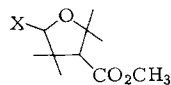


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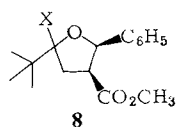


7

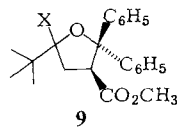
a → **b**, 67% (4 : 1)

a → **b**, 88% (6 : 1)

a → **c**, 51% (3 : 1)



8



9

a → **b**, 80% (>20 : 1)

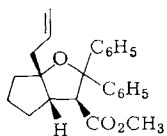
a → **c**, 59% (8 : 1)

a → **b**, 87% (>20 : 1)

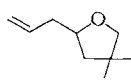
a → **c**, 84% (>20 : 1)

Scheme 1. Synthesis of methyl 5-allyl-3-tetrahydrofuran-2-carboxylates **6b-9b** ($X = \text{CH}_2-\text{CH}=\text{CH}_2$) and methyl 5-cyano-3-tetrahydrofuran-2-carboxylates **7c-9c** ($X = \text{C}\equiv\text{N}$) from the γ -lactols **6a-9a** ($X = \text{OH}$) and allyltrimethylsilane **4** or cyanotrimethylsilane **5**, respectively, in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ as promoter. The *trans*:*cis* ratios of the products are given after the yields in parentheses.

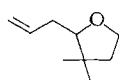
yl 3-tetrahydrofuran-2-carboxylates **6b-9b** and **7c-9c**, respectively, are isolated in good yields (Scheme 1).^[6] Because boron trifluoride etherate has been successfully used until now, the effect of other Lewis acids on yields and on the stereochemical course of the substitution has not yet been investigated. The reaction of **7a** and **9a** with silyl enol ethers or with trimethylvinylsilane was unsuccessful even in the presence of TiCl_4 . That both bicyclic compounds and simple tetrahydrofuran derivatives can be synthesized is demonstrated by the preparation of the allylated products **10-12**^[6] (yields in parentheses), which were obtained analogously from the corresponding γ -lactols with allyltrimethylsilane **4**/ $\text{BF}_3 \cdot \text{OEt}_2$.



10 (85%)



11 (57%)



12 (40%)

The substitution might take place via oxonium ions, which are formed upon treatment of the γ -lactols with Lewis acids. Preferential attack of the nucleophile from the more accessible side would then lead to the observed products. Because the structural assignments of **6b**, **7b**, **7c**, and **8c** appear to be well established on the basis of the spectroscopic data,^[7] we assume that the other main products in Scheme 1 also have the *trans* configuration. In the case of **7** and **8**, cyanotrimethylsilane **5** is less selective than allyltrimethylsilane **4** (even switching from **5** to *tert*-butyl(cyano)dimethylsilane does not change the *trans*:*cis* ratio in the case of **7c**).

Because γ -lactols are readily accessible^[8] and allyl or cyano groups are easy to modify, the synthetic method described here should allow access to a variety of tetrahydrofuran derivatives.^[9]

General Experimental Procedure

The γ -lactol was dissolved in dry dichloromethane (5 mL per mmol of γ -lactol) and treated first with 2 equivalents of **4** or **5** (1.1 equivalents are sufficient for **6** and **7**) under N_2 at -78°C and then with 2 equivalents of $\text{BF}_3 \cdot \text{OEt}_2$. The stirred reaction mixture was allowed to warm over ca. 16 h to room temperature. After aqueous workup, drying (MgSO_4), concentration, and distillation or chromatography, the substitution products shown in Scheme 1 as well as **10-12** were obtained.

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- [5] H.-U. Reissig, *Tetrahedron Lett.* 22 (1981) 2981, and unpublished results.
- [6] All new compounds isolated gave satisfactory elemental analyses and appropriate spectra.
- [7] Characteristic is, for example, the low-field shift of the $^1\text{H-NMR}$ signals of 3-H and 5-H by 0.11 and 0.73, respectively, on going from *cis*- to *trans*-**7c**. This assignment is supported by the $^{13}\text{C-NMR}$ spectrum (CDCl_3 , 22.6 MHz): *trans*-**7c**: $\delta = 169.7$ (s, C=O), 117.4 (s, C \equiv N), 84.6 (s, C-2), 75.9 (d, C-5), 60.8 (d, C-3), 51.5 (q, OCH $_3$), 46.4 (s, C-4), 30.8, 25.7, 24.7, 21.7 (4q, 4CH $_3$); *cis*-**7c**: $\delta = 169.3$ (s, C=O), 117.4 (s, C \equiv N), 83.5 (s, C-2), 75.1 (d, C-5), 61.9 (d, C-3), 51.5 (q, OCH $_3$), 46.3 (s, C-4), 29.5, 25.5, 25.3, 19.3 (4q, 4CH $_3$). Similar arguments hold also for **6b**, **7b**, and **8c**.
- [8] γ -Lactols are most easily prepared by addition of nucleophiles (e.g., hydride from diisobutylaluminum hydride) to γ -lactones.
- [9] Tetrahydrofuran substructures are found in many antibiotic natural products of the polyether type: R. E. Ireland, D. Häbich, *Chem. Ber.* 114 (1981) 1418, and references cited therein.

Complex-Induced Fragmentation of As_4S_4 : Stabilization of an As_2S_3 Ligand

By Henri Brunner, Heike Kauermann, Bernd Nuber, Joachim Wachter,* and Manfred L. Ziegler

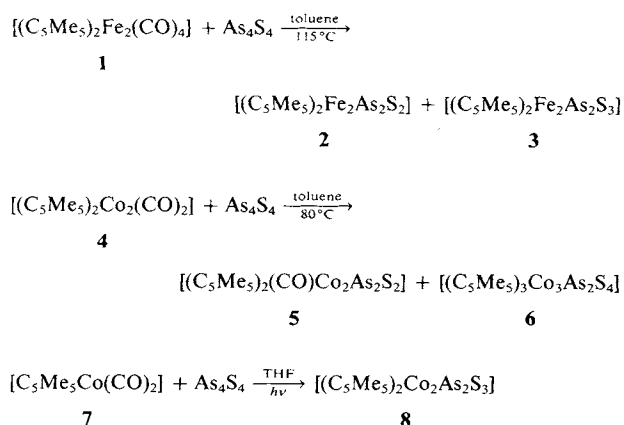
The system arsenic/sulfur provides a treasure chest of new ligands for transition-metal complexes. As_2S_3 and As_4S_4 have been employed to obtain compounds with AsS_3 ,^[1] AsS ,^[2] and $\text{As}_2\text{S}^{(3)}$ ligands. However, cage molecules as ligands were lacking, even though they are known in the phosphorus/sulfur system (P_4S_3)^[4]. During a search for complexes with AsS cage molecules as ligands, we allowed **1**, **4**, and **7** to react with As_4S_4 . Of the products **2**, **3**, **5**, **6**, and **8**, complex **8** contains an As_2S_3 ligand, the largest fragment of the As_4S_4 cage reported so far.

The complexes **2** (green) and **3** (red-violet) can be prepared by reaction of As_4S_4 with $[(\text{C}_5\text{Me}_5)_2\text{Fe}_2(\text{CO})_4]$ **1** in

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boiling toluene. On the other hand, $[(C_5Me_5)_2Co_2(CO)_2]$ ($Co=Co$) **4** reacts with As_4S_4 in toluene (80°C) to form the carbonyl-containing complex **5** and the black-brown cluster **6**.



The photochemical reaction of **1** and **7** with As_4S_4 in tetrahydrofuran (THF) gives **3** and the violet-brown complex **8**, respectively.^[5] The compositions of the diamagnetic complexes **2**, **3**, **5**, **6**, and **8** were established by field-desorption mass spectroscopy and, for **2**, **6**, and **8**, by complete elemental analysis. The reaction of $[(C_5Me_5)_2W_2(CO)_4]$ ($W \equiv W$) with As_4S_4 , on the other hand, affords solely the already known, exclusively sulfur-containing complexes $[(C_5Me_5)_2W_2(\mu-S)_2S_2]$ and $[(C_5Me_5)_2W_2(\mu-S)_2S_2]$.^[6] Common to **2**, **3**, and **5** is a side-on bonded As_2 ligand as four-electron donor,^[7] which, along with the sulfur ligands required for electron balance, appears to be better suited than mixed AsS ligands for the stabilization of lower metal oxidation states.

An X-ray structure analysis of **8**^[8] revealed that in this complex a novel As_2S_3 ligand is present as a 4e donor with two *cis*-arranged η^2 -bonded AsS units that are bridged by an S atom. This results in a "basket" with a C_2 axis through S(2) and the midpoint of the Co_2S_2 square. The structure differs from the sulfur-arsenic chains of the As_2S_3 layer lattice primarily in the all-*cis* geometry that is forced upon the molecule by the two C_5Me_5Co units. Comparison of the bond lengths for both kinds of As-S bonds reveals a surprisingly narrow range of variation of As-S distances. The mean value (2.231 Å) corresponds to

that (2.237 Å) of the μ_2, η^2 -AsS ligand in $[(C_5Me_5)_2Mo_2As_3Co(CO)_2]$ ^[2] and is comparable to those in realgar (As_4S_4) and orpiment (As_2S_3).^[9] The bond angles at S and As, although slightly expanded, more resemble those in As_2S_3 than in As_4S_4 .

The results presented here underline the importance of As_4S_4 as a starting material for new As-S ligands, but also show the difficulties in controlling the complex-induced cage fragmentation, which appears to depend crucially on the transition-metal complex used.

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1, 35344-11-7; **3**, 102284-25-3; **4**, 6965752-9; **7**, 12129-77-0; **8**, 102284-26-4; As_4S_4 , 12279-90-2.

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[5] **8**: $[C_5Me_5Co(CO)_2]$ **7** (530 mg, 2.12 mmol) and As_4S_4 (907 mg, 2.12 mmol) in 230 mL of THF were irradiated for 19 h in an immersion lamp apparatus (125-W Hg lamp). The solvent was removed and the dark brown crude product was dissolved in 15 mL of CH_2Cl_2 and chromatographed on SiO_2 (column: 40 cm \times 3 cm). **8** was eluted with toluene as a dark brown band. Re-purification on SiO_2 (column: 10 cm \times 1.5 cm; eluent: toluene/petroleum ether 1:1) afforded 16% of **8**, which was recrystallized from toluene/pentane (5:1).—¹H-NMR ($CDCl_3$): $\delta(CH_3) = 1.70$. MS (70 eV): M^+ (42%), $[M-AsS]^+$ (100).—Complexes **2**, **3**, **5**, **6** were prepared analogously [10].
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[8] The structure was determined with a SIEMENS-STOE AED2 diffractometer ($Mo_{K\alpha}$), $2.5 \leq 2\theta \leq 60^\circ$, MULTAN (As, Co) and Fourier methods. $P4_2, 2$ (D_2^2), $a = 8.996(5)$, $c = 29.92(1)$ Å, $V = 2421.4$ Å³, $Z = 4$ (dimer); 1072 reflections, 1055 reflections with $I > 3.0\sigma(I)$; anisotropic refinement, $R_w = 0.05$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD 51759, the names of the authors, and the journal citation.
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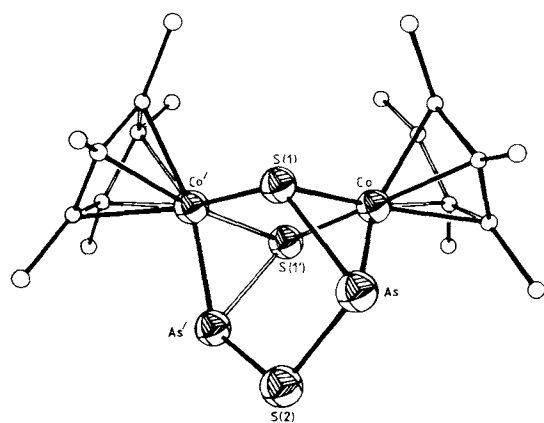


Fig. 1. ORTEP plot of the crystal structure of **8**. Selected bond lengths [Å] and bond angles [°]: Co-S1 2.224(4), Co-As 2.324(3), Co'-S1 2.267(4), As-S1 2.237(4), As-S2 2.226(2); As-Co-S1 58.3(1), S1-Co-S1' 86.3(2), Co-S1'-As' 112.4(1), As-S2-As' 104.8(1), S1-As-S2 103.3(2).

Heterogeneous Catalysis of Ammonia Synthesis at Room Temperature and Atmospheric Pressure

By Ken-ichi Aika*

The artificial fixation of nitrogen at ambient temperature and under atmospheric pressure is one of the most important goals of chemical technology. The first step toward this goal has been achieved: for example, a large number of organometallic dinitrogen complexes have been prepared,^[1] and the dissociative adsorption of N_2 occurs easily on a clean single-crystal surface of Mo ^[2] or Fe ^[3] at about room temperature. However, the catalytic synthesis of ammonia from N_2 and H_2 has not been achieved at am-

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