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 N2 at −78°C and then with 2 equivalents of BF3·OEt2. The stirred reaction mixture was allowed to warm over ca. 16 h to room temperature. After aqueous workup, drying (MgSO4), concentration, and distillation or chromatography, the substitution products shown in Scheme 1 as well as 10-12 were obtained.

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[6] All new compounds isolated gave satisfactory elemental analyses and appropriate spectra.
[7] Characteristic is, for example, the low-field shift of the 1H-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 13C-NMR spectrum (CDCl3, 22.6 MHz): trans-7c: δ = 169.7 (C = O), 117.4 (C = N), 84.6 (s, C = C), 75.9 (d, C = C), 60.8 (d, C = C), 51.5 (s, C = O), 46.4 (s, C = C), 30.8, 25.7, 24.7, 21.7 (4q, 4CH3); cis-7c: δ = 169.3 (C = O), 117.4 (s, C = N), 83.5 (s, C = C), 75.1 (d, C = C), 61.9 (d, C = C), 51.5 (s, C = O), 46.3 (s, C = C), 29.5, 25.5, 23.3, 19.3 (4q, 4CH3). Similar arguments hold also for 6b, 7b, and 8c.
[8] γ-Lactones are most easily prepared by addition of nucleophiles (e.g., hydride from diisobutylaluminum hydride) to γ-lactones.

Complex-Induced Fragmentation of As₄S₄: Stabilization of an As₄S₃ Ligand

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

The system arsenic/sulfur provides a treasure chest of molecules as ligands were lacking, even though they are known in the phosphorus/sulfur system (P₄S₃)₄. During a search for complexes with As₄S₄ cage molecules as ligands, we allowed 1, 4, and 7 to react with As₄S₄. Of the products 2, 3, 5, 6, and 8, complex 8 contains an As₄S₃ ligand, the largest fragment of the As₄S₄ cage reported so far. The complexes 2 (green) and 3 (red-violet) can be prepared by reaction of As₄S₄ with [(C₅H₅)₂Fe₃(CO)₈] 1 in

[*] Prof. Dr. M. L. Ziegler, Dr. B. Nuber
Institut für Anorganische Chemie der Universität
Im Neuenheimer Feld 270, D-6900 Heidelberg (FRG)
boiling toluene. On the other hand, \((\text{C}_2\text{Me}_3)\_2\text{Co}_2(\text{CO})_3\) (Co = Co) 4 reacts with As₄S₄ in toluene (80°C) to form the carbonyl-containing complex 5 and the black-brown cluster 6.

\[
\begin{align*}
\text{[(C}_2\text{Me}_3)_2\text{Fe}_2(\text{CO})_4]} + \text{As}_4\text{S}_4 &\quad \text{toluene} \quad \text{115°C} \\
&\quad 1 \\
\text{[(C}_2\text{Me}_3)_2\text{Fe}_2\text{As}_2\text{S}_2]} + \text{[(C}_2\text{Me}_3)_2\text{Fe}_2\text{S}_2\text{S}_2]} &\quad 2 \\
\text{[(C}_2\text{Me}_3)_2\text{Co}_2(\text{CO})_4]} + \text{As}_4\text{S}_4 &\quad \text{toluene} \quad \text{40°C} \\
&\quad 4 \\
\text{[(C}_2\text{Me}_3)_2(\text{CO})_2\text{Co}_2\text{As}_2\text{S}_2]} + \text{[(C}_2\text{Me}_3)_2\text{Co}_2\text{As}_2\text{S}_4]} &\quad 5 \\
\text{[(C}_2\text{Me}_3)_2\text{Co}(\text{CO})_3]} &\quad \text{THP} \quad \text{ref} \\
&\quad 6 \\
\text{[(C}_2\text{Me}_3)_2\text{Co}_2\text{As}_2\text{S}_2]} &\quad 7 \\
\end{align*}
\]

The photochemical reaction of 1 and 7 with As₄S₄ 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 \([(\text{C}_2\text{Me}_3)_2\text{W}_2(\text{CO})_4](\text{W} = \text{W})\) with As₄S₄ on the other hand, affords solely the already known, exclusively sulfur-containing complexes \([(\text{C}_2\text{Me}_3)_2\text{W}_2(\mu-\text{S})_2\text{S}_2] \text{ and } [(\text{C}_2\text{Me}_3)_2\text{W}_2(\mu-\text{S})_2\text{S}_2] \).[10] Common to 2, 3, and 5 is a side-on bonded As₂ ligand as four-electron donor,[7] which, along with the sulfur ligands required for electron balance, appears to be better suited than mixed As-S ligands for the stabilization of lower metal oxidation states. An X-ray structure analysis of 8[11] revealed that in this complex a novel As₄S₄ ligand is present as a 4e donor with two cis-arranged η²-bonded AsS units that are bridged by an S atom. This results in a “basket” with a C₂ axis through S(2) and the midpoint of the Co₂S₂ square. The structure differs from the sulfur-arsenic chains of the realgar (As₄S₄) and orpiment (As₂S₃). The bond angles at S and As, although slightly expanded, more resemble those in As₄S₄ than in As₄S₄.

The results presented here underline the importance of As₄S₄ 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; 9, 12129-77-0; 8, 102284-26-4; As₄S₄, 12799-90-2.

[5] 8: [C₂Me₅Co(CO)₂]‘7 (530 mg, 2.12 mmol) and As₄S₄ (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 eluted in 15 mL of CH₂Cl₂ and chromatographed on SiO₂ (column: 40 cm x 3 cm). 8 was eluted with toluene as a dark brown band. Re-purification on SI₃₃₄₃-button (1:1) afforded 16% of 8, which was recrystallized from toluene/pentane (1:1:1). — H-NMR (CDCl₃): δ(CH₃)= 1.70, 1.70 M₄ (70 eV); δ(M₄As₄) = 425.9 Nagatsuta, Midori-ku, Yokohama 227 (Japan)

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 the realization of this goal is the development of efficient catalysts for the synthesis of ammonia from nitrogen and hydrogen. However, despite many years of research, the catalytic synthesis of ammonia at ambient temperature and under atmospheric pressure has not been achieved at a...