Organometallics **1998,** *17,* 4110−4112

Notes

P_4 Activation with $[\{Cp'''(OC)_2Fe\}_2]$ ($Cp''' = C_5H_2Bu^t{}_3$-1,2,4): Exclusive Formation of the Exo/Exo-Butterfly Complex $[\{Cp'''(OC)_2Fe\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}P_4)]$

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Received February 19, 1998

Summary: The short-time cothermolysis of $[\{Cp'''(OC)_2Fe\}_2](Fe{-}Fe)$ (**1**) *and white phosphorus,* P_4, *in toluene gives the butterfly complex* $[\{Cp'''(OC)_2Fe\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}P_4)]$ (**2**), $Cp''' = C_5H_2Bu^t{}_3$-1,2,4, *as the only product in 75% isolated yield. The open-edged exo/exo-*P_4 *derivative* **2** *where one of the six P−P bonds of* P_4 *has been selectively cleaved gives, on thermolysis, the sandwich complexes* $[Cp'''Fe(\eta^5\text{-}P_5)]$ (**3**) *and* $[\{Cp'''Fe\}_2(\mu\text{-}\eta^4{:}\eta^4\text{-}P_4)]$ (**4**) *with a cisoid* P_4 *chain.*

Within the last few years, the chemistry of complexes with naked P_n ligands[1] has grown rapidly. Interestingly, little is known about the details of P_4 activation as well as the mechanistic aspects with respect to the cleavage of its P−P bonds and the degradation of the P_4 tetrahedron.[2] The successive cleavage of 1−3 P−P bonds in the P_4 molecule has been realized by its photochemical reaction with $[\{Cp''(OC)_2Fe\}_2](Fe{-}Fe)$, $Cp'' = C_5H_3Bu^t{}_2$-1,3.[3] One of the compounds detected was impure $[\{Cp''(OC)_2Fe\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}P_4)]$.[3]

Organometallic butterfly-type molecules with a tetraphosphabicyclobutane skeleton of type **2** are very rare, and until now, the described examples are of low purity and no crystals of X-ray diffraction quality could be obtained. Also known is $[\{Cp^*(OC)_2Fe\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}P_4)]$, which has been synthesized either from the diphosphene derivatives $[Cp^*(OC)_2Fe{-}P{=}P{-}R]$, R = Cp*[4] and $Fe(CO)_2Cp^*$,[5] or by the cothermolysis of $[\{Cp^*(OC)_2Fe\}_2](Fe{-}Fe)$ and P_4.[6] In all cases, the yields and purity are moderate.

Short-time thermolysis of $[\{Cp'''(OC)_2Fe\}_2](Fe{-}Fe)$ (1) and P_4 under ^{31}P NMR control affords exclusively, in ca. 75% yield, $[\{Cp'''(OC)_2Fe\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}P_4)]$ (**2**) (Figure 1) according to Scheme 1.

2 forms air-sensitive orange-yellow crystals which are scarcely soluble in pentane and very soluble in toluene. **3** and **4** form green and dark brown crystals that can be handled for a short amount of time in open air and are slightly soluble in pentane and very soluble in toluene.

Heating of **2** in decalin to 190 °C for ca. 3 h gives, after column chromatography in a yield of 25% each, the complex $[Cp'''Fe(\eta^5\text{-}P_5)]$ (**3**), a sandwich (Figure 2) with a cyclo-P_5 ligand, the all-phosphorus analogue of the cyclopentadienide ion,[1] in addition to $[\{Cp'''Fe\}_2(\mu\text{-}\eta^4{:}\eta^4\text{-}P_4)]$ (**4**) with a cisoid P_4 chain (Figure 3).

Within the P−P bonds of the P_4-butterfly skeleton of **2**, the bond length of the hinge is 2.151(2) Å, whereas the mean value of the four other P−P bonds (wing tips) is 2.21 Å, as in white phosphorus, P_4, itself. An analogous trend was found for the tetraphospabicyclobutane derivatives $(RP)_2P_2$ (**5**; **5a**, R = $N(SiMe_3)_2$ (2.13/2.22 Å);[7] **5b**, R = $C_6H_2Bu^t{}_3$-2,4,6 (2.17/2.23 Å);[8] and **5c**, R = C(R′) = PPh_3 (2.21/2.22 Å)).[9] In **2**, the folding angle between the planes P1, P2, P3/P2, P3, P4 is 100.4°; this value is slightly larger than that for the class of compounds **5** (95.2−96.6°)[7−9] with a nonmetallic substituent R on the wing-tip atoms of the butterfly. The mean value of the Fe−P−P angle is 108.1° in **2**. All X-ray structurally characterized molecules of this type possess an exo/exo-configuration of the substituents R or the ligands $Cp^RFe(CO)_2$ on the P atoms (cf. Figure 1). Also known are butterfly-like P_4 compounds with a ML_n bridge.[10]

With the synthesis of **2** (cf. Scheme 1), the selective activation of one of the six P−P bonds in P_4 by a dinuclear metal complex has been achieved in high yield (ca. 75% after column chromatography) for the first time. The only other example is $(RP)_2P_2$ (**5b**),[8] which has been synthesized besides R_2P_2 starting with P_4 in a yield of only ca. 4%.

[†] X-ray crystal structure determinations.

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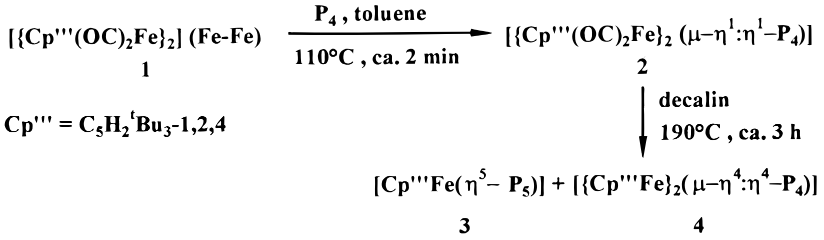
S0276-7333(98)00114-9 CCC: $15.00

Scheme 1



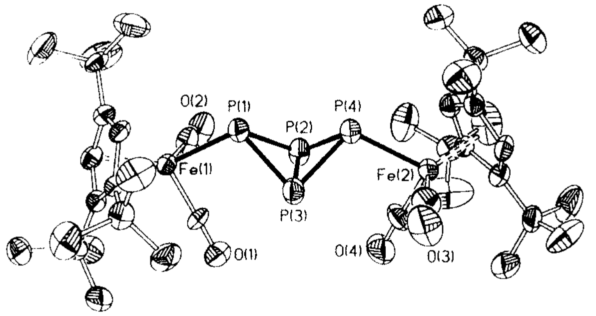


Figure 1. ORTEP diagram with labeling scheme for complex **2**. Thermal ellipsoids are drawn at 40% probability. Selected bond distances (Å) and angles (deg): Fe1−P1, 2.3552(19); Fe2−P4, 2.348(2); P2−P3, 2.151(2); P1−P2, 2.210(3); P1−P3, 2.217(3); P2−P4, 2.198(3); P3−P4, 2.209(2); P1⋯P4, 2.96, Fe1−$\text{Cp}'''_{\text{(centroid)}}$, 1.745; Fe2−$\text{Cp}'''_{\text{(centroid)}}$, 1.746; P2−P1−P3, 58.12(8); P2−P4−P3, 58.42(8); P1−P2−P3, 61.11(8); P1−P3−P2, 60.77(8); P1−P2−P4, 84.49(9); P1−P3−P4, 84.07(9); P2−P3−P4, 60.53(8); P3−P2−P4, 61.04(8); Fe1−P1−P2, 106.02(9); Fe1−P1 −P3, 109.86(9); Fe2−P4−P2, 108.45(9); Fe2−P4−P3, 107.91(9).

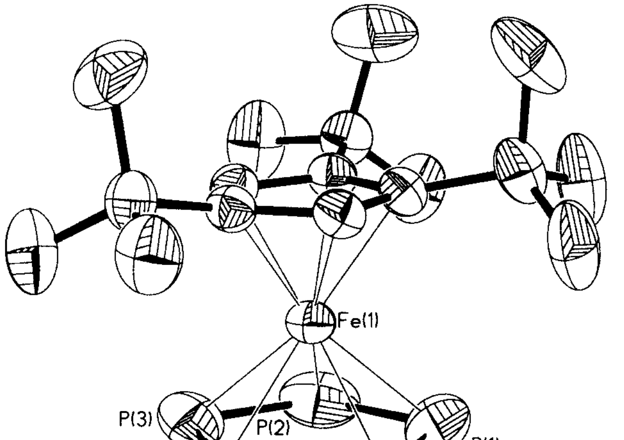


Figure 2. ORTEP diagram with labeling scheme for complex **3**. Thermal ellipsoids are drawn at 40% probability. Selected bond lengths (Å) and angles (deg): P1−P2, 2.069(6); P2−P3, 2.082(6); P3−P4, 2.076(8); P4−P5, 2.094(10); P5−P1, 2.075(9); $\text{Cp}'''_{\text{(centroid)}}$−Fe1, 1.72; $\text{P}_{5\text{(centroid)}}$−Fe1, 1.58; P2−P1−P5, 109.1(3); P1−P2−P3, 107.3 (3); P2−P3−P4, 108.5(3); P3−P4−P5, 107.7 (2); P4−P5−P1, 107.3(2); $\Sigma = 539.9$; $\text{Cp}'''_{\text{(centroid)}}$−Fe1−$\text{P}_{5\text{(centroid)}}$, 178.

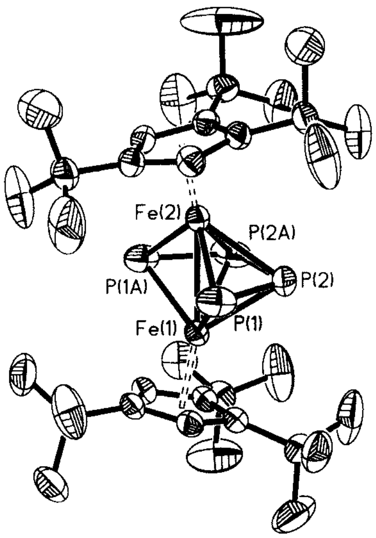


Figure 3. ORTEP diagram with labeling scheme for complex **4**. Thermal ellipsoids are drawn at 40% probability. Selected bond lengths (Å) and angles (deg): Fe1−Fe2, 2.6430(8); Fe1−P1(1′), 2.2649(8); Fe1−P2(2′), 2.3337(9); Fe2−P1(1′), 2.2678(8); Fe2−P2(2′), 2.3346(9); P1(1′)−P2(2′), 2.0877(13); P2−P2′, 2.368(2); P1⋯P1′, 3.55; Fe1(2)−$\text{Cp}'''_{\text{(centroid)}}$, 1.74; Fe1(2)−$\text{P}_{4\text{(centroid)}}$, 1.42; P1(1′)−P2(2′)−P2′(2), 106.48(3); $\text{Cp}'''_{\text{(centroid)}}$−Fe1(2)−Fe2(1), 167.9 (167.1).

In contrast to the well-studied photochemistry[11] of the compounds $[\{\text{Cp}^{\text{R}}(\text{OC})_2\text{Fe}\}_2]$(Fe−Fe), to the best of our knowledge, no detailed information on its thermal behavior is known. It is likely that on the way to the formation of **2** the radical $[\text{Cp}'''(\text{OC})_2\text{Fe}]^\bullet$ (cf. the stable radical $[(\text{C}_5\text{R}_5)(\text{OC})_2\text{Fe}]^\bullet$, R = i-C_3H_7[12]) plays an important role.

According to Scheme 1, the exo,exo-substituted butterfly molecule **2** can be used as an educt for the thermal formation of **4** and, still more surprisingly, for the preparation of the sandwich compound **3**.

3 is the second cyclo-P_5 sandwich complex characterized by X-ray crystallography. The data (Figure 2) $\bar{d}$(P−P) = 2.08 Å, $\bar{d}$(Fe1−P) = 2.38 Å, $\text{Cp}'''_{\text{(centroid)}}$−Fe1 = 1.72 Å, cyclo-$\text{P}_{5\text{(centroid)}}$−Fe1 = 1.58 Å, $\text{Cp}'''_{\text{(centroid)}}$−Fe1−$\text{P}_{5\text{(centroid)}}$ = 178° differ only slightly from those of $[\text{Cp}^{*\prime}\text{Fe}(\eta^5\text{-P}_5)]$ (**6**),[13] $\text{Cp}^{*\prime} = \text{C}_5\text{Me}_4\text{Et}$ (2.10, 2.35, 1.71, and 1.53 Å; 179°). Obviously, as a consequence of the sterically more demanding $\text{C}_5\text{H}_2\text{Bu}^t{}_3$ ligand in complex **3** ($\text{C}_5\text{Me}_4\text{Et}$ in **6**), the distance between Fe1 and the cyclo-P_5 centroid is enlargened in **3**.

The structural data (Figure 3) of the dinuclear iron complex **4** with an acyclic P_4 ligand are nearly the same as those found for $[\{\text{Cp}''\text{Fe}\}_2(\mu\text{-}\eta^4{:}\eta^4\text{-P}_4)]$ (**7**), $\text{Cp}'' = \text{C}_5\text{H}_3\text{-Bu}^t{}_2\text{-1,3}$.[3]

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Experimental Section

All experiments were carried out under an argon atmosphere in dry solvents.

$[\{Cp'''(OC)_2Fe\}_2](Fe-Fe)$(1).[14] ^{1}H and ^{31}P NMR spectra were measured on a Bruker AMX 400 (^{1}H, C_6D_5H = 7.20 ppm as the internal standard; ^{31}P, 85% H_3PO_4 as the external standard).

$[\{Cp'''(OC)_2FeP\}_2P_2]$ (2). To a solution of 240 mg (0.348 mmol) of $[\{Cp'''(OC)_2Fe\}_2](Fe-Fe)$ (**1**) in toluene (50 mL), 50 mg (0.404 mmol) of freshly dried white phosphorus, P_4, was added at room temperature. The stirred reaction mixture was heated for ca. 2 min to 110 °C, until the CO bands of **1** had disappeared in the IR spectrum in solution (new bands of **2**, 2000 and 1950 cm^{-1}). After removal of the solvent under vacuum, the residue was taken up in dichloromethane (ca. 10 mL), ca. 2 g of silylated silica gel was added, and the mixture was concentrated until it was free-flowing. Column chromatography (column, 20 × 1 cm, SiO_2(II), −20 °C, petroleum ether), starting with petroleum ether/toluene (5:1), gave a red-violet fraction (traces of **1**) after traces of a yellow fraction (P_4). With a 1:1 mixture, a bright orange fraction containing **2** was eluted. Yield: 220 mg (77.6%). ^{1}H NMR (C_6D_6, 400 MHz, 25 °C; δ, ppm): 4.69 (2H, s); 1.26 (18H, s); 1.25 (9H, s). ^{31}P NMR (C_6D_6, 25 °C; δ, ppm): −81.4 (2P, t), −324.5 (2P, t), $^1J(P, P) = -183.1$ Hz. IR(toluene), ν (CO): 2000 (vs), 1950 (vs) cm^{-1}.

Complexes $[Cp'''FeP_5]$ (3) and $[\{Cp'''Fe\}_2(P_4)]$ (4). A solution of 720 mg (0.884 mmol) of **2** in decalin (ca. 50 mL) was heated for ca. 3 h to 190 °C until no CO bands could be detected by IR. Work up was as described above (1 g of silylated silica gel; column 15 × 2 cm). With petroleum ether, green **3** was eluted. Yield: 100 mg (25%). A petroleum ether/toluene mixture 5:2 gives 160 mg (yield 25%) of dark brown **4**. ^{1}H NMR (cf. **2**): **3** 3.99 (s, 2H), 1.25 (s,18H), 1.13 (s, 9H); **4** 4.31 (s, 2H), 1.35 (s, 18H), 1.28 (s, 9H). ^{31}P NMR (cf. **2**): **3** 165.6 (s); **4** 91 (br s at 298 and 243 K).

Crystal Data for 2, 3, and 4. **2**: Crystals were obtained from a hot saturated hexane solution upon cooling to room temperature. $C_{38}H_{58}Fe_2O_4P_4$, $M_r = 814.5$, monoclinic space group $P2_1/n$, $a = 16.1344(9)$ Å, $b = 15.7131(13)$ Å, $c = 18.1964(11)$ Å, $\beta = 111.271(6)°$, $V = 4298.9(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.258$ g/cm^3, crystal dimensions 0.30 × 0.20 × 0.05 mm, $\lambda = 0.710\,73$ Å, μ (Mo Kα) = 0.858 mm^{-1}. Measured reflections 35 578, independent reflections 7282 ($R_{int} = 0.1918$), θ range 2.59−24.71°, refinement against F^2 with all data, $R_1 = 0.0451$, ([$I > 2\sigma(I)$]), w$R_2 = 0.0920$. **3**: $C_{17}H_{29}FeP_5$, $M_r = 444.1$, monoclinic space group $P2_1/c$, $a = 16.6082(13)$ Å, $b = 16.4341(15)$ Å, $c = 16.3015(11)$ Å, $\beta = 90.227(8)°$, $V = 4449.3(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.326$ g/cm^3, 0.48 × 0.18 × 0.16 mm. Measured reflections 55 780, independent reflections 7479 ($R_{int} = 0.0770$), θ range 2.75−24.71°, refinement against F^2 with all data, $R_1 = 0.0411$ ([$I > 2\sigma(I)$]), w$R_2 = 0.1096$. There are two independent molecules one of which shows rotational disorder in the cyclo-P_5 part. **4**: $C_{34}H_{58}Fe_2P_4$, $M_r = 702.4$, monoclinic space group $P2_1/m$, $a = 10.4933(11)$ Å, $b = 14.0126(12)$ Å, $c = 12.9439(11)$ Å, $\beta = 103.621(7)°$, $V = 1849.7(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.261$ g/cm^3, 0.40 × 0.32 × 0.21 mm. Measured reflections 5360, independent reflections 4245 ($R_{int} = 0.0162$), θ range 2.18−27.50°, refinement against F^2 with all data, $R_1 = 0.0404$ ([$I > 2\sigma(I)$]), w$R_2 = 0.1076$. Data were collected on a Stoe IPDS (compounds **2** and **3**) and a Siemens P4 (compound **4**) diffractometer at 293 K. Structure solutions by direct methods, SIR 92 (Giacovazzo et al. 1993), least-squares refinement: SHELXL-97.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Graduierten-kolleg: “Phosphorus Chemistry as a Link between Different Chemical Disciplines” for financial support.

Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles and figures giving additional views of **2**−**4** (24 pages). Ordering information is given on any current masthead page.

OM9801148

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