Reactions of sodium pentaphosphacyclopentadienide with half-sandwich iron complexes

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Reactions of sodium pentaphosphacyclopentadienide NaP_5 with half-sandwich iron phosphine complexes gave pentaphosphaferrocenes or ferrocenes, depending on the nature and number of substituents in the cyclopentadienyl ring.

Key words: sodium pentaphosphacyclopentadienide, cyclopentadienyl complexes of iron, pentaphosphaferrocene.

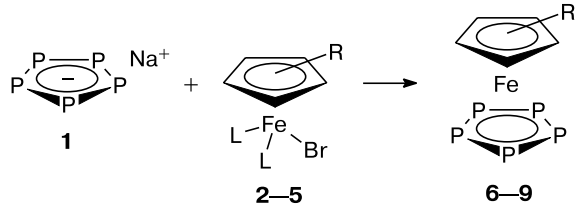
Use of principles of coordination self-assembly for construction of macromolecular compounds is a fast-developing line in coordination chemistry.[1—4] In connection with this, pentaphosphaferrocenes have a particular interest, due to presence of coplanar five P atoms creates prerequisites for design of various polymetallic systems and clusters. This has been clearly demonstrated with reactions of pentaphosphaferrocenes with a number of transition metal derivatives.[5—9]

However, the chemistry of pentaphosphaferrocenes has been mainly concerned with only two representatives of this class, namely, pentamethyl- and ethyl(tetramethyl)pentaphosphaferrocenes, owing to their accessibility. So far pentaphosphaferrocenes are prepared only by heating a mixture of iron cyclopentadienyl(carbonyl) complexes with white phosphorus in boiling xylene[10] or decalin.[7] However, this method fails to produce pentaphosphaferrocenes with fewer alkyl groups.[11] Other relevant methods[12,13] provide low yields of the target products and, consequently, have not found wide application.

Reactions of iron(II) derivatives with the pentaphosphacyclopentadienide anion, which is isolobal to the cyclopentadienide anion,[14] seem to be the most promising route to pentaphosphaferrocenes because of mild reaction conditions in this case, as illustrated with the preparation of pentamethylpentaphosphaferrocene.[15] Earlier, we have proposed a new, convenient method for the synthesis of pentaphosphaferrocenes from half-sandwich cyclopentadienyl complexes of iron and sodium pentaphosphacyclopentadienide and obtained for the first time 1,3-di-*tert*-butylpentaphosphaferrocene in high yield.[16] However, it still remains unclear how the yields of pentaphosphaferrocenes are influenced by such factors as the ligand bulkiness in the starting half-sandwich cyclopentadienyl complexes of iron and the bulkiness and number of substituents in the cyclopentadienyl ring.

To elucidate the influence of the nature of the leaving ligand on the formation of pentaphosphaferrocenes, we carried out a reaction of sodium pentaphosphacyclopentadienide (**1**) with half-sandwich iron complexes **2a—c** containing various phosphine ligands (Scheme 1). We found that the reaction rate largely depends on the nature of the phosphine ligand. For instance, heating to 70 °C is required for a reaction with trimethylphosphine complex **2a** to be completed, giving pentamethylpentaphosphaferrocene **6**.[16] At the same time, reactions with complexes

Scheme 1



Cp^R = Me_5C_5 (**2a—c**, **6**), Me_4C_5H (**3**, **7**), 1,3-$Bu^t_2C_5H_3$ (**4**, **8**), 1,3-$(Me_3Si)_2C_5H_3$ (**5**, **9**)
L = PMe_3 (**2a**), $PhPMe_2$ (**2b**, **3—5**), Ph_2PMe (**2c**)

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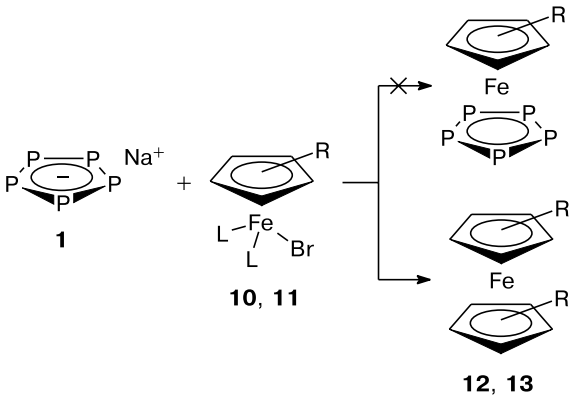
2b and **2c** (containing dimethyl(phenyl)phosphine and methyl(diphenyl)phosphine, respectively) occurred at room temperature. Thus, using cyclopentadienyl complexes of iron with Me_2PPh as a ligand in reactions with compound **1**, one can obtain new pentaphosphaferrocenes.

An analogous reaction of sodium pentaphosphacyclopentadienide **1** with iron complex **3** yielded earlier unknown tetramethylpentaphosphaferrocene **7** (see Scheme 1). The reaction pathway was different in the case of half-sandwich complexes **10** and **11** containing only three methyl groups (in positions 1, 2, and 3 and 1, 2, and 4 of the cyclopentadienyl ring, respectively). The sole products were the corresponding hexamethylferrocenes **12** and **13** (Scheme 2), probably due to transfer of the pentaphosphacyclopentadienyl ring.[13]

Scheme 2



Cp^R = 1,2,3-$Me_3C_5H_2$ (**10**, **12**), 1,2,4-$Me_3C_5H_2$ (**11**, **13**)
L = $PhPMe_2$ (**10**, **11**)

The decisive influence of the bulkiness of the substituents on the formation of pentaphosphaferrocenes was proved through a reaction of sodium pentaphosphacyclopentadienide **1** with half-sandwich iron complexes **4** and **5** containing only two bulky substituents in the cyclopentadienyl ring. 1,3-Bis(trimethylsilyl)pentaphosphaferrocene **9**, a new representative of the pentaphosphaferrocene series, was obtained in high yield.

Thus, we demonstrated that in the reactions of half-sandwich phosphine complexes of iron with sodium pentaphosphacyclopentadienide, the rate is determined by the nature of the phosphine ligand. The formation of pentaphosphaferrocenes is possible only when the starting half-sandwich iron complexes contain four methyl or two *tert*-butyl (trimethylsilyl) groups.

Experimental

All manipulations for the preparation of the starting reagents, the synthesis and the isolation of products were carried out in an inert atmosphere in standard Schlenk flasks. Solvents were distilled from Na/benzophenone immediately before use. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker MSL-400 instrument (400 (^1H), 100.6 (^{13}C), and 161.978 MHz (^{31}P)) in C_6D_6 with Me_4Si as the internal standard (^1H and ^{13}C) or with 85% H_3PO_4 as the external standard (^{31}P). The starting half-sandwich iron complexes **2**—**5**, **10**, and **11** were prepared according to a known procedure.[17]

Reactions of half-sandwich phosphine complexes 2—5 with sodium pentaphosphacyclopentadienide (1). A solution of bromobis[dimethyl(phenyl)phosphine](pentamethylcyclopentadienyl)iron (**2b**) (1.09 g, 0.002 mol) in THF was added to a 0.05 *M* solution of compound **1** in diglyme[18,19] (40 mL, 0.002 mol). The reaction mixture was stirred at ~20 °C. After 5 h, compound **1** was completely consumed (disappearance of the signal at δ 490 from the ^{31}P NMR spectrum). The mixture was evaporated to dryness in high vacuum and the residue was chromatographed on silica gel with light petroleum as an eluent. The green fraction was collected and concentrated to give pentamethylpentaphosphaferrocene (**6**) (0.51 g, 74%), m.p. 193 °C (*cf.* Ref. 10: m.p. 196 °C). Found (%): C, 34.24; H, 4.16; P, 44.23. $C_{10}H_{15}FeP_5$. Calculated (%): C, 34.72; H, 4.37; P, 44.77. ^1H NMR, δ: 1.08. ^{31}P NMR, δ: 153.

A number of pentaphosphaferrocenes were synthesized analogously. **1,2,3,4-Tetramethylpentaphosphaferrocene (7)** was obtained as a light green powder from a 0.05 *M* solution of compound **1** (40 mL, 0.002 mol) in diglyme and bromobis[dimethyl(phenyl)phosphine](1,2,3,4-tetramethylcyclopentadienyl)iron (**3**) (1.07 g, 0.002 mol). The yield was 0.51 g (77%), m.p. 124 °C (decomp.). Found (%): C, 32.14; H, 3.49; P, 46.12. $C_9H_{13}FeP_5$. Calculated (%): C, 32.57; H, 3.95; P, 46.66. ^1H NMR, δ: 1.06 (s); 3.71 (br.s). ^{31}P NMR, δ: 151 (s).

1,3-Di-*tert*-butylpentaphosphaferrocene (8) was obtained as a light green powder from a 0.05 *M* solution of compound **1** (40 mL, 0.002 mol) in diglyme and bromo(1,3-di-*tert*-butylcyclopentadienyl)bis[dimethyl(phenyl)phosphine]iron (**4**) (1.18 g, 0.002 mol). The yield was 0.52 g (67%), m.p. 112 °C (decomp.). Found (%): C, 40.06; H, 5.32; P, 39.66. $C_{13}H_{21}FeP_5$. Calculated (%): C, 40.24; H, 5.45; P, 39.91. ^1H NMR, δ: 1.06 (s); 3.71 (br.s). ^{31}P NMR, δ: 167 (s).

1,3-Bis(trimethylsilyl)pentaphosphaferrocene (9) was obtained as a light green powder from a 0.05 *M* solution of compound **1** (40 mL, 0.002 mol) in diglyme and [1,3-bis(trimethylsilyl)cyclopentadienyl](bromo)bis[dimethyl(phenyl)phosphine]iron (**5**) (1.24 g, 0.002 mol). The yield was 0.6 g (72%), m.p. 84 °C (decomp.). Found (%): C, 31.23; H, 4.88; P, 36.12. $C_{11}H_{21}FeP_5Si_2$. Calculated (%): C, 31.44; H, 5.04; P, 36.86. ^1H NMR, δ: 0.29 (s, 18 H); 4.37 (br.s, 3 H). ^{13}C NMR, δ: 2.053 (Me—Si); 87.5, 88.2, 88.7 (C_{Cp}). ^{31}P NMR, δ: 167.8 (s).

Reactions of half-sandwich phosphine complexes 10 and 11 with compound 1. A solution of bromobis[dimethyl(phenyl)phosphine](1,2,3-trimethylcyclopentadienyl)iron (**10**) (1.04 g, 0.002 mol) in THF was added to a 0.05 *M* solution of compound **1** (40 mL, 0.002 mol) in diglyme.[18,19] The reaction mixture was stirred at ~20 °C. After 5 h, compound **1** was completely consumed (disappearance of the signal at δ 490 from the ^{31}P NMR spectrum). The mixture was evaporated to dryness in high vacuum and the residue was chromatographed on silica gel with light petroleum as an eluent. The yellow fraction was collected and concentrated to give 1,2,3,1′,2′,3′-hexamethylferrocene (**12**) (0.36 g, 67%), m.p. 164 °C. Found (%): C, 71.03;

H, 8.13. $C_{16}H_{22}Fe$. Calculated (%): C, 71.12; H, 8.21. ^{1}H NMR, δ: 1.24 (s, 6 H); 1.36 (s, 3 H); 3.71 (br.s, 2 H).

An analogous reaction of bromobis[dimethyl(phenyl)phosphine](1,2,4-trimethylcyclopentadienyl)iron (**11**) with compound **1** gave 1,2,4,1′,2′,4′-hexamethylferrocene (**13**) (0.33 g, 61%), m.p. 134 °C. Found (%): C, 70.98; H, 8.26. $C_{16}H_{22}Fe$. Calculated (%): C, 71.12; H, 8.21. ^{1}H NMR, δ: 1.29 (s, 6 H); 1.16 (s, 3 H); 3.71 (br.s, 2 H).

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