Organometallics **1997,** *16,* 4954−4955

Influence of Coordinated $Cr(CO)_5$ Groups on the Fragmentation of Realgar: Synthesis and Characterization of the Novel Mixed Zintl Ion Complex $(C_5Me_4Et)Co(\eta^4\text{-}As_6S)$

Henri Brunner, Franz Leis, and Joachim Wachter*

Institut für Anorganische Chemie der Universität Regensburg, D-93040 Regensburg, Germany

Bernhard Nuber

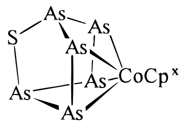
Anorganisch-Chemisches Institut der Universität Heidelberg, D-69120 Heidelberg, Germany

Received July 10, 1997[⊗]

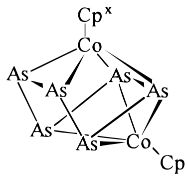
Summary: A complex containing the novel mixed Zintl ion As_6S^{2-} *is obtained from the reaction of* $Cp^x{}_2Co_2(CO)_2$ $(Cp^x = C_5Me_4Et)$ *with* $As_4S_4[Cr(CO)_5]_n$ $(n = 1, 2)$ *in boiling xylene.* Cp^xCoAs_6S (**1**) *is formed along with already known* $Cp^x{}_2Co_2As_6$ (**2**), $Cp^xCo(CO)As_4S_3$ (**3**), *and* $Cp^x{}_2Co_2As_2S_3$ (**4**). *The product distribution and nature of the products show that the* $Cr(CO)_5$ *groups play the role of sulfur-abstracting reagents rather than that of protective groups.*

The bulky $Cr(CO)_5$ fragment is very useful in the stabilization of unusual main group clusters or ring systems, e.g., $[Sn_6\{Cr(CO)_5\}_6]^{2-}$ [1] and $[Te_4\{Cr(CO)_5\}_4]^{2}$ and may, therefore, be regarded as an organometallic protective group. It is also known that the presence of $Cr(CO)_5$ groups may exert considerable influence on the coordination chemistry of white phosphorus.[3] The idea of this concept is to stabilize labile intermediates by addition of a bulky organometallic reagent as a third component to the original reaction mixture. It has not yet been used for mixed cage molecules from group 15/16 elements, e.g., realgar, As_4S_4. The latter exhibits a rich coordination chemistry which is dominated by the fragmentation of the cradle to give a variety of AsS ligands of smaller size, whereas complexation of the intact molecule is restricted to only one example.[4c]

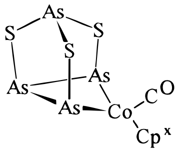
We have observed that the reaction of $Cp^x{}_2Co_2(CO)_2$ $(Cp^x = C_5Me_4Et)$ with a mixture of $As_4S_4[Cr(CO)_5]_n$ (n = 1,2)[5] in boiling toluene or xylene gives complexes of compositions Cp^xCoAs_6S (**1**),[6] $Cp^x{}_2Co_2As_6$ (**2**),[7] $Cp^xCo(CO)As_4S_3$ (**3**),[4c] and $Cp^x{}_2Co_2As_2S_3$ (**4**).[4c] Identification of the known products **2**−**4** occurs by mass spectrometry and comparison of IR and ^1H NMR spectra. Complex **1** was characterized by means of ^1H NMR, analytical methods, and X-ray crystallography.[8] The molecular structure consists of an As_6S norbornadiene-type cage to which a Cp^xCo fragment is coordinated *via* four As atoms (Figure 1). The rectangular As_4 face is formed by two short (2.333(2) Å) and two long (3.07(1) Å) As−As distances. Similar structures have been reported for $[E_7Cr(CO)_3]^{3-}$ (E = P, As, Sb),[9] which are directly derived from $E_7{}^{3-}$ Zintl ions. It is striking that in



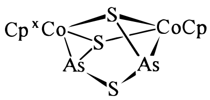
1



2



3



4

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

(1) Schiemenz, B.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 297.

(2) Blacque, O.; Brunner, H.; Kubicki, M. M.; Nuber, B.; Stubenhofer, B.; Wachter, J.; Wrackmeyer, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 352.

(3) Scheer, M.; Herrmann, E.; Sieler, J.; Oehme, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 969. Barr, M. E.; Smith, S. K.; Spencer, B.; Dahl, L. F. *Organometallics* **1991**, *10*, 3983. Scheer, M.; Becker, U.; Huffmann, J. C.; Chisholm, M. H. *J. Organomet. Chem.* **1993**, *461*, C1. Scheer, M.; Becker, U.; Matern, E. *Chem. Ber.* **1996**, *129*, 721.

(4) (a) Di Vaira, M.; Stoppioni, P. *Coord. Chem. Rev.* **1992**, *120*, 259 and cited references. (b) Brunner, H.; Poll, L.; Wachter, J.; Nuber, B. *J. Organomet. Chem.* **1994**, *471*, 117. (c) Brunner, H.; Kauermann, H.; Poll, L.; Nuber, B.; Wachter, J. *Chem. Ber.* **1996**, *129*, 657. (d) Brunner, H.; Nuber, B.; Poll, L.; Roidl, G.; Wachter, J. *Chem. Eur. J.* **1997**, *3*, 57.

(5) $As_4S_4{\cdot}[Cr(CO)_5]_n$ (n = 1, 2) was prepared by stirring a mixture of 100 mg (0.23 mmol) of β-As_4S_4 and of 1 equiv of $Cr(CO)_5THF$ in 200 mL of THF for 18 h at ambient temperature. After evaporation of the solvent, the orange residue was extracted three times with 30 mL each of CH_2Cl_2. The combined extracts were filtered from unreacted realgar and employed for the reaction after evaporation of the solvent. Analytically pure $As_4S_4{\cdot}Cr(CO)_5$ (orange) and $As_4S_4{\cdot}[Cr(CO)_5]_2$ (yellow) may be obtained in a 4:1 ratio by column chromatography on SiO_2 with a considerable loss of material.

(6) The reaction of $Cp^x{}_2Co_2(CO)_2$ with $As_4S_4{\cdot}[Cr(CO)_5]_n$ has been carried out at 115 °C in toluene or at 144 °C in *o*-xylene for 15 h. Equimolar amounts were used with respect to n = 1. Work-up of the reaction mixture was the same in both cases: After evaporation of the solvent, the brown residue was dissolved in toluene and prepurified on SiO_2 (column 15 × 3). The first band was rechromatographed on SiO_2 (column 40 × 3.0). With toluene/pentane (1:1), green-brown Cp^xCoAs_6S (**1**) was eluted first in 25% yield, followed by brown $Cp^x{}_2Co_2As_6$ (**2**; 15%), brown $Cp^xCo(CO)As_4S_3$ (**3**; 14%), and violet $Cp^x{}_2Co_2As_2S_3$ (**4**; 25%). **1** was recrystallized from toluene/pentane. Anal. Calcd for $C_{11}H_{17}As_6CoS$ (**1**): C, 19.15; H, 2.48; mol wt, 689.8. Found: C, 18.75; H, 2.72; mol wt, 689.7 (FD-MS). ^1H NMR $(CDCl_3)$: δ 0.95 (t, 3H, CH_2CH_3), 1.77 (s, 6H), 1.79 (s, 6H, CH_3), 2.34 (q, 2H, CH_2CH_3). The other samples were identified by comparison of their IR, ^1H NMR, and mass spectra with known complexes.

(7) Scherer, O. J.; Pfeiffer, K.; Heckmann, G.; Wolmershäuser, G. *J. Organomet. Chem.* **1992**, *425*, 141.

(8) Crystal data for $C_{11}H_{17}As_6CoS$: space group $P2_1/a$ with a = 11.501(2) Å, b = 12.873(2) Å, c = 12.349(2) Å, β =103.08(1)°, Z = 4, ρ = 2.57 g/cm³. The structure was solved by direct methods (SHELXTL PLUS-Release 4.2/800) using 1813 reflections having $I > 2.5\sigma(I)$ and refined to R = 0.057 and R_w = 0.044.

(9) Eichhorn, B. W.; Haushalter, R. C.; Huffmann, J. C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1032. Charles, S.; Eichhorn, B. W.; Rheingold, A. L.; Bott, S. G. *J. Am. Chem. Soc.* **1994**, *116*, 8077. Bolle, U.; Tremel, W. *J. Chem. Soc., Dalton Trans.* **1994**, 217.

S0276-7333(97)00589-X CCC: $14.00

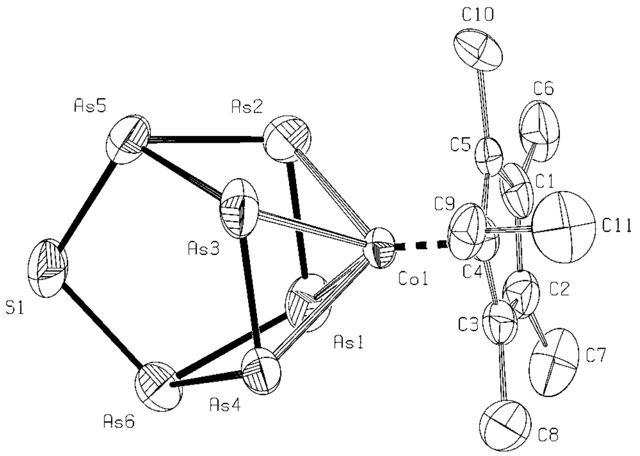
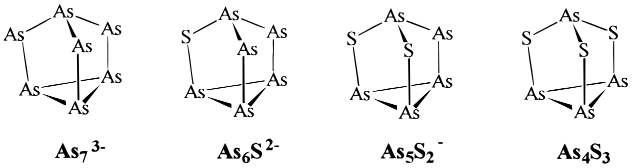


Figure 1. Structure of **1**. Selected bonding and nonbonding distances (Å) and angles (deg): Co(1)−As(1) 2.417(3), Co(1)−As(2) 2.433(3), Co(1)−As(3) 2.430(2), Co(1)−As(4) 2.419(2), As(1)−As(2) 2.331(2), As(3)−As(4) 2.336(2), As(1)−As(6) 2.450(2), As(2)−As(5) 2.454(2), As(5)−S(1) 2.210(5), As(6)−S(1) 2.211(5), As(1)···As(4) 3.040(3), As(2)···As(3) 3.108(3); As(1)−Co(1)−As(2) 57.5(1), As(2)−Co(1)−As(3) 79.5(1), As(2)−As(1)−As(6) 104.4(1), As(1)−As(6)−As(4) 76.6(1), As(5)−S(1)−As(6) 106.1(2).

$[As_7Cr(CO)_3]^{3-}$ and in **1** the As−As bonds being directly coordinated to the metal atom are about 0.12 Å shorter than the four other ones. This indicates at least in part a contribution of a metal clamp effect, which is also evident from a comparison with **3**.[4c] Here, the Cp^xCo fragment is only inserted into the basal As−As bond. Thus, the nonbonding distance As1···As4 in **1** is shorter by 0.21 Å than that in **3**, and As2−As3 is shorter by 0.41 Å than the distance between the corresponding sulfur bridges in **3**.

The influence of the $Cr(CO)_5$ groups on the nature of the products is evident from a comparison of the reaction with that of $Cp^x{}_2Co_2(CO)_2$ with As_4S_4 alone. In boiling xylene, the latter proceeds in a comparatively selective manner to give $Cp^x{}_2Co_2As_2S_3$ and $Cp^x{}_3Co_3As_2S_4$.[4c] Compounds as rich in arsenic as **1** do not form at these or lower temperatures. Interestingly, $Cp^xCo(CO)As_4S_3$ has to be directly synthesized from $Cp^x{}_2Co_2(CO)_2$ and As_4S_3, and the yields are much lower in this reaction. Therefore, the $Cr(CO)_5$ fragment serves as a sulfur-abstracting reagent. The fate of the Cr carbonyl is not known, but one may speculate that as polysulfur species with attached $Cr(CO)_5$ groups have not been observed, they finally end up as binary Cr sulfides.

Chart 1



In conclusion the reaction of $(C_5Me_4Et)_2Co_2(CO)_2$ with $As_4S_4[Cr(CO)_5]_n$ ($n = 1,2$) does not lead to the expected stabilization of labile As/S cage derivatives. Instead, **1** forms which is the first transition metal complex containing a mixed Zintl ion from two different p-block elements as a ligand. On the basis of these findings, a previous structure proposal for $[Cp^xFe(CO)_2]As_5S_2$[10] may be corrected by formal substitution of one As^- in As_6S^{2-} by S. The final substitution product in this series (Chart 1) would be the neutral cage molecule As_4S_3.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft for financial support.

Supporting Information Available: Tables of crystal structure data of **1** and ^1H NMR spectroscopic data of **1**−**4** (7 pages). Ordering information is given on any current masthead page.

OM970589J

---

[10] Brunner, H.; Poll, L.; Wachter, J. *Polyhedron* **1996**, *15*, 573.