Mendeleev Commun., 2002, 12(1), 1–2

Reactions of the pentaphospholide anion with half-sandwich complexes of iron: a new route to pentaphosphaferrocenes

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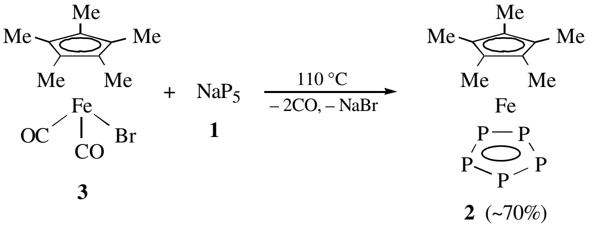
DOI: 10.1070/MC2002v012n01ABEH001517

Pentaphosphaferrocenes were prepared in good yields by the reaction of the pentaphospholide anion P_5^- with half-sandwich complexes of iron containing carbonyl groups or tertiary phosphine ligands.

The pentaphospholide anion P_5^-, which is an isolobal analogue of the cyclopentadienyl anion,[1] is of interest as a convenient reagent in organometallic and coordination chemistry.[2,3] However, only a few organometallic compounds with P_5 fragments were synthesised from NaP_5 **1**.[4,5] In particular, pentamethylpentaphosphaferrocene **2** was prepared in 12% yield by the reaction of **1** with iron(II) chloride and lithium pentamethylcyclopentadienide.[4]

Recently, we reported a new method for preparing **1** by the reaction of sodium metal with white phosphorus under the conditions of phase-transfer catalysis.[6] This simple method makes it possible to study the chemical behaviour of **1** towards various organometallic compounds. It was also of interest to develop a general high-yield route to pentaphosphaferrocenes and to determine the factors affecting the product yields. We based our approach on the well-known reaction of half-sandwich iron complexes with sodium cyclopentadienide.[7]

The reaction of **1** with pentamethylcyclopentadienyl(dicarbonyl)iron bromide† **3** in diglyme at 110 °C for 2 h gave pentamethylpentaphosphaferrocene **2** in ~70% yield.



3

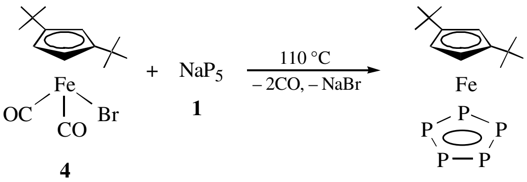
1

2 (~70%)

The structure of **2** was determined by ^1H and ^{31}P NMR spectroscopy and by a comparison with the published data.[8,9]

The reaction of **1** with 1,3-di-*tert*-butylcyclopentadienyl(dicarbonyl)iron bromide **4**† under similar conditions gave compound **5** in a yield of at most 5%.

The structure of **5** was determined by ^1H and ^{31}P NMR spectroscopy and mass spectrometry. This compound also was prepared by the interaction of $Cr(CO)_5PCl_3$ with $Cp''Fe(CO)_2K$ in a yield of about 10%.[10] The ^{31}P NMR spectrum exhibits a singlet at 167 ppm, and the ^1H NMR spectrum exhibits a singlet at 1.06 ppm due to methyl groups and a broad singlet at 3.71 ppm due to the protons of the cyclopentadienyl ring. Relative to tetra-*tert*-butylferrocene, the ^1H NMR signals are shifted by an average of 0.26 ppm.[11,12] The mass spectrum showed a peak of the molecular ion (*m*/*z* 388).



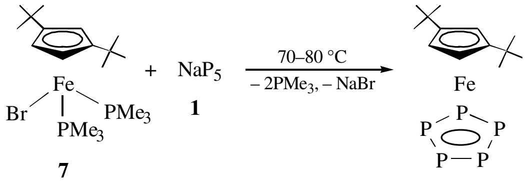
4

1

5 (~5%)

The main product of this reaction was 1,1′,3,3′-tetra-*tert*-butylferrocene **6**, which was identified by ^1H NMR spectroscopy and by a comparison of the physical properties with published data.[9] Clearly, at a reaction temperature of 110 °C, pentaphosphaferrocene **5** decomposes to give compound **6**.

We postulated that a decrease in the reaction temperature increases the yield of **5**. It is known that the replacement of CO ligands in organometallic compounds with better leaving groups, such as tertiary phosphines, facilitates the process of ligand exchange. Therefore, we treated **1** with 1,3-di-*tert*-butylcyclopentadienyl[bis(trimethylphosphine)]iron bromide **7**.‡ This reaction was conducted at 70 °C to form compound **5** in high yield (about 80%).



7

1

5

Thus, we developed a new route to pentaphosphaferrocenes based on the reaction of the pentaphospholide anion with half-sandwich iron compounds containing carbonyl or tertiary phosphine ligands.

V. Miluykov thanks the Deutsche Akademische Austauschdienst (A/00/06361) and the Sächsisches Ministerium für Wissenschaft und Kunst (SMWK, Az. 4-7531.50-04-0361-00) for financial support.

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† A solution of pentamethylcyclopentadienyl(dicarbonyl)iron bromide (260 mg, 0.8 mmol) in diglyme (20 ml) was added to a solution of NaP_5 in diglyme (40 ml, 0.02 mol dm^{-3}) at room temperature. The reaction mixture was stirred for 2 h at 110 °C. After cooling, the solvent was evaporated and the residue was purified by chromatography with light petroleum to give **2** (190 mg, 70%) as green crystals. ^1H NMR, δ: 1.08. ^{31}P NMR, δ: 153.

A solution of 1,3-di-*tert*-butylcyclopentadienyl(dicarbonyl)iron bromide (295 mg, 0.8 mmol) in diglyme (20 ml) was added to a solution of NaP_5 in diglyme (40 ml, 0.02 mol dm^{-3}) at room temperature. The reaction mixture was stirred for 2 h at 110 °C. After cooling, the solvent was evaporated and the residue was purified by chromatography with light petroleum to give **5** (15 mg, 5%) as green crystals and 1,1′,3,3′-tetra-*tert*-butylferrocene **6** (215 mg, 65%) as a yellowish orange powder (mp 193 °C; lit.,[9] 196 °C).

‡ A solution of 1,3-di-*tert*-butylcyclopentadienyl[bis(trimethylphosphine)]-iron bromide **7** (295 mg, 0.8 mmol) in diglyme (20 ml) was added to a solution of NaP_5 in diglyme (40 ml, 0.02 mol dm^{-3}) at room temperature. The reaction mixture was stirred for 2 h at 70 °C. After cooling, the solvent was evaporated and the residue was purified by chromatography with light petroleum to afford **5** (250 mg, 80%) as green crystals.

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Received: 17th September 2001; Com. 01/1843