Unexpected formation of triple-deckers: bis(cyclopentadienyliron)-μ:η$^{4:4}$-tetraphosphabutadiene complexes

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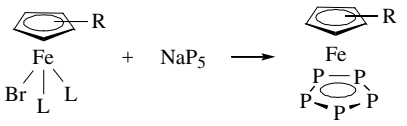
10.1070/MC2003v013n05ABEH001814

Sodium pentaphosphacyclopentadienide NaP_5 reacts with iron half-sandwich complexes to form pentaphosphaferrocenes and triple-decker complexes of iron with a P_4 middle deck.

According to the isolobal concept,[1] the cyclopentadienide anion $C_5H_5^-$ and the pentaphosphacyclopentadienide anion P_5^- are isolobal compounds and can act as six-electron donors to form sandwich complexes. For example, in the reaction of lithium pentaphosphacyclopentadienide LiP_5 with iron(II) chloride and lithium pentamethylcyclopentadienide, the sandwich complex pentamethylpentaphosphaferrocene was obtained.[2] Recently, the unusal decaphosphatitanium dianion $[Ti(P_5)_2]^{2-}$ was prepared by the reaction of P_4 with highly reduced titanium complexes.[3]

The presence of lone electron pairs at the phosphorus atoms may cause essential differences in the reactivity of the pentaphosphacyclopentadienide anion and its carbon analogue. Here we report an example of this difference, which was observed in the reaction of sodium pentaphosphacyclopentadienide with half-sandwich complexes of iron.

Previously, we found that NaP_5 reacts with half-sandwich complexes of iron containing tertiary phosphine ligands to form pentaphosphaferrocenes.[4]



1a,**b** **2a**,**b**

L = PMe_3, CO
a $Cp^R = C_5Me_5$
b $Cp^R = 1,3\text{-}Bu^t_2Cp$

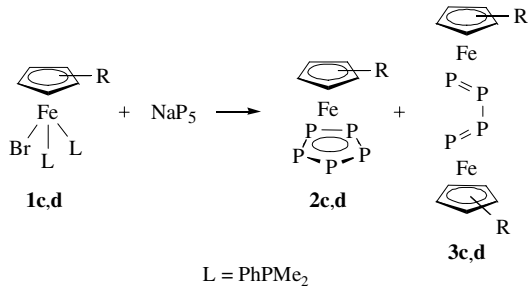
However, when trimethylsilylcyclopentadienyl iron complexes were employed in this reaction, we observed the formation of two products, the ratio between which was dependent on the stoichiometry. When iron complexes **1c**,**d** and NaP_5 reacted in a ratio of 1:1 or when an excess of NaP_5 was employed, only pentaphosphaferrocenes **2c**,**d** were obtained, which were purified by column chromatography and characterized by ^1H, ^{31}P and ^{13}C NMR spectroscopy. In the ^{31}P NMR spectra, sharp singlets at 168 ppm for **2c** and at 173 ppm for **2d** were observed.

However, when NaP_5 was treated with an excess of **1c**,**d**, a mixture of pentaphosphaferrocenes **2c**,**d** and bis(cyclopentadienyliron)-μ:η$^{4:4}$-tetraphosphabutadiene complexes **3c**,**d** was obtained, which can be separated by column chromatography.† Compounds **3c**,**d** were characterised by NMR spectroscopy, and the crystal structure of **3c** was characterised.‡

Triple-decker complexes with a P_4 fragment as a middle deck were also prepared by the photolysis of $[\{Cp^RFe(CO)_2\}_2]$ ($Cp^R = C_5H_3\text{-}1,3\text{-}Bu^t_2$, C_5Me_5) and white phosphorus; however, the yield was very low (11%).[5]

The P_4 skeleton has a trapezoidal shape with two short [P(1)–P(2), 2.090 Å and P(3)–P(4), 2.093 Å] and one long [P(2)–P(3), 2.436 Å] phosphorus–phosphorus bonds. The iron-phosphorus bond lengths can also be divided into two groups: short [Fe–P(1), Fe–P(4)] and long [Fe–P(2), Fe–P(3)].

Broad singlets were observed at 104 ppm in the ^{31}P NMR spectra of **3c**,**d** at room temperature, indicating the occurrence of a dynamic process in solution. At a low temperature (167 K),



1c,**d** **2c**,**d** **3c**,**d**

L = $PhPMe_2$
c $Cp^R = 1,3\text{-}(Me_3Si)_2C_5H_3$
d $Cp^R = 1,3,4\text{-}(Me_3Si)_3C_5H_3$

this signal splits into two broad singlets at 300 and –120 ppm with line half-widths of 15 Hz, indicating two different kinds of phosphorus atoms. A further decrease of the temperature was impossible because of the freezing point of the solvent (CD_2Cl_2).

† The NaP_5 solution was prepared according to the published procedure.[7] Iron complex **1c** or **1d** (3-fold molar excess) was added to a solution of NaP_5 (10^{-2} M, 50 ml) in diglyme, and the reaction mixture was stirred for 1 h at room temperature. After evaporation of the solvent, the residue was purified by chromatography on silica gel with light petroleum as an eluent. Green pentaphosphaferrocene **2c** or **2d** was eluted first, followed by brown **3c** or **3d**. Yields: 9% (**2c**), 12% (**2d**); 64% (**3c**) and 55% (**3d**). Crystals of **3c** were grown from pentane at –60 °C.

2c: mp 84 °C. ^1H NMR (400 MHz, C_6D_6) δ: 0.29 (s, 18H), 4.37 (br. s, 3H). ^{13}C NMR (100.695 MHz, C_6D_6) δ: 2.053 (Me–Si), 87.5, 88.2, 88.7 (C–Cp). ^{31}P NMR (161.975 MHz, C_6D_6) 167.8.

2d: mp 92 °C. ^1H NMR (400 MHz, C_6D_6) δ: 0.53 (s, 9H), 0.31 (s, 18H), 4.60 (s, 2H). ^{13}C NMR (100.625 MHz, C_6D_6) δ: 2.07, 0.97 (Me–Si), 87.1, 88.2 (C–Cp). ^{31}P NMR (161.975 MHz, C_6D_6) δ: 172.6.

3c: mp 58 °C. ^1H NMR (400 MHz, C_6D_6) δ: 0.26 (s, 18H), 4.32 (br. s). ^{13}C NMR (100.625 MHz, C_6D_6) δ: 2.06 (Me–Si), 87.7, 88.8, 88.9 (C–Cp). ^{31}P NMR (161.975 MHz, C_6D_6) δ: 104.0.

3d: mp 69 °C. ^1H NMR (400 MHz, C_6D_6) δ: 0.55 (s, 9H), 0.33 (s, 18H), 4.67 (s, 2H). ^{13}C NMR (100.625 MHz, C_6D_6) 2.09, 0.95 (Me–Si), 87.3, 88.1 (C–Cp). ^{31}P NMR (161.975 MHz, C_6D_6) δ: 104.9 (br.).

‡ *Crystal data for* **3c**: $C_{22}H_{42}Fe_2P_4Si_4$, M = 654.51, red brown needles, triclinic, space group $P\bar{1}$, a = 704.96(14), b = 1215.6(3), c = 2015.6(4) pm, α = 82.909(4)°, β = 87.089(4)°, γ = 74.160(3)°, V = 1.6488(6) nm^3, Z = 2, d_{calc} = 1.318 g cm^{-3}, λ(MoKα) = 71.073 pm, μ = 1.230 mm^{-1}, $2\theta_{max}$ = 58.54°, R_1 = 0.0996 and wR_2 = 0.1177 for 11004 collected and 7792 independent reflections, 457 parameters, maximal residual electron density of 0.67 and –0.45 eÅ^{-3}. Data were collected with a Siemens CCD (SMART) diffractometer. 885 reflections were used for the refinement of unit cell parameters. Empirical absorption correction was performed using the SADABS program.[4] The structures were solved by direct methods (SHELXS[4]), and all non-hydrogen atoms were refined anisotropically; H atoms were located by difference maps and refined isotropically.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 201801. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

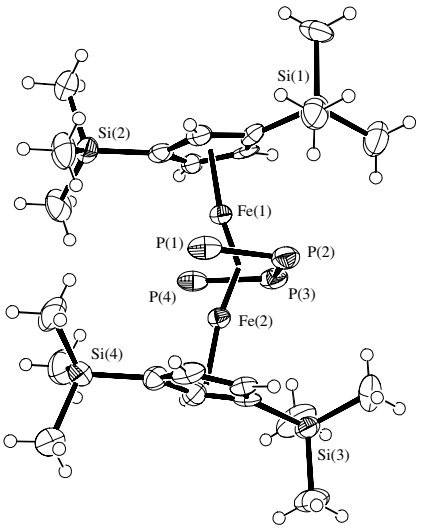
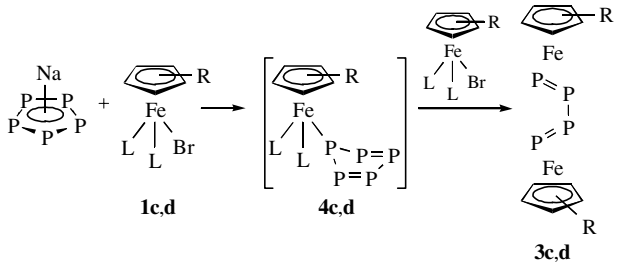


Figure 1 Molecular structure of **3c**. Selected bond lengths (Å) and angles (°): Fe(1)–P(1) 2.255(1), Fe(1)–P(2) 2.329(1), Fe(1)–P(3) 2.308(1), Fe(1)–P(4) 2.275(1), Fe(2)–P(1) 2.265(1), Fe(2)–P(2) 2.318(1), Fe(2)–P(3) 2.324(1), Fe(2)–P(4) 2.261(1), Fe(1)–Fe(2) 2.603(1), P(1)–P(2) 2.090(2), P(2)–P(3) 2.436(2), P(3)–P(4) 2.093(2), P(1)···P(4) 3.550(2), P(1)–P(2)–P(3) 105.08(6), P(2)–P(3)–P(4) 105.79 (7).

Thus, the phosphorus–phosphorus coupling constants could not be determined.

For the formation of **3c**,**d** two possible routes can be proposed. Firstly, the major product, pentaphosphaferrocene **2c**,**d**, can react with starting compounds **1c**,**d**. However, we found that the reaction of **1c**,**d** with **2c**,**d** did not take place at room temperature or on heating in toluene. The second possible pathway is the formation of Fe–P_5 σ complex **4c**,**d**, which can react with **1c**,**d** to form products **3c**,**d**. The carbon analogue of **4c**,**d** was described previously.[6]



In summary, we have found that the reaction of half-sandwich complexes of iron with NaP_5 can proceed with the formation of triple-decker iron compounds containing a P_4 fragment as a middle deck.

V. M. acknowledges the support of the Sächsisches Ministerium für Wissenschaft und Kunst (SMWK, Az.: 4-7531.50-04-0361-01/11) and DFG (Az.: 436 RUS 17/60/01).

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Received: 18th June 2003; Com. 03/2140