Experimental Section

General procedure for the alkoxycarbonylation of chloroarenes: the corresponding chloroarene (7 mmol), *n*-butanol (14 mL), $[PdCl_2(PhCN)_2]$ (13.4 mg, 0.035 mmol, 0.5 mol%), and ligand **4** (84.9 mg, 0.140 mmol, 2 mol%) were added to a Schlenk flask under argon (orange solution). Sodium carbonate (2.226 g, 21 mmol, 3 equiv) and molecular sieves (4 Å, ca. 3 g) were added to the reaction autoclave. Following evacuation and replacement with argon (three cycles) the reaction mixture was transferred with a PVC hose (∅ ≈ 2 mm) under a slight excess pressure of argon from the Schlenk flask into the autoclave. The autoclave was closed and heated to the reaction temperature (145 °C). The reaction pressure (1 bar CO) was held constant by means of a CO reservoir, connected to the autoclave by a pressure regulator. After 16 h reaction time the autoclave was cooled to room temperature and the yellow orange mixture diluted with dichloromethane (70 mL). After washing with water (70 mL) the aqueous phase was extracted with dichloromethane (2 × 20 mL), and the combined organic phases were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude product was then purified by column chromatography (silica gel, EtOAc/hexane).

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[13] In a long reaction time experiment on the alkoxycarbonylation of chlorobenzene with 5 mol% Pd catalyst a conversion of 48% (selectivity 91%) was reached after 5 days even at a reaction temperature of 90 °C.

[14] A P:Pd ratio of 80:1 was chosen for these experiments to maintain a ligand concentration 2 mol%. In earlier work on carbonylation reactions we showed that for the stabilization of the Pd catalyst the ligand concentration and not the ligand:palladium ratio is important.[9]

Synthesis, Structure, and Reactivity of a Diphosphadiferratetrahedrane with a Fe–Fe Double Bond**

Christine Eichhorn, Otto J. Scherer,* Thorsten Sögding, and Gotthelf Wolmershäuser

Dedicated to Professor Marianne Baudler
on the occasion of her 80th birthday

Whereas in the chemistry of acetylene complexes of iron, compound **1** containing a C_2Fe_2 tetrahedrane framework and a Fe–Fe double bond was prepared and crystallographically characterized already in 1976,[1] for the iso(valence)electronic and isolobal ($\mathrm{HC} \underset{o}{\longleftrightarrow} \mathrm{P}$, $\mathrm{HC{\equiv}CH} \mathrel{\hat{=}} \mathrm{{:}P{\equiv}P{:}}$) diphosphadiferratetrahedranes only the complex **2** with a Fe–Fe single bond and additional P-coordination is known.[2]

Diphosphadimetallatetrahedranes of the type $[\{L_nM\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}P_2)]$ ($L_nM = 15$ valence-electron(VE) fragment)[3] synthesized to date all display M–M single bonds, and with six skeleton electron pairs (SEPs) for the tetrahedral M_2P_2 framework are considered as *nido* clusters. According to theoretical investigations a decrease (5 SEPs) as well as an increase (7 SEPs) in the number of electrons in the skeleton lead to changes of the M_2P_2 framework.[4]

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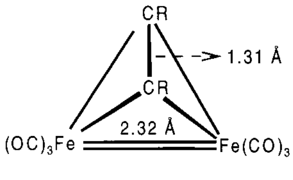
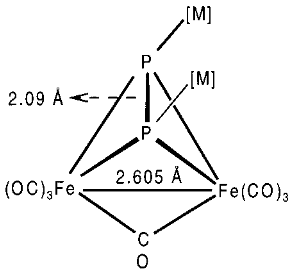
[+] Crystal structure analysis.

[**] This work was supported by the Fonds der Chemischen Industrie and by the Graduiertenkolleg „Phosphorchemie als Bindeglied verschiedener chemischer Disziplinen“.

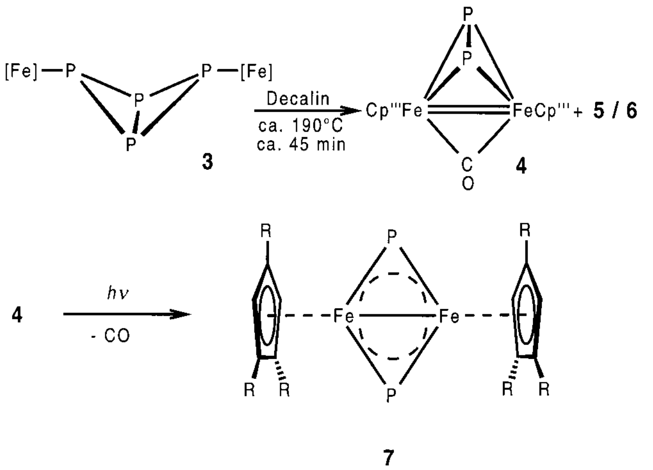


1: R = *t*Bu



2: [M] = Cr(CO)$_5$

If the thermolysis time for the reaction with butterfly molecule **3** is reduced from about 3 h to about 45 min, the diphosphadiferratetrahedrane **4** with a Fe–Fe double bond (formally a diphosphadimetallatetrahedrene) is obtained in 18 % yield together with the known complexes [Cp'''Fe-(η^5-P$_5$)] (**5**) and [{Cp'''Fe}$_2$(μ-η^4:η^4-P$_4$)] (**6**) (Scheme 1).[5]



Scheme 1. Preparation of complexes **4** and **7** from the butterfly molecule **3**. [Fe] = Fe(CO)$_2$Cp''', Cp''' = 1,2,4-*t*Bu$_3$C$_5$H$_2$, R = *t*Bu.

Complex **4** forms air- and light-sensitive green crystals,[6] which are soluble to very soluble in *n*-hexane, toluene, and dichloromethane. The μ-CO band occurs at 1761 cm^{-1} in the IR spectrum and a singlet appears at $\delta = 776.3$ in the ^{31}P{^{1}H} NMR spectrum. Compound **4** has 5 SEPs; thus, one less than **2**.[4a]

The crystal structure analysis[7] for the tetrahedral Fe$_2$P$_2$ framwork (Figure 1) of **4** revealed a P–P bond length of 2.064(2) Å (see also ref. [3]), which is therefore slightly shorter than that in **2** (2.09 Å).[2] The Fe–Fe bond length of 2.3944(10) Å lies in the range for Fe–Fe double bonds and is slightly longer than that in **1** (2.32 Å), but considerably shorter than that in **2** (2.605 Å). The iron atoms are almost symmetrically bridged (Fe1–C1 1.9236(6), Fe2–C1 1.914(6) Å) by the CO ligand; their distances to the phosphorus atoms (2.2867(16)–2.2948(17) Å) are on average 2.29 Å (2.28 Å for **2**).[2] The planar Cp''' five-membered rings deviate by 16.7° from a parallel arrangement and the Fe1-Fe2-$\mathrm{Cp'''_{centroid}}$ as well as Fe2-Fe1-$\mathrm{Cp'''_{centroid}}$ angles by 7.3 and 7.2°, respectively, from linearity.

The P$_2$ building block of **4** is split photochemically under elimination of CO to a complex with two bent μ-P ligands (→**7**, Scheme 1; the question still remains unanswered as to whether this formally involves the formation of a P$_2$Fe$_2$ tetrahedrane with a Fe–Fe triple bond). Although there are a few complexes with μ_3-P ligands,[3, 8, 10] the only comparable example with such a μ-P bridging ligand is [{(ArO)$_2$W}$_2$-(μ-P){PC*t*BuP(OAr)$_2$}] (**8**), which was prepared from *t*BuC≡P and [{(ArO)$_3$W}$_2$](*W*≡*W*).[9]

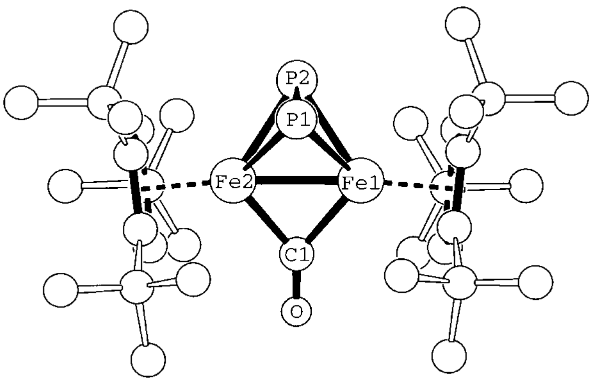


Figure 1. Structure of **4** in the crystal. Bond lengths [Å] and angles [°]: Fe1-Fe2 2.3944(10), Fe1-P1 2.2915(18), Fe1-P2 2.2867(16), Fe2-P1 2.2890(19), Fe2-P2 2.2948(17), P1-P2 2.064(2), Fe1-C1 1.923(6), Fe2-C1 1.914(6), Fe1-$\mathrm{Cp'''_{centroid}}$ 1.75, Fe2-$\mathrm{Cp'''_{centroid}}$ 1.74; Fe1-P1-Fe2 63.03(5), Fe1-P2-Fe2 63.02(5), P1-Fe1-P2 53.60(6), P1-Fe2-P2 53.53(6), Fe1-C1-Fe2 77.2(2), Fe1-Fe2-$\mathrm{Cp'''_{centroid}}$ 172.70, Fe2-Fe1-$\mathrm{Cp'''_{centroid}}$ 172.80.

The dark green crystals of **7** show solubility behavior similar to that of **4**.[6] The ^{31}P{^{1}H} NMR signal of **7** at δ=1406.9 is shifted to extremely low field (see also ref. [10]), and compared to the signal of the starting material **4** it is shifted by 630.6 ppm. The crystal structure analysis of **7** (Figure 2) reveals a rhombic Fe$_2$P$_2$ four-membered ring,[7] in which the atoms deviate from the least squares plane by at most 0.0211 Å. The normals of the Fe1-Fe2-P1 plane and that of the Fe1-Fe2-P2 plane form an angle of 2.8°. The Fe1–Fe2 bond length of 2.5004(4) Å corresponds almost exactly to the average value from that in **2** (single bond) and that in **4** (double bond). If the bent μ-P ligands are each considered as 3e$^-$ donors, then for the diamagnetic complex **7** the two Fe

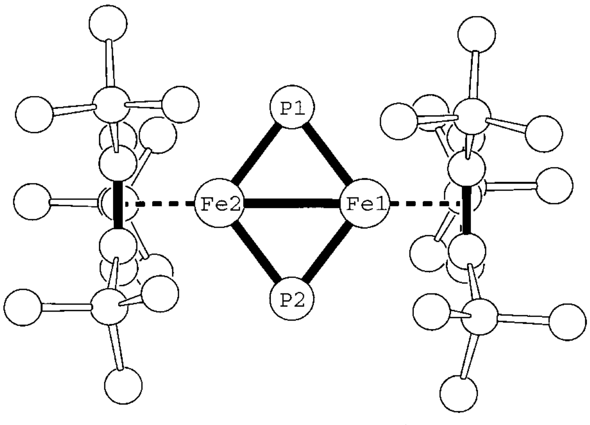


Figure 2. Structure of **7** in the crystal. Bond lengths [Å] and angles [°]: Fe1-Fe2 2.5004(4), Fe1-P1 2.1069(7), Fe1-P2 2.0994(7), Fe2-P1 2.1068(7), Fe2-P2 2.1015(8), Fe1-$\mathrm{Cp'''_{centroid}}$ 1.73, Fe2-$\mathrm{Cp'''_{centroid}}$ 1.73; Fe1-P1-Fe2 72.80(2), Fe1-P2-Fe2 73.06(2), P1-Fe1-P2 107.06(3), P1-Fe2-P2 106.99(3).

atoms achieve 18 VE when one formally postulates a Fe–Fe double bond. As expected, in the transition from **4** to **7** a considerable shortening occurs of the Fe–P distances (Fe–P 2.29 and 2.10 Å (av), respectively; multiple bond contributions). In **7** the angles at the P atoms (Fe-P-Fe 72.80(2), 73.06(2)°) are considerably smaller than those at the Fe atoms (P-Fe-P 107.06(3), 106.99(3)°). The almost ideally eclipsed Cp''' five-membered rings (Figure 2) deviate only slightly (2.3°) from a parallel orientation and are arranged almost orthogonal (91.5, 89.2°) to the four-membered ring.

Experimental Section

4: Compound **3** (970 mg, 1.19 mmol) was dissolved in decalin (ca. 150 mL) and heated under stirring to 190 °C (reflux). After about 45 min the CO bands of the starting material **3** were no longer visible by IR spectroscopy.[5] The solvent was removed under vacuum. The red-brown residue was dissolved in dichloromethane (ca. 10 mL) and the solution was treated with silylated silica gel (ca. 2 g). The mixture was transferred to a column (20 × 2 cm) filled with silica gel and petroleum ether. At −20 °C (cryostat) a pale green fraction, which contained **5** (60 mg, 12 %), was eluted with petroleum ether. Compound **6** (370 mg, 44 %) was obtained as the second, dark red fraction with petroleum ether/toluene (20/1). Compound **4** (150 mg, 18 %) was eluted as a dark green solution with petroleum ether/toluene (10/1), and was recrystallized from hexane.

7: A dark green solution of **4** (150 mg, 0.22 mmol) in toluene (ca. 120 mL) was photolyzed at room temperature (150-W mercury high-pressure lamp). After 4.5 h the band for the bridging CO ligand of the starting material was no longer detected in the IR spectrum of the reaction mixture. The solvent was removed under vacuum, and the residue was taken up in heptane. A pale brown insoluble solid was separated on a frit; owing to its poor solubility this could not be characterized further. Compound **7** (90 mg, 63 %) was obtained as a yellow-brown powder from the eluate, and was recrystallized from hexane.

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[6] Spectroscopic data of compounds **4** and **7**: ^{31}P NMR (167.97 MHz, C_6D_6, 85 % H_3PO_4 external; $T = 298$ K): **4**: $\delta = 776.3$ (s, 2P); **7**: $\delta = 1406.9$ (s, 2P); ^{1}H NMR (200.13 and 400.14 MHz, C_6D_6, C_6D_5H internal; $T = 298$ K): **4**: $\delta = 4.61$ (s, 2H), 1.34 (s, 18H), 1.13 (s, 9H); **7**: $\delta = 6.59$ (s, 2H), 1.37 (s,18H), 1.29 (s, 9H); IR (toluene): **4**: $\tilde{\nu}$(CO) = 1761 cm^{-1} (vs).

[7] Crystal structure data of **4** [**7**]: $C_{35}H_{58}Fe_2OP_2$ [$C_{34}H_{58}Fe_2P_2$], $M_r = 668.5$ [640.4], monoclinic [monoclinic], space group $P2_1/n$ [$P2_1/n$], $a = 14.15624(13)$ [11.7825(8)], $b = 14.1991(10)$ [10.4476(4)], $c = 18.171(2)$ Å [28.5310(17)], $\beta = 99.277(12)°$ [91.156(8)], $V = 3604.7(6)$ Å^3 [3511.4(3)], $Z = 4$ [4], $\rho_{calcd} = 1.232$ g cm^{-3} [1.211], $T = 293(2)$ K, $\theta = 2.04–26.08°$ [2.95–25.68], 25078 [46082] measured reflections, 7016 [6644] independent reflections ($R_{int} = 0.1449$ [0.0504]), $R1 = 0.0465$ [0.0373], $wR2 = 0.0687$ [0.0996] ($I > 2\sigma(I)$); $R1 = 0.1500$ [0.0451], $wR2 = 0.0889$ [0.1043] (all data); diffractometer: Siemens P4 [Stoe IPDS]; structure solution: direct methods; program: 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: 7016/379 [6644/361]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-163506 (**4**) and CCDC-163507 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Evidence for σ Dimerization During Anodic Redox Switching of 1,3,5-Tripyrrolidinobenzene: A New Molecular Switch**

Jürgen Heinze,* Christian Willmann, and Peter Bäuerle

The dimerization of radical ions of conjugated aromatic systems has been discussed in the literature for more than 20 years.[1–10] In the case of radical cations, experimental data have led many authors to postulate the formation of weakly reacting π dimers. This assumption, however, is not able to fully explain the experimental results. In the case of radical anions, by contrast, the formation of covalently bonded σ dimers is generally accepted.[2, 11–18] This controversy over the σ or π dimerization of radical ions is unresolved primarily as a consequence of the widely held view that because of coulombic repulsion between charged molecules only weak reactions are possible. This argument overlooked and overlooks first the presence of the counterions, which drastically diminish repulsion, and second that even in moderately polar solutions the level of coulombic interactions is low compared to the gas phase.

Interpretations of the measurements of radical cations in connection with the π-dimer hypothesis are based almost exclusively on the results for UV/Vis spectra obtained at different temperatures. Contrary to expectations, in UV spectra dimerization is usually detected in the short-wave

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