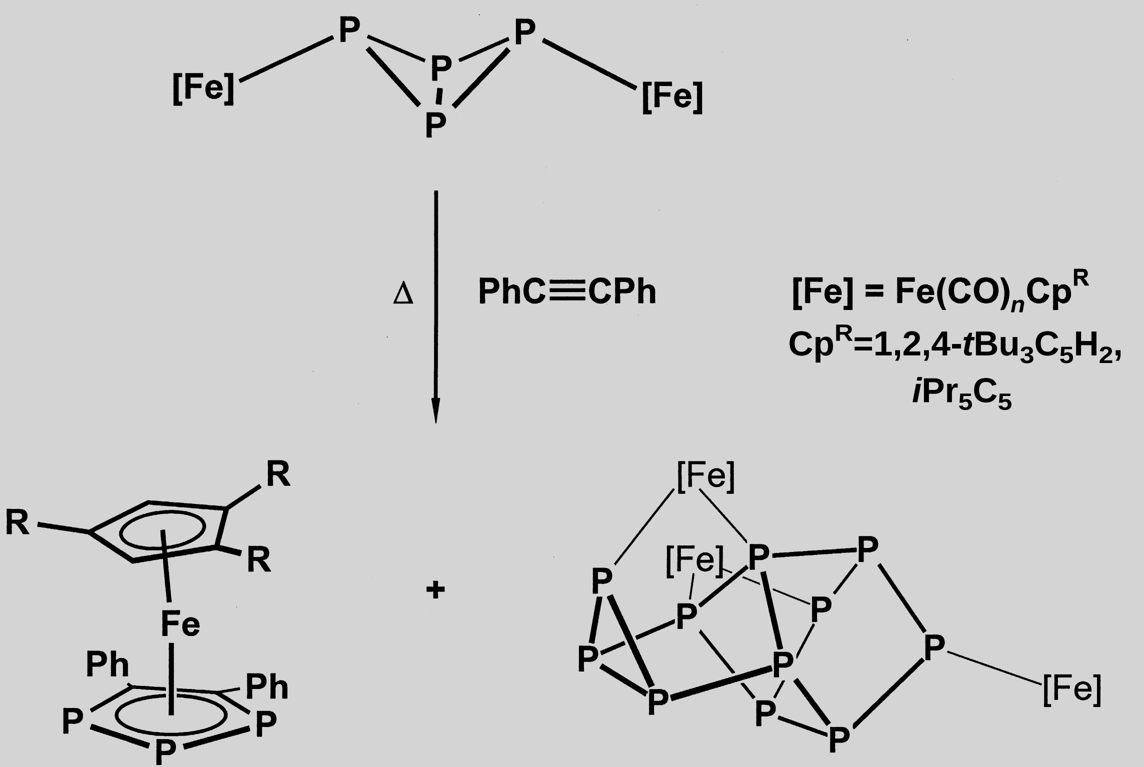
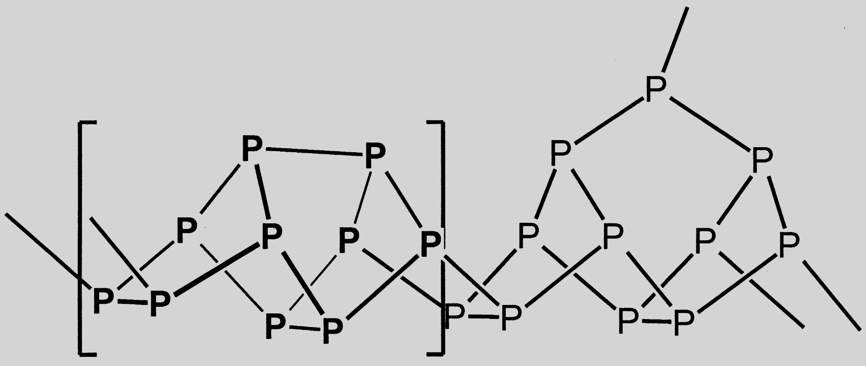


$[\{Cp^5_3(OC)_4Fe_3\}P_{11}]$



[ ] ≙ P_{10} partial motif of Hittorf´s phosphorus
with a P_2-P_8-P_2-P_9 repeat unit

Besides the desired synthesis of a sandwich complex with a 1,2,3-triphospholyl ligand, the reaction of the iron butterfly molecule with diphenylacetylene for Cp^5($i$$Pr_5C_5$) additionally affords a trinuclear iron complex, whose P_{11} framework can be derived from the P_{10} substructure of Hittorf's phosphorus by insertion of a P atom (P three-membered ring). Find out more on the following pages.

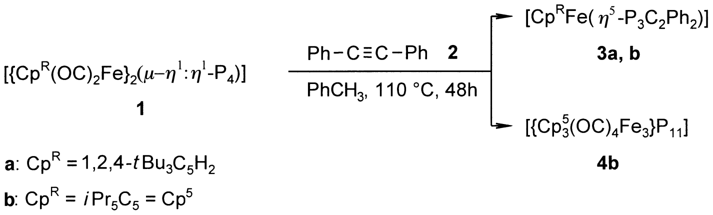
[{$Cp^R(OC)_2Fe$}$_2$(μ-η^1:η^1-P_4)]: Starting Material for the Synthesis of Iron Sandwich Compounds with a 1,2,3-Triphospholyl Ligand and of a Trinuclear Iron Complex with a P_{11} Ligand**

Otto J. Scherer,* Thomas Hilt and
Gotthelf Wolmershäuser

*Dedicated to Professor Gerd Becker
on the occasion of his 60th birthday*

Among phosphorus heterocycles with π bonds, polyphospholide ions $[(CH)_nP_{5-n}]^-$ ($n = 0-4$) as 6π systems form an important link between inorganic and organic chemistry.[1] In contrast to the well-studied 1,2,4-triphospholide ions,[1] whose first representative was prepared by Becker et al. from *t*BuCP and $LiP(SiMe_3)_2$,[2] both the parent compound of the 1,2,3-triphospholides, $[(CH)_2P_3]^-$, as well as the tetraphospholide ion $[(CH)P_4]^-$, formed, for instance, as a mixture in the thermolysis of P_4 and sodium in diglyme, were characterized by ^{31}P NMR spectroscopy.[3] A complex multistep synthesis has been described for $[(CPh)_2P_3]^-$ which contains a C_2 and P_3 building block in the five-membered ring.[4] Whereas the ligand properties of the 1,2,4-triphospholide ions have been studied in detail,[1] to the best of our knowledge there is only one complex known with the 1,2,3-triphospholyl ligand $[(CPh)_2P_3]^-$ that has been characterized by ^{31}P NMR spectroscopy.[4]

The reaction of the butterfly molecules **1a**[5a] and **1b**,[5b] which have a P_4 bicyclobutane framework, with tolane **2** leads to the sandwich complexes **3a**, **b** with a 1,2,3-triphospholyl ligand in moderate yield. In the case of **1b** the trinuclear iron compound **4b** ($Cp^5 = iPr_5C_5$) with a P_{11} ligand is formed in addition in approximately 10% yield.



In the sandwich complexes **3a**, **b** the five-membered-ring ligand $[(CPh)_2P_3]^-$ can be formally built from a P_3 building block of the butterfly molecule **1** and the alkyne **2**. At the same time **1** provides the necessary Cp^RFe fragment ($Cp^R = 1,2,4\text{-}tBu_3C_5H_2$, iPr_5C_5) for the completion of the sandwich structure of **3**.

Compounds **3a**, **b** form an anthracite to gray-green solid, which is soluble in *n*-pentane and very soluble in toluene, and can be handled in air for short periods. The ^{31}P NMR spectra[6] of **3a**, **b** each display an AX_2 spin system with identical coupling constants and slightly different chemical shifts.

The crystal stucture analysis[7] of **3a** confirms its sandwich structure (Figure 1). The distances and angles of the 1,2,3-triphospholyl ligands of **3a** were compared with the calculated value of the 1,2,3-triphospholide ion, $[(CH)_2P_3]^-$ **5**,[8] as well as those of the complex $[CpFe(\eta^5\text{-}P_3C_2tBu_2)]$ **6**[9a,b] with a 1,2,4-triphospholyl ligand. The P–P, P–C, and C–C distances and the P-P-P angles differ only slightly (P–P 2.12 (**3a**, average), 2.137 (**5**), 2.061 (**6**),[9a] 2.144 Å (**6**);[9b] P–C 1.77 (**3a**, average), 1.76 (**5**, average), 1.76 Å (**6**, average); C–C 1.413 (**3a**), 1.388 Å (**5**); P-P-P 99.04 (**3a**), 99.25° (**5**).[8] In **3a** the planes of the five-membered rings deviate from a parallel orientation by 7.6° ($Cp^R_{centroid}\text{-}Fe\text{-}(P_3C_2)_{centroid} = 173.5°$).

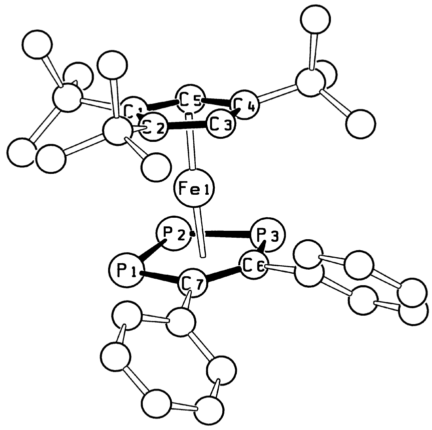


Figure 1. Structure of **3a** in the crystal. Selected bond lengths [Å] and angles [°]: P1-P2 2.1287(14), P2-P3 2.1193(15), P1-C7 1.766(4), P3-C6 1.783(3), C6-C7 1.413(5), Fe1-$(P_3C_2)_{centroid}$ 1.655, Fe1-$Cp^R_{centroid}$ 1.712; P1-P2-P3 99.04(5), P2-P1-C7 99.48 (12), P2-P3-C6 99.74(13), P3-C6-C7 120.1(3), P1-C7-C6 121.4(3).

For complexes with P_n ligands thus far examples have only been found with even values of n (8, 10, 12, and 14) for $n \geq 7$.[10] P_{11} has now been coordinatively stabilized for the first time in the trinuclear iron complex **4b**. Compound **4b**[6] forms red-brown crystals, which are poorly soluble in pentane and well soluble in toluene and dichloromethane; they can be handled for short periods in air.

The crystal structure analysis[7] shows (Figure 2) that the P_{11} framework of **4b** comprises a P_8P_2 substructure of Hittorf's phosphorus,[11] in which the P9–P10 edge is bridged in addition by the P11 atom.

The structurally characterized molecules Na_3P_{11} **7a**,[12a] $(Me_3EtN)_3P_{11}$ **7b**,[12b] $(Me_3Si)_3P_{11}$ **7c**, [12c] and $(iC_3H_7)_3P_{11}$ **7d**[12d,e] reveal exlusively a "ufosane"-type structure (polycycle consisting of six annelated P_5 rings) for the P_{11} framework. Interestingly, in theoretical studies on $P_{11}{}^+$[13a,b] and P_{11}[13a,c], the P_{11} framework, which has been confirmed for the first time by crystal structure analysis for **4b**, is discussed as a further structural alternative. The P–P bond lengths of **4b** lie in the range between 2.181(3) (P3–P8) and 2.268(3) Å (P5–P6), which is also found in **7d** (2.176 to 2.264 Å) with a

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[*] Prof. Dr. O. J. Scherer, Dr. T. Hilt, Dr. G. Wolmershäuser[+]
Fachbereich Chemie der Universität
Erwin-Schrödinger-Strasse, 67663 Kaiserslautern (Germany)
Fax: (+49) 631-205-2187
E-mail: oscherer@rhrk.uni-kl.de

[+] Crystal structure analyses.

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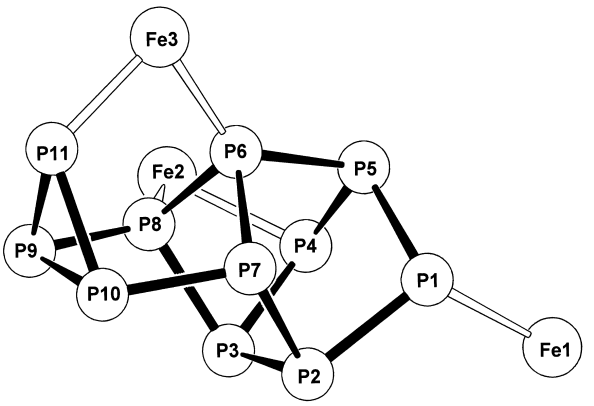

Figure 2. Structure of the framework of **4b** in the crystal (the Cp^5 ligands are omitted for clarity). Selected bond lengths [Å] and angles [°] (Fe1 = $Fe(CO)_2Cp^5$ (17 VE), Fe2, Fe3 = $Fe(CO)Cp^5$ (15 VE)): P1-P2 2.224(3), P1-P5 2.198(3), P2-P3 2.233(3), P3-P4 2.224(3), P4-P5 2.232(3), P5-P6 2.268(3), P6-P7 2.192(3), P6-P8 2.226(3), P2-P7 2.199(3), P3-P8 2.181(3), P7-P10 2.218(3), P8-P9 2.213(3), P9-P10 2.230(3), P9-P11 2.227(3), P10-P11 2.246(3), P1-Fe1 2.322(2), P4-Fe2 2.335(2), P8-Fe2 2.247(3), P6-Fe3 2.228(2), P11-Fe3 2.290(3); P10-P9-P11 60.52(10), P9-P10-P11 59.68(10), P7-P10-P9 108.78(14), P5-P6-P8 93.03(11), P5-P6-P7 102.03(10), P7-P6-P8 96.78(11), P8-P9-P10 98.90(11), P2-P7-P6 100.21(13), P2-P7-P10 109.34(13), P6-P7-P10 96.67(10), P3-P8-P6 100.64(10), P3-P8-P9 111.76(12), P6-P8-P9 98.49(12), P8-P9-P11 101.27(11), P7-P10-P11 98.67(12).

"ufosane" framework[12e] as well as in the P_8P_2 substructure (2.201 to 2.299 Å) of Hittorf's phosphorus.[11] The average values $\bar{d}$(P–P) do not differ significantly (2.22 (**4b**), 2.21 (**7b** and **7d**),[12b,e] 2.219 Å (Hittorf's phosphorus)[11]). Whereas the lengths of the Fe–P σ bonds (Fe1–P1, Fe2–P4, and Fe3–P11) range from 2.290(3) to 2.335(2) Å, the two-electron bonds between the phosphorus donor center (lone pair of electrons) and the bridging 15-valence-electron (VE) iron fragments (P8–Fe2 2.247(3), P6–Fe3 2.228(2) Å) are significantly shorter (Figure 2), a trend that also occurs in $[(\eta^5\text{-}C_5H_4Me)_4Fe_4(CO)_6P_8]$ **8**.[14]

The mass spectrum of **4b**[6] displays the ions $[\{Cp^RFe\}_2P_n]^+$ ($n = 3-5$), which can be assigned to a series of cationic 30-, 29-, and 28VE-triple-decker complexes. Formally $[\{Cp^RFe\}_2P_5]^+$ can be built up from the atoms P1 to P5 and the decarbonylated fragment Cp^RFe of the iron atoms Fe1 and Fe2 (Figure 2). The cationic sandwich complex $[Cp^RFeP_5]^+$ as well as that of the molecule with two less P atoms $[Cp^RFeP_3]^+$ are possible fragments of an undetectable $[Cp^R(OC)FeP_6]^+$ species (P_6 = P6 to P11, Fe = Fe3 (see Figure 2), $Cp^R = i Pr_5C_5$).

Experimental Section

3a [**3b**, **4b**]: Diphenylacetylene **2** (70 mg) [170 mg] was added at room temperature under stirring to a solution of **1a** (320 mg, 0.39 mmol) [860 mg][5a] [**1b** 0.96 mmol][5b] in toluene (ca. 100 mL) [250 mL], and the orange-red reaction mixture was heated to reflux at 110 °C. After 48 h the CO bands of the starting material **1a** [**1b**] were no longer visible in the IR spectra. After removal of the solvent in vacuo, the residue was dissolved in dichloromethane (ca. 10 mL), treated with silylated silica gel (ca. 2 g) and transferred to a column (20 × 1 cm) packed with Al_2O_3 and petroleum ether. With petroleum ether a gray-green fraction was eluted that contained **3a** (90 mg, 41 %) [**3b** (210 mg, 36 %)]. With petroleum ether/toluene (5/1) a pale brown fraction was isolated in each case, which according to ^{31}P NMR spectroscopy was composed of a mixture of substances, which to date has not been possible to separate. In the case of **1b**, with petroleum ether/toluene (1/1) **4b** (140 mg, 10 %) was isolated in addition as a dark red fraction. Compound **4b** was recrystallized from pentane.

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[6] Spectroscopic data of the compounds **3a, b** and **4b**: ^{31}P NMR (167.97 MHz, C_6D_6, 85 % H_3PO_4 external; $T = 298$ K): **3a**: $\delta = 78.1$ (d, 2P), –18.5 (t, 1P), $^1J(P,P) = -412.0$ Hz; **3b**: $\delta = 80.3$ (d, 2P), –22.4 (t, 1P), $^1J(P,P) = -412.0$ Hz; **4b**: partially unsatisfactory resolved signal groups in the region from 200 to –100 ppm; ^1H NMR (400.14 MHz, C_6D_6, C_6D_5H internal, $T = 298$ K): **3a**: $\delta =$ 7.55 (m, 5H), 7.00 (m, 5H), 4.26 (br.s, 2H), 1.36 (s, 9H), 1.28 (s, 9H), 1.18 (s, 9H); **3b**: $\delta = 7.42$ (m, 5H), 7.02 (m, 5H), 2.93 (br.s, 5H), 1.31 (br.s, 30H); IR (toluene): **4b**: $\tilde{\nu}$(CO) [cm^{-1}] = 1996 (vs), 1953 (vs), 1938 (vs), 1910 (vs); MS (EI, 70 eV): **4b**: *m/z*: 817 [$Cp^5_2Fe_2P_5^+$, 100], 786 [$Cp^5_2Fe_2P_4^+$, 19], 755 [$Cp^5_2Fe_2P_3^+$, 24], 486 [$Cp^5FeP_5^+$, 57], 424 [$Cp^5FeP_3^+$, 25], 211 [FeP_5^+, 11 %].

[7] Crystal structure data of **3a** [**4b**]: $C_{31}H_{39}FeP_3$ [$C_{64}H_{105}Fe_3O_4P_{11} \cdot 0.75\,C_5H_{12}$], $M_r = 560.4$ [1497.8], orthorhombic [triclinic], space group $Pna2_1$ [$P\bar{1}$], $a = 14.326(2)$ [15.1159(16)], $b = 14.422(1)$ [16.7864(15)], 13.826(2) [17.9137(16)] Å, [$\alpha = 94.642(10)$, $\beta = 105.711(11)$, $\gamma =$ 106.723(12)°], $V = 2856.6(6)$ [4127.9(7)] Å^3, $Z = 4$ [2], $\rho_{calcd} = 1.303$ [1.205] g cm^{-3}, $T = 293(2)$ K, $\theta = 2.04-27.50$ [2.91–23.82]°, measured reflections: 4263 [41 494], independent reflections: 3685 [11 976] ($R_{int} = 0.0223$ [0.1517]); $R1 = 0.0342$ [0.0529], $wR2 = 0.0692$ [0.1089] (($I > 2\sigma(I)$); $R1 = 0.0491$ [0.1553], $wR2 = 0.0744$ [0.1293] (all data); diffractometer: Siemens P4 [Stoe IPDS]; structure solution: direct methods; programs: SHELXS-97 [SIR 92 (A. Altomare, G. Cascarano, G. Giacovazzo, A. Gualiardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435)]; structure refinement: full-matrix least-squares methods against F^2; Program: SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**); data/parameters: 3685/326 [11976/791]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136248 (**3a**) and CCDC-136249 (**4b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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