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Preliminary communication

INVESTIGATION OF THE FORMATION OF NEW BIMETALLIC CLUSTERS OF THE TYPE $(\eta\text{-}C_5Me_5)_2M_2M'_2(\mu_3\text{-}S)_4(CO)_2$ (M = Cr, Mo; M′ = Co), CONTAINING THE $M_2M'_2S_4$ CORE

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Summary

The reaction of the sulfur rich pentamethylcyclopentadiene complexes $(C_5Me_5)_2Cr_2S_5$ and $(C_5Me_5)_2Mo_2S_4$ with $Co_2(CO)_8$ results in the formation of new bimetallic clusters of composition $(C_5Me_5)_2M_2Co_2(\mu_3\text{-}S)_4(CO)_2$ (M = Cr, Mo), containing the $M_2Co_2S_4$ core.

Attempts to synthesize cubane-like molecules of the type $(C_5H_5)_4M_4S_4$ (M = Cr, Mo, Fe, Co) have been focussed onto the structures and the chemistry of $(CpFeS)_4$ [1] and $(CpCoS)_4$ [2]. Distortions from the cubane structure have been predicted [3] for $(CpMS)_4$ (M = Cr, Mo) [4] due to the formation of metal—metal bonds, as recently found in the related cluster $(CpCrO)_4$ [5]. Relatively little is known about mixed metal clusters of this type although there is considerable interest in the synthesis of clusters which resemble the Fe_3MoS_4 unit, the presumed biologically active part of nitrogenase [6]. In order to find a new route to such complexes a CpM unit (M = VIB metal) can be regarded as isoelectronic with a $Mn(CO)_2$, Fe(NO), Co(CO) unit, respectively. Thus it should be possible to combine various of such groups with the desired sulfur skeleton. In this work we describe the first attempt to realize this concept. As sulfur-rich substrates the pentamethylcyclopentadiene complexes $(C_5Me_5)_2Cr_2S_5$ (I) [7] and $(C_5Me_5)_2Mo_2S_4$ (II) [8] were used in the reaction with $Co_2(CO)_8$ (eq. 1).

$$(C_5Me_5)_2M_2S_n + Co_2(CO)_8 \rightarrow (C_5Me_5)_2M_2S_4Co_2(CO)_2 \qquad (1)$$

(I: M = Cr, n = 5; II: M = Mo, n = 4)
(III: M = Cr; IV: M = Mo)

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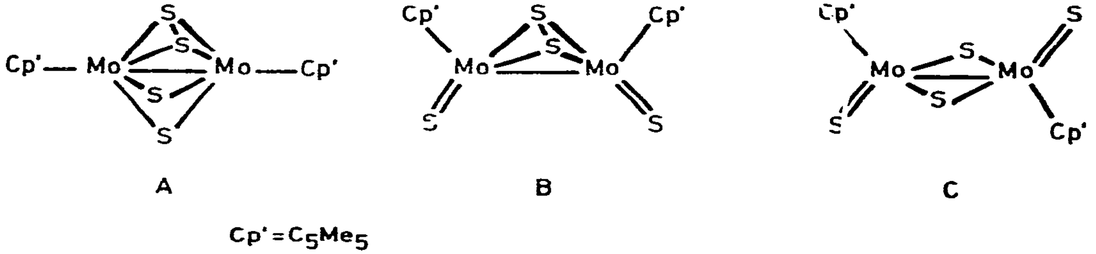
The reaction is carried out in toluene at room temperature and takes place with spontaneous CO-evolution to give the neutral, violet-brown compounds III and IV. From all three isomers A, B and C of $(C_5Me_5)_2Mo_2S_4$ (Scheme 1) employed, the same product is formed, but there is evidence from monitoring the reaction by IR spectroscopy that IIC reacts considerably more slowly than the other two isomers. In the latter case a carbonyl-rich intermediate was observed, but attempted isolation of this failed even at −30°C.

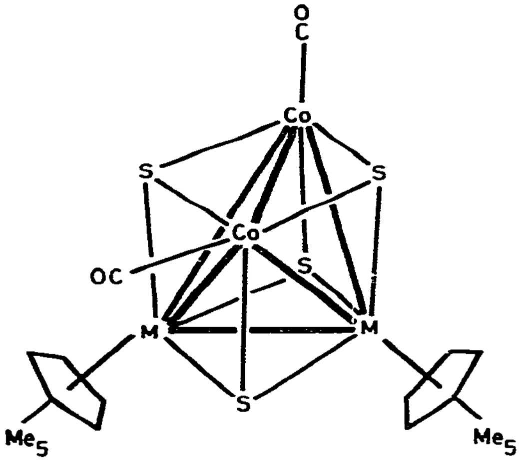


SCHEME 1

The composition of III and IV is confirmed by elemental analysis and mass spectra to be $(C_5Me_5)_2Co_2M_2S_4(CO)_2$. Prominent ions of the 70 eV mass spectra are besides the parent ion M^+, the fragments $[M - CO]^+$, $[M - 2CO]^+$, $[M - 2CO - C_5Me_5]^+$, $[M - 2CO - 2C_5Me_5]^+$, as well as M^{2+}. Characteristic IR absorptions (KBr) are ν(CO) frequencies at 1985 and 1960 (III) and 1975 and 1950 cm^{-1} (IV), respectively. Whereas weak absorptions at 515 and 375 cm^{-1} are common for both complexes, the relatively strong terminal Mo=S frequencies at 480 cm^{-1} of IIB and IIC have disappeared as well as the absorptions characteristic for the μ-S_2 and the iso-μ,η^1-S_2 ligand in I (the metal—sulfur bonds of IIA are IR inactive). The sharp CH_3 resonances in the ^1H NMR spectra (1.87 (III) and 1.96 ppm (IV), $CDCl_3$) are both shifted 0.26 ppm to higher field compared with the starting complexes I and II. This is due to an increase of the metal to sulfur ratio from 2/4 in the reagents to 4/4 in the products.

Although suitable single crystals of III and IV have not yet been obtained, their structures can be assumed to involve equal distribution of the four sulfurs over all metal atoms, so that they serve as μ_3 ligands. This is supported by the disappearance of the terminal M—S double bond in IIB and IIC, as well as by a change of the character of the μ-S_2 ligand in I and, obviously, in IIA and IIB. A corresponding transformation of one μ-S_2 group into two μ_3-S ligands has been demonstrated for $Fe_2(CO)_6(\mu$-$S_2)$ in its reactions with $C_5H_5Co(CO)_2$ [9] or $[C_5H_5M(CO)_2]_2$ (M = Cr, Mo) [10]. A μ_3 ligand may also be formed by the loss of sulfur from the iso-μ,η^1-S_2 group in I as shown by the transformation of $(C_5Me_5)_2Cr_2S_5$ into $(C_5Me_5)_4Cr_4S_4$ upon heating of a toluene solution of I [11].

Thus, the C_5Me_5 ligands being assumed to be present as monoanions and the sulfurs as dianions, each of the Cr or Mo atoms is left in M^{III} d^3 configuration and each of the Co atoms in a Co^{II} d^7 configuration. In order to explain the diamagnetism of III and IV, formation of three metal—metal bonds is required for each metal atom, and this finally results in the formation of an all metal bonded tetrahedron. These considerations are supported by the structure of the isoelec-



M = Cr, Mo

Fig. 1. Proposed structure for $(\eta\text{-}C_5Me_5)_2M_2M'_2(\mu_3\text{-}S)_4(CO)_2$.

tronic cluster $Fe_4(NO)_4(\mu_3\text{-}S)_4$, for which an X-ray study has confirmed a distorted cubane structure containing a tetrametal cluster with four Fe—Fe bonds [12].

Experimental

All manipulations were carried out under dry nitrogen with solvents freshly distilled from appropriate drying agents. As a typical procedure which can be applied to the other reagents I, IIA and IIC, the reaction of *syn*-$(C_5Me_5)_2Mo_2(\mu\text{-}S_2)S_2$ (IIB) with $Co_2(CO)_8$ is described.

$(\eta\text{-}C_5Me_5)_2Mo_2Co_2(\mu_3\text{-}S_4)(CO)_2$. To a brown solution of 0.11 g (0.19 mmol) of IIB in 50 ml toluene 65 mg (0.19 mmol) $Co_2(CO)_8$ were added. The mixture was stirred at room temperature for 30 min, concentrated to 10 ml and then transferred to a column (20 × 3 cm, SiO_2). A red-brown band was eluted with toluene and yielded 97 mg (72%) of product IV. Recrystallization from toluene/ether (2/1) gave dark violet-brown thin plates. Analyses: III: Found: C, 38.54; H, 4.38; mol. wt. (mass spectrosc.), 676. $C_{22}H_{30}Co_2Cr_2O_2S_4$ calcd.: C, 39.05; H, 4.47%; mol. wt. 676.6. IV: Found: C, 34.24; H, 3.59; Co, 15.72; S, 16.87; mol. wt. (mass spectroscop.), 756 (with respect to ^{92}Mo). $C_{22}H_{30}Co_2Mo_2O_2S_4$ calcd.: C, 34.56; H, 3.96; Co, 15.43; S, 16.77%; mol. wt. 764.6.

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