

ucts with *cis*-hexahydroindane framework in the hydrogenation of **1**. This was explained in terms of hydrogenation of the 3,3a-double bond of the intermediary dienol and not of the 3a,4-double bond (see Scheme 1, analogue A). If this were true the formation of a dienol would lead to a planarization of the symmetry center at C-3. Thus, on addition of hydrogen the C³-epimer of **5** should be formed. However, this inversion is not observed.

The acetate **7** obtainable from **1** is a molecule which exhibits the same relative stereochemistry at the centers **3**, **3a**, and **7a** as observed in the naturally occurring prostaglandins.

Experimental

2: A solution of **1** (11.1 g, 4.1 mmol) and NBS (10 g, 5.6 mmol) in CCl₄ (300 mL) was heated to boiling for 2.5 h. After cooling, succinimide was filtered off, the filtrate evaporated down in a vacuum, and the residue taken up in a little ether. 9.7 g of **2** (68%) crystallized out within about 12 h on cooling the filtrate in a refrigerator at ca. 0°C. Colorless crystals, m.p. 154°C; IR: 1750, 1640, 1605 cm⁻¹ (CO); ¹H-NMR: δ = 1.18 (s, 9H, *t*Bu), 1.52 (s, 3H, 7a-CH₃), 3.58 (dd, 1H, J_{1,2} = 10.1, J_{1,2'} = 7.6 Hz, C¹-H), 5.87 (dd, 1H, J_{3,2} = 8.9, J_{3,2'} = 7.4 Hz, C³-H).

3: The isomeric bromide **3** can also be isolated (in smaller amounts than 10%) from the mother liquor on silica gel with ether. Colorless crystals, m.p. 132°C (ether/petroleum ether); IR: 1745, 1640 cm⁻¹ (CO); ¹H-NMR: δ = 1.16 (s, 1H, 7a-CH₃), 1.24 (s, 9H, *t*Bu), 4.28 (dd, 1H, J_{1,2} = 10.0, J_{1,2'} = 6.3 Hz, C¹-H), 6.04 (dd, 1H, J_{3,2} = 5.0, J_{3,2'} = 1.2 Hz, C³-H).

4: A solution of **2** (3.4 g, 1 mmol) and silver acetate (2 g, 1.2 mmol) in glacial acetic acid (100 mL) was heated to boiling for 3.5 h. After cooling, silver bromide was filtered off, the solvent removed in a vacuum, and the residue crystallized from ether/petroleum ether (1:1); yield 1.8 g (56%). Colorless crystals, m.p. 131–132°C; IR: 3300–2400 (br.), 1750, 1710, 1690 cm⁻¹ (CO); ¹H-NMR: δ = 1.19 (s, 9H, *t*Bu), 1.21 (s, 1H, 7a-CH₃), 2.03 (s, 3H, acetate), 3.90 (dd, 1H, J_{1,2} = 11.5, J_{1,2'} = 6.5 Hz, C¹-H), 6.24 (dd, 1H, J_{3,2} = 8.5, J_{3,2'} = 2 Hz, C³-H).

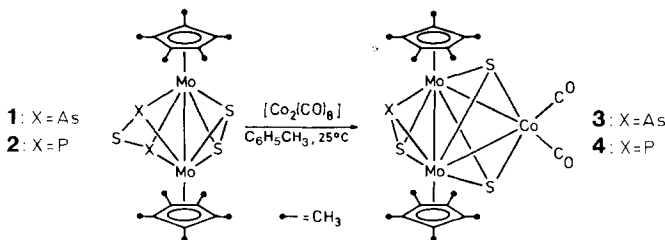
Received: October 26, 1984 [Z 1050 IE]
German version: *Angew. Chem.* 97 (1985) 129

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[2] All compounds were characterized by elemental analyses as well as IR and NMR data. All NMR spectra were recorded in CDCl₃ on a 200-MHz instrument, all IR spectra in KBr.
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[4] **2** can be esterified with diazomethane in ether. 2-Me-ester: colorless crystals, m.p. 121°C (ether/petroleum ether), ¹H-NMR: δ = 1.18 (s, 9H, *t*Bu), 1.44 (s, 3H, 7a-CH₃), 3.77 (s, 3H, ester), 3.56 (dd, 1H, J_{1,2} = 10.5, J_{1,2'} = 7.5 Hz, C¹-H), 5.06 (dd, 1H, J_{3,2} = 9, J_{3,2'} = 7 Hz, C³-H).
[5] We thank Dr. K. Pachler (Analytisches Zentrallabor, E. Merck Darmstadt) for recording and discussing the ¹H-NMR spectra.
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[7] Overall yields for all four compounds: quantitative. The product distribution is variable (CO₂-cleavage!).—**5**: colorless crystals, m.p. 118.5°C (ether), IR: 3300–2500 (br.), 1740, 1650, 1603 cm⁻¹ (CO); ¹H-NMR: δ = 1.04 (s, 3H, 7a-CH₃), 1.14 (s, 9H, *t*Bu), 1.97 (s, 3H, acetate), 3.73 (dd, 1H, J_{1,2} = 7.9, J_{1,2'} = 9.2 Hz, C¹-H), 5.04 (ddd, 1H, J_{3,2} = 10.0, J_{3,2'} = 4.2, J_{3,3a} = 9.6 Hz, C³-H), 2.37 (dd, 1H, J_{3a,3} = 9.6, J_{3a,4} = 13.1 Hz, C^{3a}-H), 3.44 (d, 1H, J_{4,3a} = 13.1 Hz, C⁴-H).—**6**: colorless crystals, m.p. 104°C (ether/petroleum ether), IR: 3400–2500 (br.), 1730, 1700, 1640, 1595 cm⁻¹; ¹H-NMR: δ = 0.98 (s, 3H, 7a-CH₃), 1.17 (s, 9H, *t*Bu), 1.94 (s, 3H, acetate), 2.85 (d, 1H, J_{3a,3} = 6.8 Hz, C^{3a}-H), 3.66 (dd, 1H, J_{1,2} = 6.7, J_{1,2'} = 6.7 Hz, C¹-H), 5.46 (m, 1H, C³-H).—**7**: colorless crystals, m.p. 94°C (ether/petroleum ether), IR: 1740, 1720 cm⁻¹ (CO); ¹H-NMR: δ = 1.03 (s, 3H, 7a-CH₃), 1.14 (s, 9H, *t*Bu), 1.9 (m, 1H, C^{3a}-H), 2.02 (s, 3H, acetate), 3.66 (dd, 1H, J_{1,2} = 7.8, J_{1,2'} = 9.2 Hz, C¹-H), 4.88 (ddd, 1H, J_{3,2} = 9.8, J_{3,2'} = 4.3, J_{3,3a} = 9.2 Hz, C³-H).—**8**: colorless crystals, m.p. 77°C (ether/petroleum ether), ¹H-NMR: δ = 1.14 (s, 3H, 7a-CH₃), 1.16 (s, 9H, *t*Bu), 1.94 (s, 3H, acetate), 2.3 (m, 1H, C^{3a}-H), 3.81 (dd, 1H, J_{1,2} = 6.2, J_{1,2'} = 5.4 Hz, C¹-H), 5.31 (ddd, 1H, J_{3,2} = 6.1, J_{3,2'} = 3.4, J_{3,3a} = 5.7 Hz, C³-H).
[8] The methyl esters of **5** and **6** can be prepared by esterification with diazomethane: 5-Me-ester: colorless crystals, m.p. 119–121°C (petroleum ether), ¹H-NMR: δ = 1.05 (s, 3H, 7a-CH₃), 1.14 (s, 9H, *t*Bu), 1.98 (s, 3H, acetate), 3.7 (s, 3H, OMe).—6-Me-ester: colorless oil, ¹H-NMR: δ = 0.97 (s, 3H, 7a-CH₃), 1.16 (s, 9H, *t*Bu), 1.91 (s, 3H, acetate), 3.74 (s, 3H, OMe). Positions and couplings of the remaining protons as in **5** and **6** [7].

Synthesis of [(C₅Me₅)₂Mo₂XS₃Co(CO)₂] Clusters (X = P, As) and Structural Characterization of a μ₂,η²-AsS Ligand

By Henri Brunner, Heike Kauermann, Ulrich Klement, Joachim Wachter*, Thomas Zahn, and Manfred L. Ziegler

Spectroscopic investigation of the complexes **1** and **2**, which were synthesized from [(C₅Me₅)₂Mo₂] and As₄S₄ or P₄S₃, revealed the possible presence of an unusual μ₂,η²-XSX-structural unit^[1]. Since it has so far proven impossible to confirm the presence of such a unit by single-crystal X-ray structural analyses, we attempted the preparation of clusters via a secondary reaction with Co₂(CO)₈ in the hope that their mode of synthesis might throw some light on the structure of **1** and **2**.



However, according to elemental analyses and mass spectra, the diamagnetic clusters **3** and **4**^[2] formed on reaction of **1** and **2** respectively with Co₂(CO)₈ surprisingly contained one X-atom less than expected. An X-ray structure analysis carried out on **3** showed the presence of

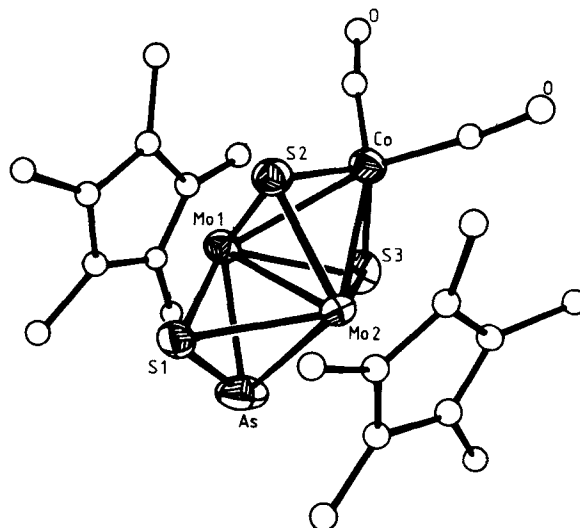


Fig. 1. Molecular structure of **3** in the crystal (ORTEP diagram). Selected bond lengths [Å] and angles [°]: Mo1–Mo2 2.610(1), Mo1–Co 2.722(2), Mo1–As 2.533(2), Mo1–S1 2.517(2), Mo1–S2 2.406(3), Mo1–S3 2.416(4), Mo2–Co 2.725(2), Co–S2 2.178(3), Co–S3 2.165(4), As–S1 2.237(3); Mo2–Mo1–Co 61.4(0), Mo2–Mo1–As 58.7(0), Mo2–Mo1–S1 58.6(1), Mo2–Mo1–S2 57.3(1), Mo1–Co–S2 57.5(1). The As and S1 positions are each 50% statistically occupied by arsenic and sulfur.

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an Mo₂Co-triangle bridged by two μ₃-sulfur ligands and a new structural unit, an η²-AsS ligand as bridge between two Mo atoms. The AsS-ligand, the two S-bridges and the Co-atom lie in a plane bisecting the molecule. The carbonyl groups are located in the plane of the three-membered ring of metal atoms (Fig. 1). Hence, **3** constitutes the first example of a molecule containing complex-stabilized arsenic monosulfide, which, in the free state, is unstable. With the proviso that there is a 50% statistical distribution of arsenic and sulfur at the As and S1 sites, the As–S1 distance in **3** can be said to be 2.237(3) Å, a value which corresponds to the average length of the As–S single bond in α-As₄S₄^[4]. We conclude, therefore, that the new ligand has a bond order of 1 and functions as a 5e-donor. Furthermore, if we consider the μ₃-S atoms as 4e-donors and the remaining ligands as 5e-donors (C₅Me₅-moieties) and 2e-donors (CO groups), then each metal atom acquires noble-gas configuration by formation of M–M single bonds. The experimentally determined metal-metal distances lend support to this conclusion.

Remarkably, the Co(CO)₂-fragment is incorporated exclusively in the η²-S₂-group of **1** and **2**, even though there are several sites open to attack in the ligand sphere of the starting complex. The S₂-bridge over the Mo atoms is thereby enlarged to an SCoS unit, while elimination of X from the XSX-bridge leads to formation of the bridging XS-ligand. This apparent lability of an Mo–X bond is confirmed by the sensitivity of **1** towards oxidation: Only the previously reported arsenic-free complexes [(C₅Me₅)₂Mo₂O₂S₂] and [(C₅Me₅)₂Mo₂OS₃] can be isolated from toluene solutions of **1** in presence of air.

Received: October 10, 1984;
revised: November 22, 1984 [Z 1034 IE]
German version: *Angew. Chem.* 97 (1985) 122

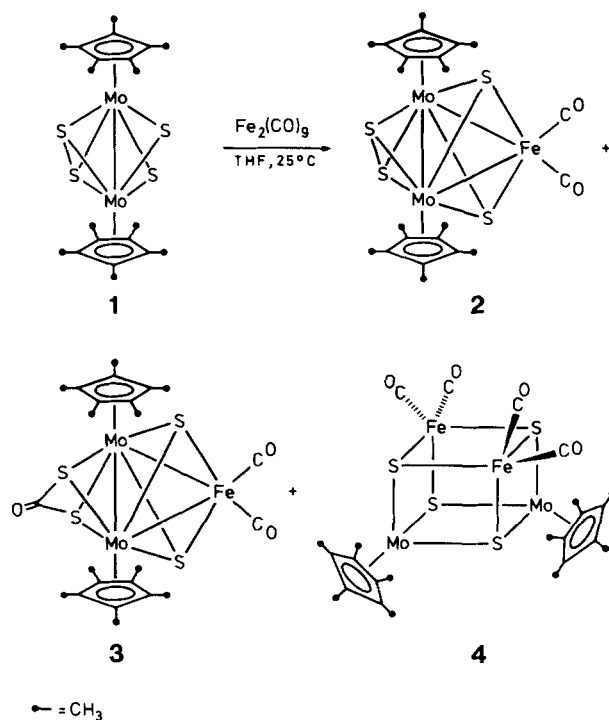
CAS Registry numbers:

1, 90790-24-2; **2**, 94570-20-4; **3**, 94570-21-5; **4**, 94570-22-6;
[(C₅Me₅)₂Mo₂OS₃], 94570-23-7; [(C₅Me₅)₂Mo₂O₂S₂], 94570-24-8; [Co₂(CO)₈],
10210-68-1.

Novel MoFeS Clusters from [(C₅Me₅)₂Mo₂S₄] and Fe(CO)₅ or Fe₂(CO)₉

By Henri Brunner, Norbert Janietz, Joachim Wachter*, Thomas Zahn, and Manfred L. Ziegler

Thio-transition-metal clusters containing various metal atoms serve as model compounds, both in the catalysis of industrially important desulfurization reactions as well as in the deciphering of bioinorganic reactions. Of particular importance is the coupling of Mo and Fe with sulfur to give "heterocubanes", among which, compounds with a Mo₂Fe₂S₄ core are still very poorly represented in the literature. The first such cluster to be prepared and spectroscopically characterized was [(C₅Me₅)₂Mo₂Fe₂(NO)₂S₄]^[1]. But "mixed" trinuclear clusters with a trigonal pyramidal M₂M'S₂ core and a μ₂,η²-di-(main group element) ligand are also still relatively rare^[2].



The three new diamagnetic MoFeS clusters **2–4** are formed on reaction of the complex **1** with Fe₂(CO)₉ in tetrahydrofuran (THF) (molar ratio 1 : 1.3). **2** and **4** are also formed in the photochemical reaction of **1** with Fe(CO)₅ (in the molar ratio 1 : 2) in THF^[3a]. The composition of each product has been confirmed by elemental analysis and mass spectra. The ¹H-NMR and IR spectra^[3b] are consistent with the results of the X-ray structure analysis.

Characteristic of the structures of **2** and **3**^[4] (Figs. 1 and 2) is a trigonal-bipyramidal Mo₂FeS₂ core; the Mo₂Fe(CO)₂ moiety is perpendicular to the plane of the sulfur ligands. As 48e-clusters, **2** and **3** each contain three metal-metal single bonds, consistent with the observed

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- [2] a) A mixture of 0.60 mmol **1** or **2** and 0.64 mmol Co₂(CO)₈ in 50 mL toluene is stirred for 1 h (**1**) or 2.5 h (**2**) at room temperature. Chromatographic purification on SiO₂ with toluene/petroleum ether (1 : 1) afforded the red-brown complexes **3** and **4** in 60 and 28% yield, respectively. The complexes can be recrystallized from toluene/pentane (5 : 2).—b) IR (KBr, [cm⁻¹]): **3**: ν(CO) = 1975 (vs), 1927 (s); **4**: ν(CO) = 1982 (vs), 1932 (s). ¹H-NMR (δ(CH₃), CDCl₃): **3**: 1.88; **4**: 1.90.
- [3] P2₁/n, a = 11.529(7), b = 15.348(9), c = 15.588(5) Å, β = 107.28(3)°, V = 2633.75 Å³, Z = 4, Syntex P3 diffractometer (MoKα), 3° ≤ 2θ ≤ 55°, 2490 observed reflections with I ≥ 2.5σ(I), Patterson (Co, Mo, As, S) and Fourier methods, anisotropic refinement to R_w = 0.04. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 51104, the names of the authors, and the full citation of the journal.
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- [5] If a solution of **1** in toluene is stirred for 48 h in presence of air, subsequent chromatographic work-up enables isolation of [(C₅Me₅)₂Mo₂OS₃] (green, 46% yield; IR (KBr, [cm⁻¹]): ν(Mo=O) = 900 (vs), ν(Mo=S) = 482 (s); ¹H-NMR (δ(CH₃), CDCl₃): 2.03, 1.96) and [(C₅Me₅)₂Mo₂O₂S₂] (orange, 39% yield; IR (KBr, [cm⁻¹]): ν(Mo=O) = 898 (vs), ν(Mo=S) = 451 (w); ¹H-NMR (δ(CH₃), CDCl₃): 2.00.
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