

fore decisive for the enantiomeric purity of the products derived therefrom, and hence in this respect efforts at improvement must be made. In contrast, the problem of obtaining educts **4** in high enantiomeric purity can be regarded as being solved: The constant *ee* values of 90–93% for **8a–d** prove that **4** exhibits at least this *ee*-value. Furthermore, the constancy of the *ee*-value for the compounds **8** examined indicates that the transfer of chirality from **4** to **8** is cogent.

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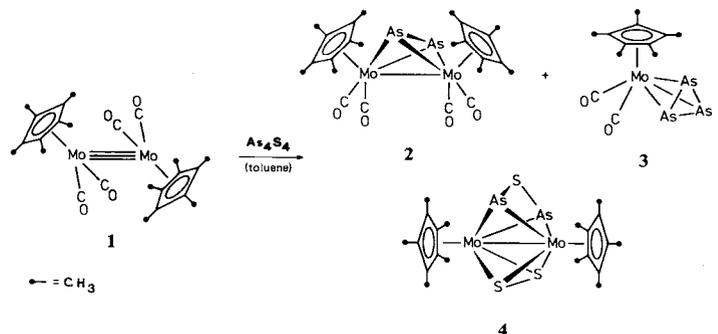
Ligand Extrusion from the As_4S_4 -Cage by $[C_5Me_5(CO)_2Mo]_2$: Formation of $(C_5Me_5)_2Mo_2(CO)_4(\mu, \eta^2-As_2)$, $C_5Me_5(CO)_2Mo(\eta^3-As_3)$, and $(C_5Me_5)_2Mo_2As_2S_3^{**}$

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The chalcogenide-rich binuclear complexes of the type $(C_5Me_5)_2Mo_2X_4$ ($X = S, Se$) can be prepared by complete exchange of the CO groups of $[C_5Me_5(CO)_2Mo]_2$ **1**, which contains one $Mo \equiv Mo$ bond, by reaction with elemental sulfur or selenium^[1]. Since a similar synthetic principle has also been found for $(C_5H_5)_2Mo_2As_3$, a combination of arsenic with sulfur or selenium should lead to previously unknown arsenide/chalcogenide ligands. In fact, realgar (As_4S_4), which is moderately soluble in organic solvents, proves to be a suitable synthetic reagent. Surprisingly, reaction of As_4S_4 with **1** also gives rise to a η^3-As_3 complex which belongs to the still less researched monosubstituted derivatives of yellow arsenic.

The two arsenic-containing complexes **2** and **3** as well as the arsenic- and sulfur-containing complex **4** are formed by heating an equimolar mixture of **1** and As_4S_4 in toluene^[3]; no complex containing only sulfur could be detected. The compositions of all the products have been verified by elemental analysis (C, H, As, S) and mass spectro-

scopy. The spectroscopic data of **2** [IR: $\nu_{CO} = 1976, 1913, 1897, 1823 \text{ cm}^{-1}$ (toluene solution); ^1H-NMR : $\delta_{CH_3} = 1.98$ ($CDCl_3$)] indicate a tetrahedral Mo_2As_2 cluster, as previously established by X-ray crystallography for $(C_5H_5)_2Mo_2(CO)_4(\mu, \eta^2-As_2)$ ^[4].



X-Ray structure analysis of **3**^[5] indicates that the Mo atom forms the apex of a tetrahedron with a practically equilateral As_3 triangle as base (cf. Fig. 1). A crystallographically stipulated mirror plane through the atoms $As1$, Mo , $C2$, and $C3$ bisects the bonds $As2-As2'$ and $C6-C6'$ as well as the angle $C1-Mo-C1'$. Just as in $As_3Co(CO)_3$, the $As-As$ distances (2.375 Å) are shorter than in the free As_4 molecule^[6]. In order to account for this result, a reduction in the mutual repulsion of the lone pairs of electrons by transfer of electron density to the central metal atom and the other ligands^[6] or an increase in bonding and a decrease in antibonding interactions within the As_3 -ring by coordination to the metal^[7] have been postulated.

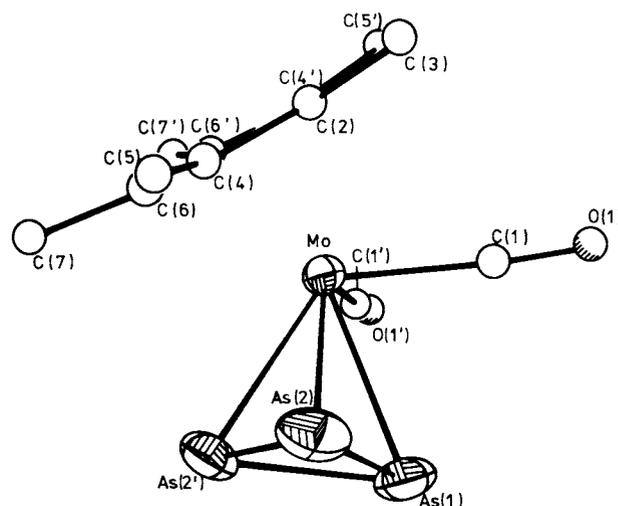


Fig. 1. Molecular structure of the complex **3** in the crystal (ORTEP representation). Selected bond lengths [pm] and angles [°]: $Mo-As1$ 270.6(2), $Mo-As2$ 263.9(1), $Mo-C1$ 200.7(7), $Mo-C2$ 227(1), $Mo-C4$ 233(1), $Mo-C6$ 239(1), $As1-As2'$ 237.2(1), $As2-As2'$ 237.7(2); $As2-Mo-C1$ 87.4(2), $C1-Mo-C1'$ 90.5(4), $C_5Me_5(\text{cent})-Mo-As_3(\text{cent})$ 136(2), $C_5Me_5(\text{cent})-Mo-C1$ 96.4(4), $As_3(\text{cent})-Mo-C1$ 113.5(2), $As2-As1-As2'$ 60.2(1), $As1-As2-As2'$ 59.9(0).

Experimental proof for an increased charge density at the central metal is provided, for the first time, for **3** by comparison with the isoelectronic complex $C_5Me_5Mo(CO)_2NO$ ^[8]. Correspondingly, in **3** a more "obli-

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[**] Reactivity of the M-M Multiple Bond in Metal Carbonyl Derivatives, Part 9. - Part 8: J. Wachter, J. G. Riess, A. Mitschler, *Organometallics*, in press.

quely" arranged C_5Me_5 -ring is found in which the distances of the atoms C6 and C6', which are *cis* to the As_3 -ligand, to Mo are ca. 0.12 Å more than that of C2, and the Mo–C distances for the CO ligands are at least ca. 0.065 Å longer. The ν_{CO} frequencies in **3** [1964, 1904 cm^{-1} (KBr)], which are over 20 cm^{-1} lower, are consistent with this.

To date, single crystals of the air-sensitive, red-violet complex **4** have eluded isolation. In addition, the IR spectrum—weak absorptions at 422 and 388 cm^{-1} suggest Mo–ligand bridging functions—cannot be interpreted in more detail; nevertheless the 1H -NMR spectrum [$\delta_{CH_3} = 2.03$ in $CDCl_3/[D_8]toluene$ (1:2) at $-26^\circ C$] indicates a symmetric structure. By analogy to the previously known structures of $(C_5Me_5)_2Mo_2(\mu, \eta^2-S_2)(\mu-S)_2$ ^[1a] and $(C_5Me_5)_2Mo_2(\mu, \eta^2-As_3)(\mu, \eta^2-As_2)$ ^[2], **4** probably contains a $\mu, \eta^2-As_2S_2$ and a μ, η^2-S_2 ligand, which should both lie in a plane between the two Mo atoms. The sum of valence electrons from all the ligands therefore amounts to 10 per Mo atom, which enables the latter to attain the noble gas configuration upon inclusion of the corresponding metal d-orbitals. This scheme is corroborated by studies on the reactivity. Thus, no weakly bonded sulfur is eliminated by PPh_3 , for example, and, even under mild conditions, S_8 displaces the As_2S_2 ligand to form the blue complex $(C_5Me_5)_2Mo_2(\mu, \eta^2-S_2)(\mu-S)_2$ ^[1a].

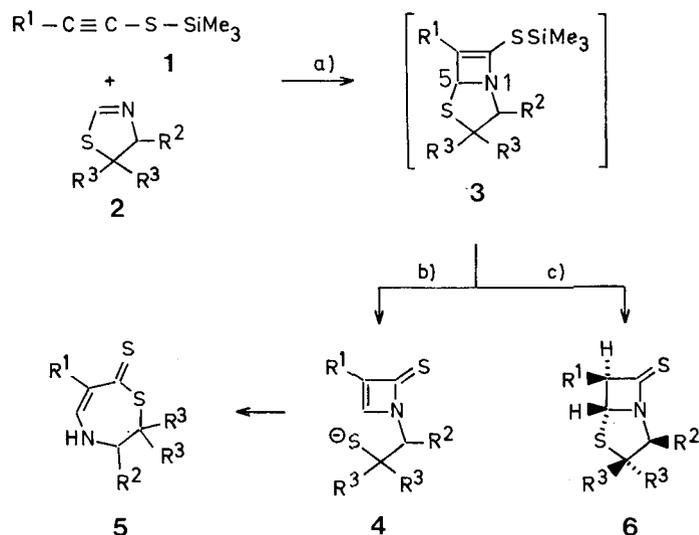
No statements can be made at present about the mechanism of fragmentation of the As_4S_4 -cage since the complexation of intact realgar has not yet proved possible. However, the novel compounds **2–4** appear to be relatively thermodynamically stable, as also indicated by the decomposition of the structurally totally different P_4S_3 into $C_5Me_5(CO)_2MoP_3$, $(C_5Me_5)_2Mo_2P_2S_3$, etc.^[9]

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Thiopenam Derivatives from Alkynyl Silyl Sulfides and 4,5-Dihydrothiazoles**

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Although β -lactam antibiotics have been modified in a variety of ways^[1], the replacement of the oxo group in the four-membered ring by hetero-substituents has so far not been studied in detail. As previously described in the literature, a tosylimino group can easily be introduced^[2], whereas the sulfuration of biologically active β -lactams



Scheme 1. a) $20^\circ C$, 7 d, without solvent; b) H_2O , CsF or SiO_2 ; c) Ultrasonication (20 min), then H_2O .

	R ¹	R ²	R ³		R ¹	R ²	R ³
1a	<i>t</i> Bu			5a, 6a	<i>t</i> Bu	H	H
1b	Ph			5b	Ph	H	H
2a		H	H	5c	<i>t</i> Bu	COOMe	H
2b		COOMe	H	5d, 6b	<i>t</i> Bu	COOMe	Me
2c		COOMe	Me	5e	Ph	COOMe	Me

gives only poor yields of the desired sulfurated products^[3]. We have now investigated the possibility of obtaining β -thiolactams as part of a penicillin skeleton ("thiopenam derivatives") by reaction of the readily accessible alkynyl silyl sulfides **1a, b**^[4], which are highly reactive toward nucleophiles, with the 4,5-dihydrothiazoles **2a, b** and (*S*)-**2c**^[5].

The alkynes **1** react with the heterocycles **2** at room temperature to give adducts which may be formulated as silylthio derivatives **3**. Desilylation by hydrolysis, cesium fluoride or silica gel does not furnish the thiopenam system **6**, but leads, with cleavage of the S4–C5 bond, via **4** to dihydro-1,4-thiazepinethione **5**.

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