6.57 (t, 2H)], underwent the expected[5,6] photoisomerization to cyclobutanedione 7 [UV (methylcyclohexane): $\lambda_{max} = 496$ nm (110); IR (methylcyclohexane : CH_2Cl_2 1 : 1) $\nu_{max} = 1770$, 1795 cm^{-1}] upon irradiation at 404 or 436 nm, with isosbestic behavior in the early stages of the reaction (305, 374 and 482 nm).

Irradiation of 7 in methylcyclohexane at room temperature ($\lambda = 496$ nm) resulted in its conversion into benzene, presumably via the intermediacy of **5**. The quantum efficiency for this reaction is greater than the maximum value observed for formation of **7** from **6**. When the irradiation was performed at −80°C, the spectrum of a new compound was obtained with maxima in the ultraviolet at 294, 282, 271 and 260 nm (sh). The extinction coefficients were of the order of 3000. The new compound is stable indefinitely at −80°C (cf. Fig. 1).

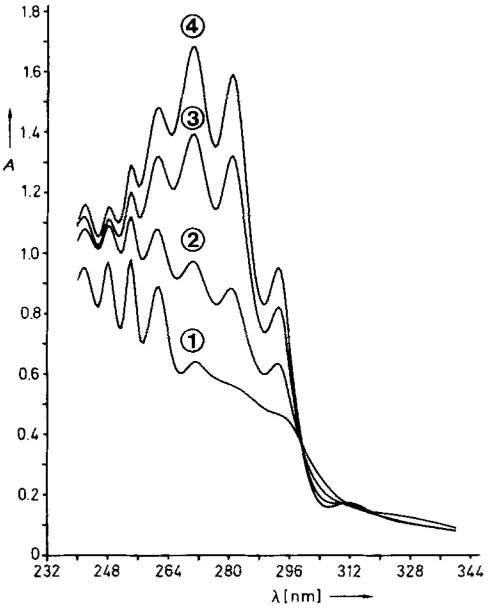

Fig. 1. UV spectroscopic monitoring of the generation of **5** from **7** at −80°C. Spectra after 10 ②, 30 ③, and 60 min ④ irradiation at $\lambda > 380$ nm. ①: Spectrum after warming to −50°C (complete decomposition of **5** to benzene).

The above absorptions are assigned to *o,p'*-dibenzene (**5**), on the following grounds: On the one hand, the spectrum is almost identical to that of the benzene-naphthalene adduct,[7,8] and, on the other, benzene is formed rapidly and quantitatively upon warming. The kinetics of this retro-Diels-Alder reaction were measured by following the disappearance of the maxima mentioned above at five temperatures in the range −68 to −52°C. Good first-order behavior was observed in all cases and identical rate constants were obtained from measurements at different wavelengths at a given temperature. The results obtained fit the Arrhenius expression:

$$\lg k\,[s^{-1}] = (11.78 \pm 0.5) - \frac{(14.7 \pm 0.4)}{2.303\,RT}\,[\text{kcal mol}^{-1}]$$

with $\Delta H^{+} = 14.3$ kcal mol^{-1}, $\Delta S^{+} = -6$ cal mol^{-1} K^{-1}, $\Delta G^{+} = 15.6$ kcal mol^{-1} (errors are double standard deviations). The minimal entropy change observed is consistent with a rigid transition state for this highly exothermic reaction. Comparison of the activation parameters for the thermolysis of **5** with those reported for the thermal decomposition of the formal [4+2] addition products of benzene and naphthalene **8**[7] or anthracene **9**[8] is instructive. The entropies of activation (25°C) for **8** and **9** are −5 and −3 cal mol^{-1} K^{-1}, respectively but the activation energies (19.5 kcal mol^{-1} for **8** and 24.9 kcal mol^{-1} for **9**) differ markedly, reflecting the difference between formation of two molecules of benzene from **5** vis-à-vis one of benzene and one of naphthalene from **8** or one of benzene and one of anthracene from **9**. We also note that the reported[2a] half-life of **2** at 40°C is 5.75 h, while $t_{1/2}$ for **5** is of the order of 5 ms at this temperature. Irradiation of **5** through quartz at −80°C resulted in almost quantitative conversion (>95% by UV spectroscopy) into benzene. In addition, poorly defined bands of low intensity were observed at 355, 379, and 390 nm. Thus, the excited state of **5**, which has, a priori, many reaction paths available to it, proceeds to the same product as the thermal reaction (possibly in a stepwise fashion).

Received: July 30, 1985;
revised: September 23, 1985 [Z 1407 IE]
German version: *Angew. Chem. 97* (1985) 1054

CAS-Registry-numbers:
5, 7322-47-6; 6, 99096-99-8; 7, 99097-00-4; benzene, 71-43-2; barrelene, 500-24-3; *o*-benzoquinone, 583-63-1.

---

[1] D. Bryce-Smith, *Chem. Commun. 1969*, 806; R. Engelke, P. J. Hay, D. A. Kleier, W. E. Wadt, *J. Am. Chem. Soc. 106* (1984) 5439.

[2] a) H. Röttele, W. Martin, J. Oth, G. Schröder, *Chem. Ber. 102* (1969) 3985; J. A. Berson, R. F. Davis, *J. Am. Chem. Soc. 94* (1972) 3658; b) H. D. Martin, P. Pföhler, *Angew. Chem. 90* (1978) 901; *Angew. Chem. Int. Ed. Engl. 17* (1978) 847.

[3] W. Grimme, E. Schneider, *Angew. Chem. 89* (1977) 754; *Angew. Chem. Int. Ed. Engl. 16* (1977) 717.

[4] R. Braun, *Diplomarbeit*, Universität Düsseldorf 1982. R. Braun, H. D. Martin, in preparation.

[5] M. B. Rubin, M. Weiner, H. D. Scharf, *J. Am. Chem. Soc. 98* (1976) 5699; M. B. Rubin, *Topics Curr. Chem. 129* (1985) 1.

[6] Quantum yields for this reaction exhibited wavelength, concentration, temperature, and solvent dependence (cf. M. B. Rubin in *Xth IUPAC Symposium on Photochemistry* (Interlaken, July, 1984), Presses Polytechniques Romandes, Lausanne 1984, p. 173. Optimal yields of **7** were obtained by irradiation of ca. 0.001 M solutions in methylcyclohexane at 50°C and 436 nm.

[7] W. Grimme, H. G. Köser, *Angew. Chem. 92* (1980) 307; *Angew. Chem. Int. Ed. Engl. 19* (1980) 307.

[8] N. C. Yang, M. J. Chen, P. Chen, *J. Am. Chem. Soc. 106* (1984) 7310.

$[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4]$ and $[(\eta^5\text{-}C_5Me_5)_2Co_2S_4]$, Two Novel Bis(pentamethylcyclopentadienylmetal) Complexes Rich in Sulfur

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

The electronic and structural properties of $[Cp_2M_2S_4]$ complexes (Cp: C_5H_5, MeC_5H_4 or C_5Me_5) depend, like their reactivity, upon the transition metal M. Each of the elements V,[1] Cr, Mo, W,[2] and Fe[3] can be assigned to a particular structural type. So far, nothing has been reported about a corresponding Co compound.

The complex $[C_5Me_5(CO)Co]_2$, containing a Co=Co bond, reacts with sulfur in toluene at room temperature with formation of the green complex **1** in 23-39% yield.[4]

$$[C_5Me_5(CO)Co]_2 + 1/2\,S_8 \xrightarrow[20^\circ C]{\text{toluene}} [(C_5Me_5)_2Co_2S_4] \quad \mathbf{1}$$

---

[*] Dr. J. Wachter, Prof. Dr. H. Brunner, N. Janietz, W. Meier
Institut für Anorganische Chemie der Universität
Universitätsstrasse 31, D-8400 Regensburg (FRG)

G. Sergeson, Dipl.-Chem. T. Zahn, Prof. Dr. M. L. Ziegler
Anorganisch-chemisches Institut der Universität
Im Neuenheimer Feld 270, D-6900 Heidelberg (FRG)

Elemental analyses and mass spectrum (dominating ions in the 70 eV spectrum: M^+, $[M-S]^+$, $[M-S_2]^+$) support this formulation. Compound **1**, which according to its ^{1}H-NMR spectrum ($\delta(CH_3) = 1.62$, in $CDCl_3$) is symmetrical and is configurationally stable in solution, at least at room temperature. An IR absorption at 502 cm^{-1} is characteristic for disulfide ligands, whose multiple coordination possibilities have already been described in detail.[5] According to an X-ray structure analysis,[6] **1** has a center of inversion, the two Co atoms are bridged by two disulfide ligands (Fig. 1). These η^1,η^2-S_2 ligands are indeed primarily known as bridging elements,[5] but not in this step-like (*anti*-) arrangement of two such moieties. A relatively large Co-Co distance (3.38 Å) supports the assumption that the Co atoms achieve noble gas configuration without the necessity of Co-Co bonding. Hence, **1** represents a novel type of structure within the $[Cp_2M_2S_4]$-class of compounds.

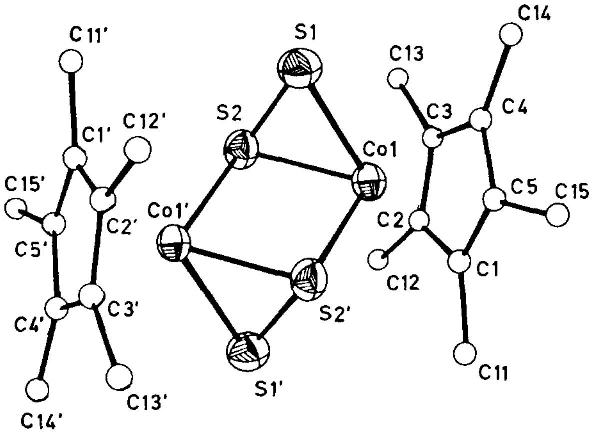

Fig. 1. Molecular structure of **1** (ORTEP plot). Selected bond lengths [Å] and angles [°] Co1-S1 2.247(4), Co1-S2 2.245(4), Co1-S2' 2.244(4), S1-S2 2.062(6), Co1···Co1' 3.38; S1-Co1-S2 54.7(2), S2-Co1-S2' 83.1(2), Co1'-S2-Co1 96.9(1), Co1'-S2-S1 102.6(2).

Common to all compounds of this type is that their structures can only be elucidated with the aid of an X-ray structure analysis. Thus, the synthesis of two isomers of the composition $[(C_5H_5)_2Fe_2S_4]$, which are formed in moderate yields upon photolysis of $[C_5H_5(CO)_2Fe]_2$ with S_8 has recently been reported.[3] We have now found a high-yield synthesis of the permethylated derivative **2** by reaction of $[C_5Me_5(CO)_2Fe]_2$ with an excess of sulfur in boiling toluene.[7]

$$[C_5Me_5(CO)_2Fe]_2 + 1/2\,S_8 \xrightarrow[115^\circ C]{\text{toluene}} [(C_5Me_5)_2Fe_2S_4] \quad \mathbf{2}$$

2 is formed as the sole isomer in 55-78% yield. Extension of this method to $[C_5H_5(CO)_2Fe]_2$, however, leads to formation of $[(C_5H_5)_4Fe_4S_4]$.[8] Owing to a lack of unequivocal IR spectroscopic data for comparison, an X-ray structure analysis also had to be carried out on **2**.[6] Complex **2** contains two disulfide ligands oriented perpendicularly to each other (Fig. 2). The bond lengths and bond angles are essentially in accord with those in $[(C_5H_5)_2Fe_2(\eta^1$-$S_2)(\eta^2$-$S_2)]$.[3] The influence of the pentamethylcyclopentadienyl moiety manifests itself in only a slight extension (0.01-0.03 Å) of the Fe-Fe, Fe-S, and S-S distances. Interestingly, in the two complexes **1** and **2**, both of which contain no direct metal-metal bond, the methyl residues of the two C_5Me_5 rings are staggered, whereas in $[(C_5Me_5)_2Mo_2S_4]$ they are eclipsed.[2c]

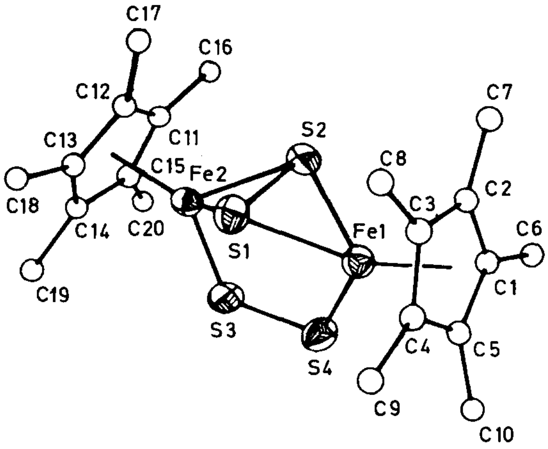

Fig. 2. Molecular structure of **2** (ORTEP plot). Selected bond lengths [Å] and angles [°]: Fe1-S1 2.282(1), Fe1-S2 2.273(1), Fe1-S4 2.129(1), Fe2-S1 2.269(1), Fe2-S2 2.268(2), Fe2-S3 2.122(2), S1-S2 2.055(2), S3-S4 2.021(2), Fe1···Fe2 3.53; S1-Fe1-S2 53.6(0), S1-Fe2-S2 53.9(0), Fe1-S1-Fe2 101.6(1), Fe1-S2-Fe2 101.9(1), Fe2-S3-S4 110.7(1), Fe1-S4-S3 110.8(1).

A comparison of **1** and **2** strikingly reveals the same overall contribution of eight valence electrons by the sulfur ligands in both cases. Nevertheless, the difference in the ligand combinations, as is also reflected in compounds of the 5th and 6th subgroups,[1,2] is impressive, and should also be observable in other systems.

Received: August 1, 1985 [Z 1409 IE]
German version: *Angew. Chem. 97* (1985) 1056

---

[1] C. M. Bolinger, T. B. Rauchfuss, A. L. Rheingold, *J. Am. Chem. Soc. 105* (1983) 6321.

[2] a) H. Brunner, H. Kauermann, W. Meier, J. Wachter, *J. Organomet. Chem. 263* (1984) 183; b) M. Rakowski DuBois, D. L. DuBois, M. C. Van DerVeer, R. C. Haltiwanger, *Inorg. Chem. 20* (1981) 3064; W. Danzer, W.-P. Fehlhammer, A. T. Liu, G. Thiel, W. Beck, *Chem. Ber. 115* (1982) 1683; c) H. Brunner, E. Guggolz, W. Meier, J. Wachter, T. Zahn, M. L. Ziegler, *Organometallics 1* (1982) 1107.

[3] H. Chanaud, A. M. Ducourant, C. Giannotti, *J. Organomet. Chem. 190* (1980) 201; R. Weberg, R. C. Haltiwanger, M. Rakowski DuBois, *Organometallics 4* (1985) 1315.

[4] A solution of $[C_5Me_5(CO)Co)]_2$ (333 mg, 0.75 mmol) in toluene (100 mL) was treated with S_8 (98 mg, 0.38 mmol) and stirred for 90 min at room temperature. The dark green mixture was filtered over Al_2O_3, and the filtrate concentrated to 15 mL and chromatographed on Al_2O_3 (Activity II-III). The green complex **1** was eluted with toluene. The complex could be recrystallized from toluene.

[5] A. Müller, W. Jaegermann, J. E. Enemark, *Coord. Chem. Rev. 46* (1982) 245.

[6] **1**: $P2_1/n$, $a = 8.112(9)$, $b = 14.236(11)$, $c = 10.301(9)$ Å, $\beta = 110.71(7)^\circ$, $V = 1112.70$ Å^3, $Z = 2$. Stoe-Siemens diffractometer ($Mo_{K\alpha}$) $3^\circ \leqslant 2\theta \leqslant 30^\circ$, 739 measured reflections with $I > 3.0\sigma(I)$, Patterson (Co, S) and Fourier methods, anisotropic refinement to $R_w = 0.045$. **2**: $P2_1/a$, $a = 14.980(6)$, $b = 10.496(5)$, $c = 15.315(5)$ Å, $\beta = 109.36(3)^\circ$, $V = 2271.82$ Å^3, $Z = 4$, Siemens diffractometer ($Mo_{K\alpha}$) $3^\circ < 2\theta < 60^\circ$, 3374 observed reflections with $I > 2.5\sigma(I)$, Patterson (Fe, S) and Fourier methods, anisotropic refinement to $R_w = 0.035$. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen2, on quoting the depository number CSD-51547, the names of the authors, and the full citation of the journal.

[7] $[C_5Me_5(CO)_2Fe]_2$ (600 mg, 1.20 mmol) was allowed to react with S_8 (380 mg, 1.50 mmol) for 20 h in boiling toluene (100 mL). Chromatography on SiO_2 (eluent toluene) gave brown $[(C_5Me_5)_2Fe_2S_4]$. The complex could be recrystallized from CH_2Cl_2/Et_2O (1 : 1).—IR (KBr, [cm^{-1}]): $\nu(S-S) = 520$. ^{1}H NMR ($CDCl_3$): $\delta(CH_3) = 1.70$.

[8] R. A. Schunn, C. J. Fritchie, C. T. Prewitt, *Inorg. Chem. 5* (1966) 892.