Triferriothioxophosphoranes: First Structural Characterization of a μ_3-P=S Complex☆

Ingo-Peter Lorenz*, Wolfgang Pohl, and Kurt Polborn

Institute of Inorganic Chemistry, University of Munich,
Meiserstraße 1, D-80333 München, Germany
Telefax: (internat.) +49(0)89/5902258

Received August 11, 1995

Key Words: Triferriophosphane sulfide / Metallothioxophosphorane / PS complex / Spiro compounds / Decarbonylation

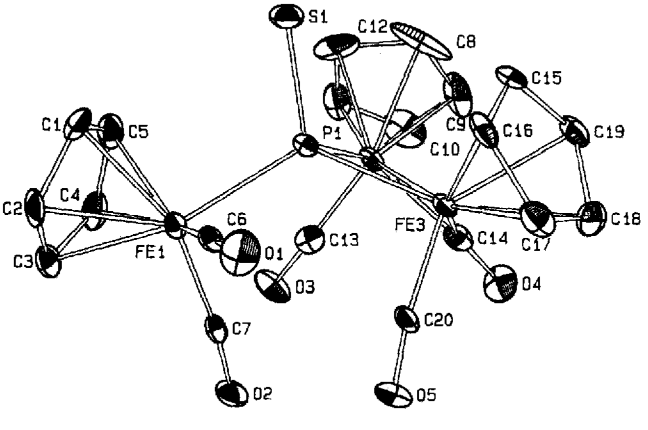
The P-H-functional triferriophosphonium salts $[\{CpFe(CO)_2\}_3PH]_2FeCl_4$ (**1**) and $[\{\mu\text{-}CO(CpFeCO)_2\}\{CpFe(CO)_2\}PH]_2FeCl_4$ (**4**) are easily deprotonated by DBU to the corresponding unstable triferriophosphanes **2**, **5**, which subsequently are oxidized by sulfur to the triferriophosphane sulfides $\{CpFe(CO)_2\}_3P{=}S$ (**3**) and $\{\mu\text{-}CO(CpFeCO)_2\}\{CpFe(CO)_2\}P{=}S$ (**6**), respectively. The photolysis of **3** results only in its decomposition by elimination of $[CpFe(CO)_2]_2$, whereas the photolysis of **6** cleaves off one CO ligand to give the new spiro compound $(CpFeCO)(\mu\text{-}\eta^2\text{-}PS)\{\mu\text{-}CO(CpFeCO)_2\}$ (**7**), where the P=S unit is η^2-bonded to the 15-electron CpFeCO fragment, and the phosphorus atom bridges two 17-electron fragments. Compound **7** shows a new coordination mode of the PS unit where sulfur is also bound to one of the metal atoms. Compounds **6** and **7** can be regarded as first examples of a new class of PS complexes of transition metals. All compounds were characterized by IR, $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR spectroscopy as well as mass spectrometry; for **6** the X-ray analytical data are given.

Although the coordination chemistry of the ligands NO[1] and NS[2] is well-known, the homologous diatomic molecules PO and PS as complex ligands are quite unexplored. In the literature only two examples of μ_3-PO complexes were hitherto reported[3]. One complex was prepared by Scherer et al. by oxidation of a P_2 complex with $(Me_3SiO)_2$ giving $[(\eta^5\text{-}Cp^4)_2Ni_2W(CO)_4(\mu_3\text{-}PO)_2]$ ($Cp^4 = C_5H\textit{i}Pr_4$)[3a]. The other route for obtaining also a μ_3-PO complex is the hydrolysis of a μ_3-$PN\textit{i}Pr_2$ complex with H_2O to give the *closo*-$[Ru_4(CO)_{12}(\mu_3\text{-}P{=}O)][\textit{i}Pr_2NH_2]$ salt[3c]. In conformity with the isolobal analogy both compounds can also be described as trimetallophosphane oxides. Analogously, the few known, but not well characterized PS complexes can also be regarded as trimetallophosphane sulfides[4]. The first one was prepared from $Na[Co(CO)_4]$ and $SPCl_3$ to give the tetrahedral cluster $Co_3(CO)_9(\mu_3\text{-}PS)$ and was identified only by IR spectroscopic data[4a]. The trimetallothioxophosphorane $\{CpMo(CO)_3\}_3P{=}S$ without a metal-metal bond was postulated by Rehder et al.[4b]. We now report on three new "PS" complexes and the X-ray structural analysis of the first new "closed" trimetallothioxophosphorane having one metal-metal bond and one CO bridge.

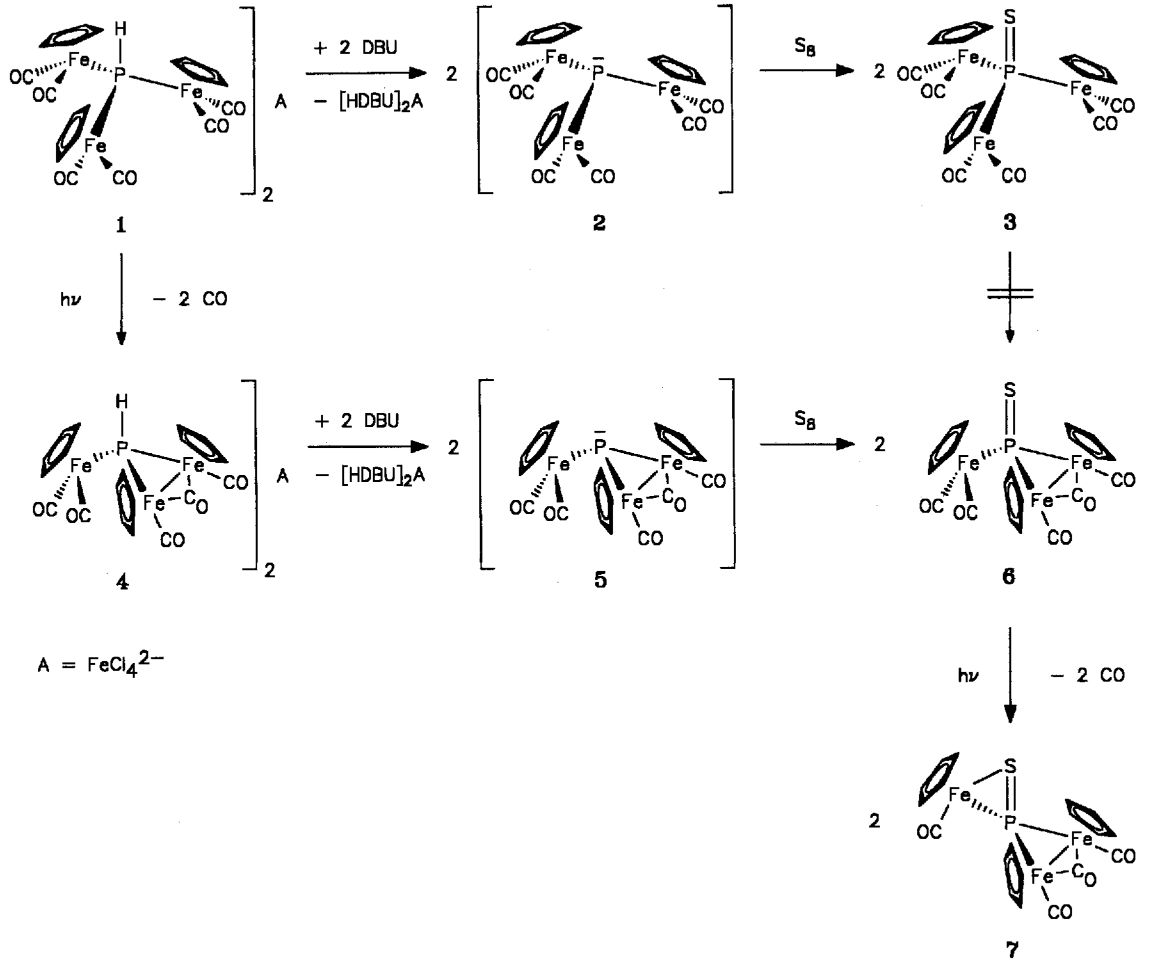
Results and Discussion

Our starting material for the synthesis of the triferriothioxophosphoranes was the triferriophosphonium salt $[\{CpFe(CO)_2\}_3PH]_2FeCl_4$ (**1**)[5] which we recently characterized by X-ray structural analysis[6]. It is easily deprotonated by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to the triferriophosphane $\{CpFe(CO)_2\}_3P$ (**2**)[6] which is subsequently oxidized by sulfur to the corresponding triferriophosphane sulfide $\{CpFe(CO)_2\}_3P{=}S$ (**3**). This compound is very unstable so that we could only obtain NMR- and IR-spectroscopic data. Once isolated at low temperature decomposition takes place within several hours. It is an example of a so-called *open* trimetallophosphane sulfide without a metal-metal bond. The P=S system in compound **3** should be more stable if the molecule contained one or more metal-metal bonds. That is why we used the partially *closed* triferriophosphonium salt $[\{CpFe(CO)_2\}\{\mu\text{-}CO(CpFeCO)_2\}PH]_2FeCl_4$ (**4**) – available by photoinduced decarbonylation of **1** – with one Fe–Fe bond and a bridging CO group as a new starting compound. The reaction of **4** with DBU in THF gives the intermediate *closed* triferriophosphane $\{CpFe(CO)_2\}\{\mu\text{-}CO(CpFeCO)_2\}P$ (**5**)[6], which – analogously to the *open* compound **2** – can easily be sulfurized to the corresponding triferriophosphane sulfide $\{CpFe(CO)_2\}\{\mu\text{-}CO(CpFeCO)_2\}P{=}S$ (**6**). Sulfide **6** is much more stable than **3**, and we could get single crystals by recrystallization of **6** from a solution in CH_2Cl_2/pentane (1:1) at −30 °C. The result of the X-ray structural analysis is shown in Figure 1.

Figure 1. The molecular structure of $\{CpFe(CO)_2\}\{\mu\text{-}CO(CpFeCO)_2\}P{=}S$ (**6**). – Selected bond lengths [Å] and angles [°]: Fe1–P1 2.316(4), Fe2–P1 2.265(4), Fe3–P1 2.274(3), Fe2–Fe3 2.606(2), S1–P1 2.008(5), Fe2–C14 1.91(1), Fe3–C14 1.93(2); Fe1–P1–Fe2 122.2(2), Fe1–P1–Fe3 121.7(1), Fe2–P1–Fe3 70.1(1), P1–Fe2–Fe3 55.12(9), P1–Fe3–Fe2 54.8(1), Fe1–P1–S1 106.5(2), Fe2–P1–S1 117.1(2), Fe3–P1–S1 116.2(2), Fe2–C14–Fe3 85.4(5)



0009–2940/96/0101–0011 $ 10.00+.25/0



The P=S bond length in **6** was determined to be 2.008(5) Å which is in the range of a double bond. The structure of **6** can be compared with that of **4**[6]. The Fe−P distances range from 2.265(4) to 2.316(4) Å which are a bit longer than those found in **4** (2.213−2.241 Å). With 2.606(2) Å the Fe2−Fe3 distances in **4** and **6** are exactly the same. The $^{31}P\{^1H\}$-NMR spectrum of **6** shows a signal at $\delta = 439.9$ which is markedly shifted downfield in comparison with those of the starting material **4** ($\delta = 266.2$[6]) and the *open* compound **3** ($\delta = 174.3$). The cyclopentadienyl groups give rise to two signals in the ^1H-NMR and $^{13}C\{^1H\}$-NMR spectra in the expected ratio of 1:2 at $\delta = 5.10$, 4.83 and 90.2, 92.7.

Photolysis of **6** induces a further decarbonylation reaction to give **7**. There is, however, no evidence for the formation of a second CO bridge and a second Fe−Fe bond. The spectroscopic data of **7** indicate that a new spiro compound being not very stable formed. During the photolysis the absorptions of the two carbonyl stretching modes at 2024 and 1985 cm^{-1} in the IR spectrum are shifted to 1998 and 1966 cm^{-1}, whereas the band of the μ_2-CO group at 1780 cm^{-1} is shifted to 1794 cm^{-1}. The first indication of the formation of the Fe−P−S triangle is the new ν(CO) band at the very low frequency of 1915 cm^{-1}. We earlier reported on an analogous photolytically induced CO elimination reaction of the differrio compound $\{CpFe(CO)_2\}_2PPh(S)$ where $\{CpFe(CO)_2\}$-$\{CpFeCO\}(Ph)P{=}S$ with an Fe−P−S triangle formed; the latter shows the same characteristic low ν(CO) absorption at 1908 cm^{-1} in its IR spectrum[7]. Another interesting fact is that the three cyclopentadienyl groups give rise to three signals in both the ^1H- and $^{13}C\{^1H\}$-NMR spectra of **7**. So **7** cannot be symmetrical as it should be in the case of a second Fe−Fe bond and CO bridge.

Compound **7** is the first example of a P=S complex where the P=S unit is coordinated only to metals and acts as a bridging 2-electron donor to the $\{\mu\text{-CO(CpFeCO)}_2\}$ unit and as a η^2-bonded 3-electron donor to the 15-VE metal-complex fragment CpFeCO.

The first example of a complex with a *terminal* PS ligand was published after this paper has been submitted: $Mo(PS)(NRAr)_3$ [$R = C(CD_3)CH_3$; $Ar = 3,5\text{-}C_6H_3Me_2$][9]

Experimental

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR: Jeol GSX 270 or Jeol EX 400, internal standard TMS or 85% H_3PO_4 for ^1H and ^{13}C or ^{31}P in $CDCl_3$. − IR: Nicolet 520 FT-IR. − All reactions were performed under dry Ar. Compounds **1** and **2** as well as **4** and **5** were synthesized as described in ref.[6].

Tris[dicarbonyl-(η⁵-cyclopentadienyl)ferrio]thioxophosphorane (**3**): To a suspension of 0.35 g (0.27 mmol) of **1** in 3 ml of THF was added at −20 °C 0.09 ml (0.54 mmol) of DBU, whereby a dark brown solution of the triferriophosphane **2** formed. Then 17 mg (0.54 mmol) of sulfur was added, and after stirring for 1 h the mixture was concentrated, and the residue was dissolved in 10 ml of CH_2Cl_2. After addition of 10 ml of pentane to the solution all impurities were collected in an oily phase and separated. From the solution pure **3** was isolated at −20 °C as a dark brown solid by concentration of the solution. Since **3** decomposes at about −10 °C a melting point and elemental analyses could not be obtained. Yield 0.20 g (62%). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2032 (s) cm^{-1}, 2013 (s), 1982 (s) (CO). − ^1H NMR (−20°C): δ = 5.07 (s, Cp). − ^{13}C NMR (−20°C): δ = 212 (CO), 89.7 (Cp). − ^{31}P NMR (−20°C): δ = 174.3. − $C_{21}H_{15}Fe_3O_6PS$ (593.9): EI-MS, *m/z*: 354 [[CpFe(CO)$_2$]$_2$], 240 [CpFeCO(PS)].

{μ-Carbonyl-bis[carbonyl-(η^5-cyclopentadienyl)ferrio]}-[dicarbonyl(η^5-cyclopentadienyl)ferrio]thioxophosphorane (**6**): To a suspension of 0.31 g (0.25 mmol) of **4** in 3 ml of THF at −20°C 0.075 ml (0.50 mmol) of DBU was added, whereby a dark brown solution of the intermediate triferriophosphane **5** formed. Then 16 mg (0.50 mmol) of sulfur was added, and after stirring for 1 h the mixture was concentrated and the residue dissolved in 10 ml of CH_2Cl_2. After addition of 10 ml of pentane the solution was filtered, and the filtrate was concentrated to give **6** as a black solid. Recrystallization from CH_2Cl_2/pentane (1:1) at −30°C afforded single crystals. Yield 0.23 (83%), m.p. 128°C (dec.). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2024 (s) cm^{-1}, 1985 (s), 1960 (m), 1780 (m) (CO), 749 (w, PS). − ^1H NMR: δ = 5.10 (s, Cp, 5H), 4.83 (s, Cp, 10H). − ^{13}C NMR (−20°C): δ = 213.3 [d, ^2J(PC) = 20 Hz, CO], 211.5 [d, ^2J(PC) = 10 Hz, CO], 92.7 (Cp, 10 C), 90.2 (Cp, 5 C). − ^{31}P NMR: δ = 439.9. − $C_{20}H_{15}Fe_3O_5PS$ (565.9): calcd. C 42.45, H 2.67, S 5.67; found C 42.10, H 2.56, S 6.21. − EI-MS, *m/z*: 566 [M^+].

{μ-Carbonyl-bis[carbonyl-(η^5-cyclopentadienyl)ferrio]}-[carbonyl(η^5-cyclopentadienyl)ferrio]thioxophosphorane (**7**): A solution of 0.20 g (0.35 mmol) of **6** in 30 ml of CH_2Cl_2 was irradiated with a 150-W Hg high-pressure lamp (Original Quarzlampen GmbH, Hanau) for 45 min under continuous IR control. After filtration the solution was concentrated to give **7** as a black solid. Yield: 0.17 g (90%), m.p. 98°C (dec.). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1998 (s) cm^{-1}, 1966 (m), 1915 (m), 1794 (m) (CO). − ^1H NMR: δ = 4.81 (s, Cp, 5H), 4.69 (s, Cp, 5H), 4.68 (s, Cp, 5H). − ^{13}C NMR (−20°C): δ = 89.9, 89.4, 80.3 (Cp). − ^{31}P NMR: δ = 468.0. − $C_{19}H_{15}Fe_3O_4PS$ (537.9): FAB-MS, *m/z* (%): 538 (10) [M^+], 510 (32) [M^+ − CO], 454 (12) [M^+ − 3 CO], 426 (100) [M^+ − 4 CO].

X-Ray Structure Determination of **6**[8]: Diffractometer: Enraf-Nonius CAD4 (Mo-K_α, λ = 0.71073 Å). − Formula $C_{20}H_{15}Fe_3O_5PS$, M_r = 565.91, black single crystal, size 0.16 × 0.20 × 0.37 mm, monoclinic, a = 1525.3(6), b = 911.4(3), c = 1561.0(6) pm, β = 109.89(3)°, V = 2.0405 nm^3, Z = 4, space group $P2_1/c$, d(calcd.) = 1.842 g cm^{-3}, μ = 23.114 cm^{-1}, F(000) = 1136.00. − Data collection: T = 23(1)°C; 2Θ = 4 − 46° in $\pm h$, $+k$, $+l$; ω scan; scan range 1.00° + 0.35 tan Θ; 3157 reflections collected; 3033 independent and 1825 observed reflections with $I > 3\sigma(I)$. − Structure solution and refinement: SIR, MolEN. R = 0.0681; R_w = 0.0797 [$w^{-1} = \sigma^2(F_o)$]; GOF = 2.05; residual electron density 1.38/−0.412 · 10^6 e pm^{-3} between Fe2 and Fe3.

☆ Dedicated to Prof. Dr. *M. Herberhold* on the occasion of his 60th birthday.

[1] D. M. G. Mingos, D. J. Sherman, *Adv. Inorg. Chem.* **1989**, *34*, 293.

[2] M. Herberhold, *Nachr. Chem. Tech. Lab.* **1981**, *29*, 365.

[3] [3a] O. J. Scherer, J. Braun, P. Walther, G. Heckmann, G. Wolmershäuser, *Angew. Chem.* **1991**, *103*, 861; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 852. − [3b] W. A. Herrmann, *Angew. Chem.* **1991**, *103*, 835; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 826. − [3c] J. F. Corrigan, S. Doherty, N. J. Taylor, A. J. Carty, *J. Am. Chem. Soc.* **1994**, *116*, 9799.

[4] [4a] A. Vizi-Orosz, G. Pályi, L. Markó, *J. Organomet. Chem.* **1973**, *60*, C25. − [4b] V. Grossbruchhaus, D. Rehder, *Inorg. Chim. Acta* **1988**, *141*, 9.

[5] G. Effinger, W. Hiller, I.-P. Lorenz, *Z. Naturforsch., Part B*, **1987**, *42*, 1315.

[6] I.-P. Lorenz, W. Pohl, M. Schmidt, H. Nöth, *Z. Naturforsch., Part B*, in press.

[7] I.-P. Lorenz, P. Mürschel, W. Pohl, K. Polborn, *Chem. Ber.* **1995**, *128*, 413.

[8] Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59088, the names of the authors, and the journal citation.

[9] C. E. Laplaza, W. M. Davis, C. C. Cummins, *Angew. Chem.* **1995**, *107*, 2181; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2042.

[95122]