Synthesis and Structure of the First Dimetalated Diphosphane Disulfide $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP(H)(S)]_2$

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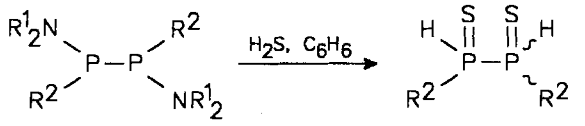
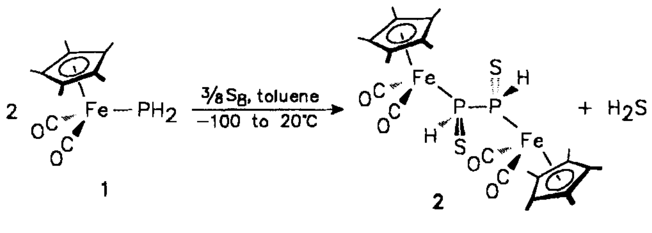
The first transition metal derivative *meso*-$[(\eta^5\text{-}C_5Me_5)(CO)_2\text{-}FeP(H)(S)]_2$ (**2**) of the unknown diphosphane disulfide $[PH_2(S)]_2$ results from treatment of $(\eta^5\text{-}C_5Me_5)(CO)_2FePH_2$ (**1**) with 1.5 equivalents of elemental sulfur. Compound **2** was characterized by means of spectroscopy (IR, ^{31}P, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^1H NMR) as well as X-ray diffraction analysis.

In contrast to the parent compound $H_2(S)P-P(S)H_2$, tetraorganodiphosphane disulfides are easily available by a number of synthetic routes including the oxidation of the corresponding diphosphanes with elemental sulfur[1-3] or the treatment of thiophosphoric trichloride or alkyl thiophosphonic halides with Grignard reagents[3-6]. There is only one report in the patent literature, that is focused on the synthesis of disecondary diphosphane disulfides[7]. They were prepared by reaction of $R^1_2N(R^2)P-P(R^2)NR^1_2$ with an excess of H_2S, where R^2 = alkyl, aralkyl, cycloalkyl, or aryl.



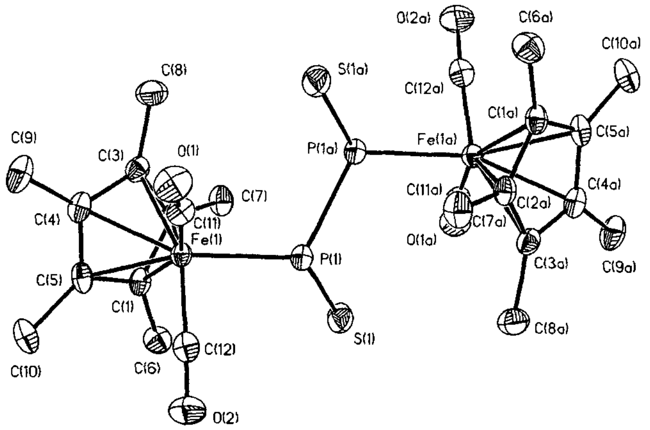
During the course of our studies on the chemical behavior of metallophosphanes complex **1**[8] was allowed to react with 3/8 equivalents of S_8 in the temperature range of −100 to 20°C. The chalcogene dissolved at about 0°C with effervescense of H_2S, whereupon the color of the solution turned to deep red. Deep red microcrystalline **2** was isolated in 61% by crystallization.



According to the $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture, which is dominated by a singlet at $\delta = -3.50$ for compound *meso*-**2**, the formation of other products, e.g. the (*R,R*) or (*S,S*) diastereoisomers, can be excluded. The ^1H-coupled spectrum features a 1:2:1 triplet at $\delta = -3.50$ with $J_{P,H} = 363.9$ Hz. Obviously, the ^{31}P nucleus experiences two magnetically equivalent ^1H atoms. In the ^1H-NMR spectrum a doublet at $\delta = 6.72$ ($^1J_{P,H} = 363.8$ Hz) is attributed to the hydrogen atoms at phosphorus. The presence of integral $(\eta^5\text{-}C_5Me_5)(CO)_2Fe$ building blocks is manifested by a singlet for the C_5Me_5 ring protons at $\delta = 1.32$ and singlets at $\delta = 8.7$ and 97.4 for the ring carbon atoms, respectively. The two intense bands of the carbonyl stretching modes in the IR spectrum of **2** ($\tilde{\nu}$ = 2016, 1966 cm^{-1}) are markedly shifted in comparison with the starting material ($\tilde{\nu}$ = 1987, 1936 cm^{-1})[8].

The molecular structure of *meso*-**2** was established by an X-ray diffraction study. The molecule is best described as a diphosphane 1,2-disulfide which is functionalized at each phosphorus atom by an $(\eta^5\text{-}C_5Me_5)(CO)_2Fe$ group via Fe−P single bonds of 2.2647(11) Å. Usually, Fe−P distances in low-valent carbonyliron complexes range from 2.12−2.39 Å[9]. A P−P distance of 2.234(2) Å is consistent with a single bond[10]. The PS double bond length in **2** was determined to be 1.9899(13) Å which is at the upper end of such distances found in a number of phosphane sulfides (1.87−1.97 Å[11]).

Figure 1. ORTEP-type representation of the molecular structure of **2** in the crystal. Thermal ellipsoids are represented on a 50% probability level. Selected bond lengths [Å]: Fe−P 2.2647(11), P1−S1 1.9899(13), P−P 2.234(2), P−H 1.37(4), Fe−C11 1.773(3), Fe−C12 1.763(3), Fe−C_{Ring} = 2.112(3)−2.155(3). − Selected bond angles [°]: Fe−P−S 118.63, Fe−P−P 114.69(5), P−P−S 110.65(6), P−Fe−C11 93.72(10), P−Fe−C12 86.38(10), C11−Fe−C12 95.79(13), P−P−H1 92(2), Fe−P−H1 109(2), S−P−H1 109.(2)



The severe distortions of the P tetrahedra are evident by bond angles varying fom 92° (P−P−H) to 118.63° (Fe−P=S). The atoms Fe1−P1−P1a−Fe1a are located in the same plane (torsion angle = 180°), whereas the torsion angle Fe1−P1−P1a−S1a amounts to

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42.5°. To the best of our knowledge **2** is the first dinuclear transition metal complex with a bridging diphosphanyl disulfide ligand.

Experimental

All manipulations were performed under dry N_2. Solvents were rigorously dried with an appropriate drying agent and distilled before use. Complex **1** was prepared as described[8]. – IR: Mattson Polaris (FT-IR)/Atari 1040 STF. – ^1H, ^{31}P, ^{13}C NMR: Bruker AC 100 (^1H, 100.131; ^{13}C, 25.180; ^{31}P, 40.539 MHz) and Bruker AM 300 (100; ^1H, 300.1; ^{13}C, 75.5; ^{31}P, 121.7 MHz). Standards: $SiMe_4$ (^1H, ^{13}C), 85% H_3PO_4 (^{31}P).

1,2-Bis[dicarbonyl(pentamethylcyclopentadienyl)ferrio]diphosphane 1,2-Disulfide (**2**): A solution of 0.44 g (1.57 mmol) of (η^5-C_5Me_5)$(CO)_2FePH_2$ (**1**) in 2.5 ml of toluene was rapidly cooled to −100°C before the addition of 0.076 g (2.36 mmol) of elemental sulfur. The well stirred mixture was allowed to warm to ambient temp. At about 0°C the color of the mixture changed to deep red. All of the sulfur dissolved, and evolution of H_2S was observed. When the H_2S evolution had ceased, the solution was stored at −30°C for 24 h. A red microcrystalline precipitate of **2** was filtered and dried in vacuo. Yield: 0.34 g (61%), m.p. 120°C. – IR (cm^{-1}, C_6D_6): $\tilde{\nu} = 2016, 1966$ (C≡O). – ^1H NMR (C_6D_6): $\delta = 1.32$ (s, 30H, C_5Me_5), 6.72 [d, $^1J_{(P,H)} = 363.8$ Hz, 2H, PH). – $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 8.7$ [s, $C_5(CH_3)_5$], 97.4 [s, $C_5(CH_3)_5$], 213.2 (s, CO), 213.5 (s, CO). – ^{31}P NMR (C_6D_6): $\delta = -3.50$ ["t", $^1J_{(P,H)} = {}^2J_{(P,H)} = 363.9$ Hz]. – $C_{24}H_{32}Fe_2O_4P_2S_2$ (622.3): calcd. C 46.32, H 5.18; found C 46.40, H 5.33.

X-Ray Analysis of **2** · 2 C_7H_8[12]: Single crystal from toluene; 0.5 × 0.4 × 0.3 mm; Siemens P2(1) diffractometer; Mo-K_α (graphite monochromator, $\lambda = 0.71073$ Å), empirical formula $C_{24}H_{32}Fe_2O_4P_2S_2 \times 2\ C_7H_8$, space group $P\bar{1}$; unit cell dimensions: $a = 7.541(2)$, $b = 10.408(4)$, $c = 13.185(4)$ Å; $\alpha = 75.23(3)$, $\beta = 75.89(2)$, $\gamma = 83.38(3)°$; $d_{calcd.} = 1.382$ g cm^{-3}, $V = 968.9(5)$ Å^3, $Z = 1$; μ(Mo-K_α) = 0.976 mm^{-1}; range for data collection $2\Theta_{max} = 55°$; ω scan; index ranges: $0 \leq h \leq 9$, $-13 \leq k \leq 13$, $-16 \leq l \leq 17$; reflections collected 4809; independant reflections 4473; parammeters 227; no absorption correction. Structure solution: direct methods, structure refinement: Full-matrix least-squares on F^2, $R_F = 0.0443$, $wR_F^2 = 0.0992$ based on 3350 reflexions with $I > 2\sigma(I)$, with $w = 1/[\sigma^2(F_o^2) + (0.0555P)^2]$ where $P = (F_o^2 + 2\ F_c^2)/3$.

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[12] Additional details on the crystal structure determination are deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, and may be reguested by quoting the depository number CSD-58906, the names of the authors, and the literature citation.

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