts with CS_2 to give the dinuclear copper(I) complex $[(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2]$; a complete *X*-ray crystal structure determination has shown that the two $(PPh_3)_2Cu$ fragments are held together by a bridging $S_2CSCH_2SCS_2{}^{2-}$ ligand, formed from a double head-to-tail condensation of three CS_2 molecules.

Transition-metal species can promote the condensation of carbon disulphide molecules *via* a head-to-tail $S_2C\text{–}SCS$[1] or a head-to-head $S_2C\text{–}CS_2$ mechanism.[2] The complexes obtained invariably contain a C_2S_4 moiety, displaying various stereochemistries and anchoring modes to metals. In addition to the metal centres, other groups can contribute in the stabilisation of the C_2S_4 fragment (Figure 1).

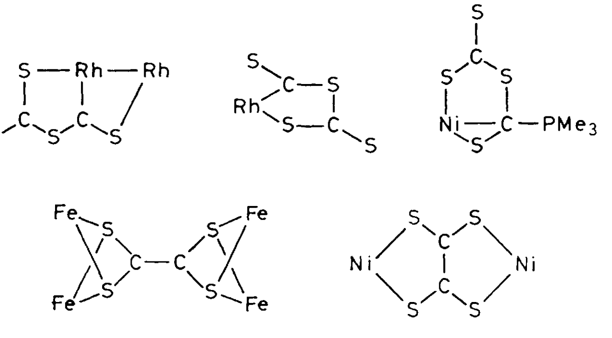

Figure 1. In these sketches of structures only connectivity is shown. There is no attempt to define bond orders.

To our knowledge, there are no previous reports of a metal-promoted trimerization of CS_2. Herein we report the synthesis and stereochemical characterization of the complex $[(PPh_3)_2\text{-}Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2]$ (**1**) formed from a double head-to-tail condensation of three CS_2 molecules.

$[(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2]$
(**1**)

$[(PPh_3)_2Cu(\eta^2\text{-}BH_4)]$
(**2**)

On allowing a methylene chloride solution of $[(PPh_3)_2\text{-}Cu(\eta^2\text{-}BH_4)]$[3] (**2**) to react with an excess of CS_2 for 3 h at 30 °C a yellow-orange solution resulted. Upon addition of ethanol and slow evaporation of the solvent, yellow crystals of (**1**) were precipitated in 80% yield.†

Crystal data: $C_{75}H_{62}Cu_2P_4S_6$, M = 1406.7, monoclinic, space group $C2/c$, a = 53.573(30), b = 12.759(9), c = 22.856(15) Å, β = 104.6(1)°, U = 15119.1 Å^3, Z = 8, D_c = 1.236 g

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† Satisfactory elemental analytical data were obtained; i.r. (Nujol) ν_{asym} (SCS) 1010, ν_{sym} (C–S) 880 cm^{-1}.

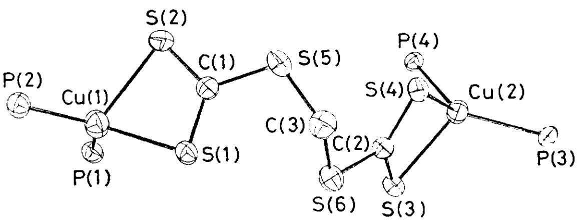

Figure 2. Perspective view of the inner skeleton of $[(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2]$. ORTEP drawing with 30% probability ellipsoids. Selected bond distances: Cu–P 2.254(4)—2.276(6), Cu–S 2.412(5)—2.479(5), S(1)–C(1) 1.65(2), S(2)–C(1) 1.70(2), S(3)–C(2) 1.72(2), S(4)–C(2) 1.65(2), S(5)–C(1) 1.76(2), S(5)–C(3) 1.79(2), S(6)–C(2) 1.73(2), and S(6)–C(3) 1.81(2) Å.

cm^{-3}, $\mu(\text{Cu-}K_\alpha) = 33.16\ \text{cm}^{-1}$, $\lambda(\text{Cu-}K_\alpha) = 1.5418$ Å. Intensity data were collected on a Philips PW 1100 automatic diffractometer, using the ω–2θ scan technique and graphite monochromated Cu-K_α radiation. An absorption correction was applied, the transmission coefficients ranging from 0.78 to 0.35. The structure was solved by the heavy atom method and refined by the full-matrix least-squares technique. During the refinement the phenyl rings were treated as rigid bodies. The present conventional R factor is 0.092 for 4573 reflections ($2\theta \leqslant 100°$) having $I \geqslant 4\sigma(I)$.‡

The crystal structure consists of dimeric complex molecules $[(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2]$, a perspective view of the inner skeleton being given in Figure 2.

In the dimeric complex two $(PPh_3)_2Cu$ units are held together by a bridging $S_2CSCH_2SCS_2^{2-}$ ligand. Each copper atom displays a distorted tetrahedral geometry, being surrounded by the phosphorus atoms of two phosphine ligands and by the two sulphur atoms of one S_2C– fragment. The distortion from the idealized tetrahedral geometry is mainly due to the short bite of the S_2C– group, the value of the S–Cu–S bond angles being 73.5(2) and 73.6(2)°. The Cu–P and Cu–S bond distances compare well with those reported for a variety of copper(I) complexes with a P_2S_2 donor atom set.[4] In the $S_2CSCH_2SCS_2^{2-}$ bridging ligand, the C–S bond distances in the terminal CS_2 fragments are systematically shorter than those of the central C atom, as expected from the different hybridization states of the carbon atoms. Also the values of the S–C–S bond angles [S–C(1)–S (av.) 120(3), S–C(2)–S (av.) 120(3), and S(5)–C(3)–S(6) 113.6(10)°] agree with sp^2 and sp^3 hybridization states for the C atoms.

Since CS_2-like heteroallenes often display close chemical analogies in their reactions with transition metal centres,[5] current studies are underway to test the reactivity of complex (**2**) and other η^1- and η^2-borohydride copper(I) complexes towards carbon dioxide, carbonyl sulphide, carbon diselenide, organoisothiocyanates, isocyanates, and carbodi-imides. Preliminary results have indicated that both the nature of the ancillary phosphine-ligands and the binding mode of the tetrahydroborate group are important. In particular, the complex $[(\text{tppme})Cu(\eta^1\text{-}BH_4)]$ [tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane] has been found to effect the reduction of CO_2, COS, and CS_2 to η^1-co-ordinated formate, thioformate, or dithioformate groups, respectively.[6]

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.