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Supplementary Material Available: Table SI consists of final positional parameters with estimated standard deviations and B_{eq} (4 pages). Ordering information is given on any current masthead page.

Unprecedented Rearrangement of a Diphosphene $\eta^1\eta^2$-Bonded to Iron. Synthesis and X-ray Structure of Fe_4 Complexes Containing Either a μ_4 Spiro Phosphorus Atom or a 1,1,2-Trimetalladiphosphorus Ligand $>$P=P—

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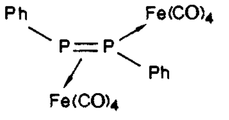
Free and complexed diphosphenes exhibit an interesting and diversified reactivity which has been the subject of numerous articles.[1] In contrast very few papers deal with their thermal behavior. Indeed thermolysis of the dinuclear $\eta^1\eta^1$-$[(CO)_5M]_2$-$(Me_3Si)_2CH$—P=P—$CH(SiMe_3)_2$ (M = Cr, W) or trinuclear $\eta^1\eta^2\eta^1$-$[(CO)_5Cr]_3$Ph—P=P—Ph complexes proceeds only with partial decomplexation and leads to the corresponding mononuclear η^1- or dinuclear $\eta^1\eta^1$-diphosphene complexes, $[(CO)_5M]$-$(Me_3Si)_2CH$—P=P—$CH(SiMe_3)_2$ (M = Cr, W)[2] or $[(CO)_5Cr]_2$Ph—P=P—Ph,[3] respectively.

Because of the better tendency of group 8 complexes to form clusters, we investigated the thermolytic behavior of the $\eta^1\eta^2$-diiron diphosphene **1**,[4] expecting unusual rearrangements of the diphosphene ligands assisted by cluster formation.



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We report here (i) the preparation and X-ray structure of the original, and unique so far, complex **3** in which one P atom acts as a spiro center between three cyclic fragments, (ii) the synthesis of a tetrairon cluster **4** possessing four phosphorus atoms in four different coordination modes, and (iii) the first structural information on a P=P unit $\mu_4\eta^2$ bonded.

Compound **1** was refluxed in benzene for 1 h, infrared monitoring showing the disappearance of **1**. The solvent then was removed, and a chromatography on Florisil (eluent hexane/toluene, 1/1) was allowed to separate the derivative $Fe_3(CO)_9(\mu$-$PPh)_2$, **2**,[5] isolated as traces from the major product $[Fe_4(CO)_{12}(PPh)_4]$, **3**. **3** was isolated in 70% yield as air-stable yellow crystals.[6] The first indication of an unusual structure came from the $^{31}P\{^1H\}$ NMR spectrum which appeared as an ABCX system. Computer simulation by routine methods afforded the following parameters: P_X δ 440.5, P_A δ 138.6, P_B δ 136.5, P_C δ 122.7 ppm ($J_{P_XP_A} = 95.7$, $J_{P_XP_B} = 249.5$, $J_{P_CP_X} = 175.7$, $J_{P_AP_B} = 1.7$, $J_{P_AP_C} = 41.4$, $J_{P_BP_C} = 99.8$ Hz). The structure of the complex was solved by single-crystal X-ray diffraction,[7] and one of the two independent molecules is shown in Figure 1. It consists of a spiranic molecule with one of the four phosphorus atoms P(1) acting as a μ_2 spiro center linked to two $Fe(CO)_3$ moieties and two phosphorus atoms, P(3) and P(4). This is the first example of such a derivative in which a P atom is the joining center between one three-membered P(1)Fe(1)Fe(2) and two four-membered P(1)P(4)Fe(4)P(3) and P(1)P(3)Fe(3)P(4) rings.[8] All the phosphorus atoms occupy a conventional phosphido bridging position between $Fe(CO)_3$ groups. The phosphorus–phosphorus distances are in the range expected for P–P single bonds: P(1)–P(3) = 2.250 (2) and 2.300 (2) Å, P(1)–P(4) = 2.245 (2) and 2.247 (2) Å. These data suggest the following attributions for the ^{31}P NMR spectrum; P_X = P(1), P_A = P(2), P_B or P_C = P(3), P_C or P_B = P(4).

Heating compound **3** at a higher temperature in refluxing xylene or direct heating of **1** in the same solvent for 1 h afforded a new complex **4**. After removal of the volatile products followed by chromatography on Florisil (eluent hexane/toluene, 1/1), **4** is obtained as air-stable black crystals by crystallization in CH_2Cl_2/C_5H_{12} at -20 °C (yield, 30% in each case). The IR spectrum of **4** in the ν_{CO} stretching region gives evidence of terminal carbonyl groups only. Mass spectrometry (m/z = 936 with successive loss of 10 CO groups) and chemical analysis[10] are in good agreement with a $(CO)_{10}Fe_4(PPh)_4\cdot{}^1/_2C_5H_{12}$ formulation.

The structure of **4** was determined by single-crystal X-ray diffraction[11] and is illustrated in Figure 2. **4** consists of a metallic slightly distorted square containing four iron atoms, two of them being surrounded by two terminal carbonyl groups and the other two by three terminal carbonyl groups. To this square is coordinated a phosphanediyl group PhP(1) acting as a four-electron donor. All four P(1)–Fe bond lengths are virtually the same. The phosphorus atom P(2) is bonded to two phenyl groups and to the two adjacent $Fe(CO)_2$ groups.

The main feature of interest in the molecule involves the P(3)P(4) fragment. Each of the two phosphorus atoms is coordinated to an $Fe(CO)_2$ and an $Fe(CO)_3$ moieties. Furthermore the phosphorus atom P(3) is linked to a phenyl group. The

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[1] For a general review, see: (a) Cowley, A. H. *Polyhedron* **1984**, *3*, 389. (b) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 924.

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[4] (a) Mathieu, R.; Caminade, A.-M.; Majoral, J.-P.; Attali, S.; Sanchez, M. *Organometallics* **1986**, *5*, 1914 and references therein. (b) Caminade, A.-M.; Majoral, J.-P.; Sanchez, M.; Mathieu, R.; Attali, S.; Grand, A. *Organometallics* **1987**, *6*, 1459.

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[6] $Fe_4(CO)_{12}[PPh]_4$, **3**: IR ν_{CO} (hexane solution) 2067 (m), 2049 (s), 2027 (vs), 2002 (s), 1990 (m), 1972 (s) cm^{-1}, Ms, m/z = 992 with successive loss of 12 CO. Anal. Calcd for $C_{36}H_{20}Fe_4O_{12}P_4$: C, 43.55; H, 2.01. Found: C, 43.74; H, 1.77.

[7] Crystal data for **3**: $C_{36}Fe_4H_{20}O_{12}P_4$, Fw = 991.4, orthorhombic, space group $Pna2_1$, a = 20.781 (2) Å, b = 37.222 (3) Å, c = 10.378 (1) Å, V = 8027 (2) Å^3, D_x = 1.641 g·cm^{-3}, Z = 8. X-ray diffraction data were measured on a CAD4 Enraf-Nonius diffractometer by using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Reflections (5941) were collected up to 2θ = 47° by the θ–2θ scan technique. The crystal structure was solved by direct methods (SHELXS-86) (Sheldrick, G. M. SHELXS-86. *Program for Crystal Structure Solution*; University of Göttingen, FRG, 1986) and refined by full-matrix least-squares (SHELX 76) (Sheldrick, G. M. SHELX 76. *Program for Crystal Structure Determination*; University of Cambridge, England, 1976) by using the 5139 observed reflections $[F_o^2 > 2\sigma(F_o^2)]$ to the R factor of 0.024 including anisotropic temperature factors, except for phenyl rings refined as isotropic rigid groups (hydrogen atoms included but not refined).

[8] To our knowledge, only one other spiranic phosphorus species has been reported;[9] in this case phosphorus is included in two three-membered rings.

[9] Huttner, G.; Mohr, G.; Pritzlaff, B.; von Seyerl, J.; Zsolnai, L. *Chem. Ber.* **1982**, *115*, 2044.

[10] $Fe_4(CO)_{10}(PPh)_4\cdot{}^1/_2C_5H_{12}$, **4**: IR ν_{CO} (CH_2Cl_2 solution) 2057 (m), 2021 (s), 2011 (s), 1992 (m), 1962 (w). Anal. Calcd for $C_{36.5}H_{26}Fe_4O_{10}P_4$: C, 45.06; H, 2.67. Found: C, 44.92; H, 2.63.

[11] Crystal data for **4**: $(C_{34}Fe_4H_{20}O_{10}P_4)\cdot{}^1/_2C_5H_{12}$, Fw = 971.4, monoclinic, space group $P2_1/c$, a = 11.926 (1) Å, b = 16.631 (2) Å, c = 21.900 (3) Å, β = 103.09 (2)°, V = 4230.8 (9) Å^3, D_x = 1.525 g·cm^{-3}, Z = 4. The 6240 reflections were collected up to 2θ = 47° by the θ–2θ scan technique as for **3**. Same programs were used. Full-matrix refinement using 3332 reflections $[F_o^2 > 3\sigma(F_o^2)]$ led to the R factor of 0.025 (anisotropic temperature factors, isotropic phenyl rigid groups with hydrogen atoms not refined, isotropic solvent molecule).

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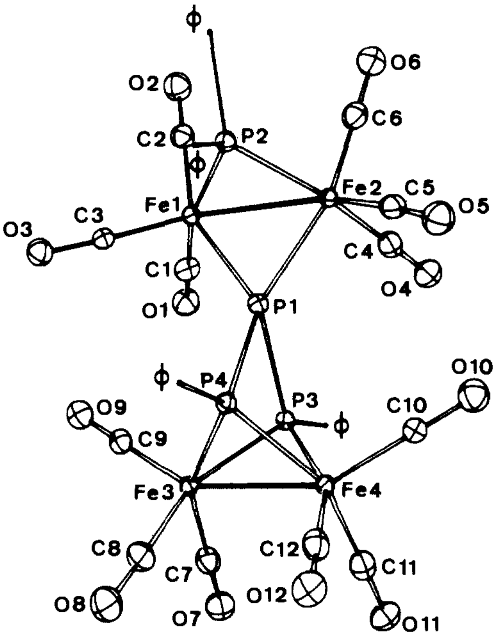

Figure 1. ORTEP view of **3**. Bond distances (Å) and angles (deg) of interest for the two independent molecules: Fe(1)–Fe(2), 2.6918 (9), 2.655 (1); Fe(3)–Fe(4), 2.629 (1), 2.619 (1); Fe(1)–P(1), 2.224 (1), 2.171 (1); Fe(1)–P(2), 2.243 (1), 2.252 (1); Fe(2)–P(1), 2.232 (1), 2.162 (2); Fe(2)–P(2), 2.199 (1), 2.205 (1); Fe(3)–P(3), 2.198 (1), 2.249 (2); Fe(3)–P(4), 2.245 (1), 2.224 (2); Fe(4)–P(3), 2.184 (2), 2.185 (1); Fe(4)–P(4), 2.206 (2), 2.184 (1); P(1)–P(3), 2.250 (2), 2.300 (2); P(1)–P(4), 2.245 (2), 2.247 (2); Fe(1)–P(1)–Fe(2), 74.34 (5), 75.57 (5); P(3)–P(1)–P(4), 69.37 (6), 67.57 (6); Fe(3)–P(3)–Fe(4), 73.73 (5), 72.38 (5); Fe(3)–P(4)–Fe(4), 72.40 (5), 72.90 (5); Fe(1)–P(2)–Fe(2), 74.59 (4), 73.13 (4).

relatively short P(3)–P(4) distance, 2.126 (2) Å, compares well with the values found in various diphosphene complexes η^2-bonded.[1a,4] Therefore the P(3)P(4) fragment can be described as the first $\mu_4\eta^2$ complexed $\sigma^2\lambda^3,\sigma^4\lambda^5$ diphosphorus unit (—P═P<) which promises to lead to new reactivity patterns.

The $^{31}P\{^1H\}$ NMR spectrum confirms the presence of four phosphorus atoms—each of them being coupled with the other three— and is assigned as follows: P(3) δ 117.3 (d, d, d $J_{P_3P_4} = 357$, $J_{P_3P_2} = 5$, $J_{P_3P_1} = 20$ Hz), P(4) δ 169.5 (d, d, d $J_{P_4P_3} = 357$, $J_{P_4P_2} = 5$, $J_{P_4P_1} = 22$ Hz), P(2) δ 264.7 (d, t $J_{P_2P_3} = 5$, $J_{P_2P_4} = 5$, $J_{P_2P_1} = 22$ Hz), P(1) δ 515.7 (d, t $J_{P_1P_3} = 20$, $J_{P_1P_4} = J_{P_1P_2} = 22$ Hz). The large $J_{P_3P_4}$ value suggests that atoms P(3) and P(4) are doubly bonded.

In summary thermal activation of **1** leads to a succession of unexpected and interesting transformations: the transformation of **3** implies without prejudging the order of reactions the cleavage of the phosphorus–phosphorus double bond of the diphosphene ligand with the insertion of the $Fe_2(CO)_6$ fragment, the migration of one phenyl group from one phosphorus to another phosphorus group, and the insertion of a "P" fragment into the two phosphorus of a second $Fe_2(CO)_6(PPh)_2$ entity. The precise mechanism of these rearrangements is difficult to establish, but several examples of migration of phenyl group from phosphorus to a metal center have been described in the literature, and it can be suggested that this migration is metal assisted.[12] To our knowledge this is the first case where migration occurs from a phosphorus atom to another phosphorus atom.

Finally the 3 → 4 transformation implies the departure of two CO ligands, the P(1)P(4) or P(1)P(3) bond breaking with simultaneous association of the two Fe_2 fragments and generation of a P═P—Ph fragment.

To conclude, this unprecedented thermal activation of a diphosphene complex is probably the consequence of a synergic effect between the diphosphene ligand and $Fe(CO)_n$ units rearrangements.

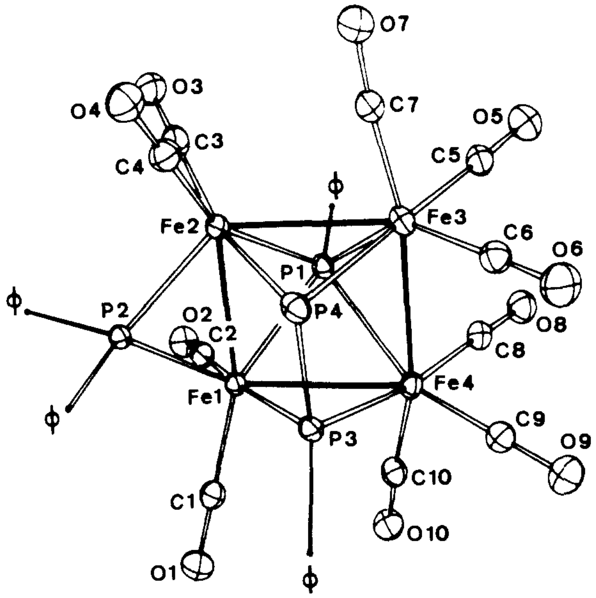

Figure 2. ORTEP view of **4**. Bond distances (Å) and angles (deg) of interest: Fe(1)–Fe(2), 2.7249 (2); Fe(2)–Fe(3), 2.726 (1); Fe(3)–Fe(4), 2.824 (1); Fe(4)–Fe(1), 2.7601 (9); Fe(1)–P(1), 2.266 (2); Fe(2)–P(1), 2.250 (2); Fe(3)–P(1), 2.241 (2); Fe(4)–P(1), 2.261 (2); Fe(1)–P(2), 2.196 (2); Fe(2)–P(2), 2.189 (2); Fe(1)–P(3), 2.205 (2); Fe(4)–P(3), 2.247 (2); Fe(2)–P(4), 2.297 (2); Fe(3)–P(4), 2.342 (2); P(3)–P(4), 2.126 (2); Fe(1)–Fe(2)–Fe(3), 91.12 (3); Fe(2)–Fe(3)–Fe(4), 89.58 (3); Fe(3)–Fe(4)–Fe(1), 88.53 (3); Fe(4)–Fe(1)–Fe(2), 90.95 (3); Fe(1)–P(1)–Fe(3), 119.41 (7); Fe(2)–P(1)–Fe(4), 120.24 (7); Fe(1)–P(2)–Fe(2), 76.84 (5); Fe(1)–P(3)–Fe(4), 76.64 (6); Fe(2)–P(4)–Fe(3), 71.95 (6); C(29)–P(3)–P(4), 113.1 (1).

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and interatomic bond distances and angles for **3** and **4** (7 pages); tables of observed and calculated structure factors for **3** and **4** (25 pages). Ordering information is given on any current masthead page.

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Effect of Molecular Dimension on the Rate of Return Electron Transfer within Photoproduced Geminate Radical Ion Pairs

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Photoinduced electron transfer to form radical ion pairs and separated radical ions is a common process,[1] and numerous chemical reactions of the so-formed radical ions have been identified.[1] The quantum yields of these reactions vary over a very wide range,[2] mainly because of differences in the rate con-

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