Hexaphosphaferrocene $[\mathrm{Fe}(\eta^5\text{-}\mathrm{P_3C_2}t\mathrm{Bu_2})_2]$ as a Connecting Moiety in Oligomeric and Polymeric Compounds

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The hexaphosphaferrocene complex $[\mathrm{Fe}(\eta^5\text{-}\mathrm{P_3C_2}t\mathrm{Bu_2})_2]$ (**1**) derived from the corresponding 1,2,4-triphosphospholyl anion reacts with CuX (X = Cl, Br, I) in a 1 : 1 stoichiometry to give the isostructural, one-dimensional polymeric compounds $[\{\mathrm{Cu}(\mu_3\text{-X})\}_4\{\mathrm{Fe}(\mu,\eta^5{:}\eta^1\text{-}\mathrm{P_3C_2}t\mathrm{Bu_2})_2\}_2]_n$ (X = Cl (**2**), Br (**3**), I (**4**)), which display a unique sinusoidal $(\mathrm{CuX})_n$ ladder structure. In the reaction with CuI a second one-dimensional polymeric compound $[\{\mathrm{Cu_3}(\mu\text{-I})(\mu_3\text{-I})_2\}(\mathrm{CH_3CN})\{\mathrm{Fe}(\mu,\eta^5{:}\eta^1\text{-}\mathrm{P_3C_2}t\mathrm{Bu_2})(\mu_3,\eta^5{:}\eta^1\text{-}\mathrm{P_3C_2}t\mathrm{Bu_2})\}]_n$ (**5**) is formed. The reaction of **1** with CuX (X= Cl, Br, I) in a 1 : 2 stoichiometric ratio leads only in the case of CuCl to the formation of the new, oligomeric compound $[\{\mathrm{Cu}(\mu_3\text{-Cl})\}_4(\mathrm{CH_3CN})_2\{\mathrm{Fe}(\mu,\eta^5{:}\eta^1\text{-}\mathrm{P_3C_2}t\mathrm{Bu_2})_2\}_2]$ (**6**), whereas in the case of CuBr and CuI the polymeric compounds **3** and **5** were isolated. The reaction of **1** with $\mathrm{Ag[Al\{OC(CF_3)_3\}_4]}$ in a 1 : 1 stoichiometric ratio results in the formation of $[\mathrm{Ag}\{\mathrm{Fe}(\mu,\eta^5{:}\eta^1\text{-}\mathrm{P_3C_2}t\mathrm{Bu_2})_2\}_2][\mathrm{Al\{OC(CF_3)_3\}_4}]$ (**7**), which shows dynamic behaviour in solution.

Key words: Copper Halides, Phosphaferrocene Complexes, Phospholyl Ligands, Self Organisation, Silver Complexes

Introduction

The self organisation of discrete units to form supramolecular aggregates and networks is still a fascinating area of contemporary research [1]. Within this area of chemistry, phosphaferrocene complexes can be readily used as connecting moieties between metal cations, *e. g.* Cu(I) and Ag(I), because the lone pairs of electrons on the ring phosphorus atoms are available for further coordination [2]. The most famous representative of this class of compounds, the pentaphosphaferrocene, $[\mathrm{Cp^*Fe}(\eta^5\text{-}\mathrm{P_5})]$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$), which belongs to the group of compounds carrying “naked” phosphorus ligands, was widely used in coordination chemistry. In its reaction with CuCl, the formation of a one-dimensional polymeric compound $[\mathrm{Cu}(\mu\text{-Cl})\{\mathrm{Cp^*Fe}(\eta^5{:}\eta^1{:}\eta^1\text{-}\mathrm{P_5})\}]_n$ is observed [3]. Two-dimensional polymeric compounds $[\mathrm{CuX}\{\mathrm{Cp^*Fe}(\eta^5{:}\eta^1{:}\eta^1{:}\eta^1\text{-}\mathrm{P_5})\}]_n$ (X = Br, I) [3] were isolated in the case of both CuBr and CuI. Furthermore, by using the appropriate stoichiometry and working under diluted conditions, the formation of spherical, nano-sized complexes $[\{\mathrm{Cp^*Fe}(\eta^5{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}\mathrm{P_5})\}_{12}\{\mathrm{CuX}\}_{10}\{\mathrm{Cu_2X_3}\}_5\{\mathrm{Cu(CH_3CN)_2}\}_5]$ (X = Cl, Br) with fullerene-like symmetry was achieved [4], which possess a 90-vertex inorganic framework. The first example of a carbon-free analogue of the icosahedral $\mathrm{C_{80}}$ molecule was obtained when reacting the pentaphosphaferrocene with CuCl in presence of *ortho*-carborane [5]. The product of this reaction, $(\mathrm{C_2B_{10}H_{12}})@[\{\mathrm{Cp^*Fe}(\eta^5\text{-}\mathrm{P_5})\}_{12}(\mathrm{CuCl})_{20}]$, displays an icosahedral fullerene-like structure with an encapsulated carborane molecule. Another example for such an encapsulation reaction was obtained in the presence of $\mathrm{C_{60}}$, resulting in the huge spherical compound $\mathrm{C_{60}}@[\mathrm{Cu_{26}Cl_{26}L_2}\{\mathrm{Cp^*Fe}(\eta^5\text{-}\mathrm{P_5})\}_{13}\text{-}(\mathrm{CH_3CN})_9]$ ($\mathrm{L = H_2O}$), in which a whole fullerene molecule is surrounded by another inorganic spherical molecule [6]. The reaction of $[\mathrm{Cp^*Fe}(\eta^5\text{-}\mathrm{P_5})]$ with $[\mathrm{Ag\{Al(OC(CF_3)_3)_4\}}]$ results in the formation of a 1D

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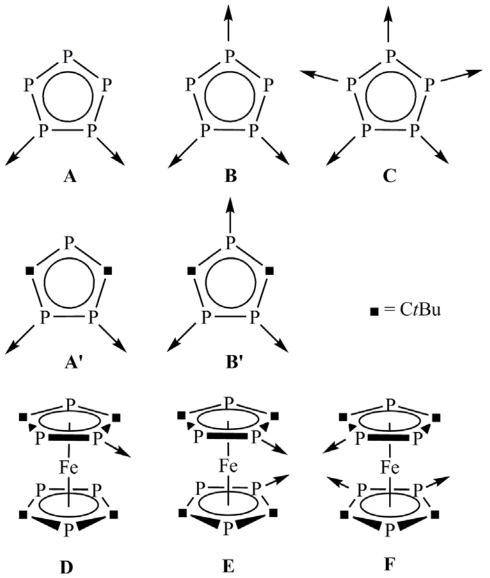
polymer, which depolymerises into the monocationic compound [{Cp*Fe(μ,η^5:η^2-P_5)}$_2$Ag]$^+$ when dissolved in CH_2Cl_2 [7]. This compound shows a dynamic behaviour in solution, changing from the monocationic to the dicationic species.

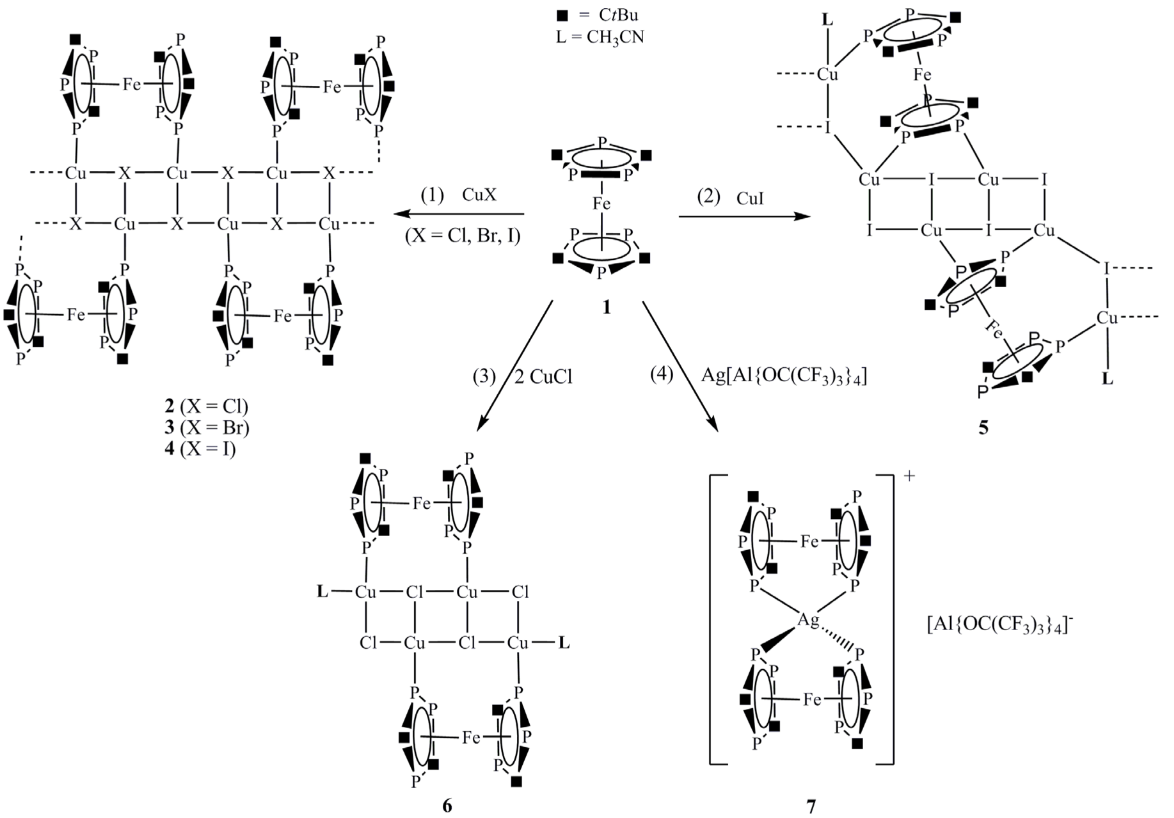
In the above mentioned examples with Cu(I) halides, the pentaphosphaferrocene shows either a 1,2- (type **A**), a 1,2,4- (type **B**) or a 1,2,3,4,5- (type **C**) coordination mode of the *cyclo*-P_5-ring. The related coordination types **A′** and **B′** can be expected, if, instead of employing the pentaphosphaferrocene as connecting unit, the isolobally related (P is isolobal with CR) triphosphaferrocenes [Cp^{R}Fe(η^5-P_3C_2tBu$_2$)] [Cp^R = Cp, η^5-C_5H_2tBu$_3$ (Cp‴)] would be used. The influence of the *t*Bu groups attached to the neighbouring carbon atoms on the potential coordination abilities of the triphosphaferrocenes was recently investigated [8]. However, only coordination mode **A′** was found so far. Furthermore, the question arose, which coordination types would occur towards Cu(I) or Ag(I) centres, if the hexaphosphaferrocene [Fe(η^5-P_3C_2tBu$_2$)$_2$] (**1**) is used [9], since this ligand carries six phosphorus atoms (three on each tri-phospholyl unit). As yet, the coordination ability of **1** has been studied only towards organometallic moieties. For example, in the reaction of **1** with [$Fe_2(CO)_9$] or [W(CO)$_5$thf] coordination type **D** was observed, whereas in the reaction with $Ru_3(CO)_{10}$ the hexaphosphaferrocene acts as chelating ligand displaying coordination mode **E** [10].

Herein we report on the synthesis and characterisation of the first one-dimensional polymers [{Cu(μ_3-X)}$_4${Fe(μ,η^5:η^1-P_3C_2tBu$_2$)$_2$}$_2$]$_n$ (X = Cl (**2**), Br (**3**), I (**4**)), [{Cu_3(μ-I)(μ_3-I)$_2$}(CH_3CN){Fe(μ,η^5:η^1-P_3C_2tBu$_2$)(μ_3,η^5:η^1-P_3C_2tBu$_2$)}]$_n$ (**5**), and the oligomeric compound [{Cu(μ_3-Cl)}$_4$(CH_3CN)$_2$-{Fe(μ,η^5:η^1-P_3C_2tBu$_2$)$_2$}$_2$] (**6**) formed in the reactions of hexaphosphaferrocene **1** with Cu(I) halides. Furthermore, we describe the synthesis and discuss the NMR spectroscopic data of the coordination dimer [Ag{(Fe(μ,η^5:η^1-P_3C_2tBu$_2$)$_2$}$_2$][Al{OC(CF_3)$_3$}$_4$] (**7**), which was obtained from the reaction of **1** with Ag[Al{OC(CF_3)$_3$}$_4$].



Results and Discussion

Complexes **2**–**6** are formed in the reaction of **1** with CuX (X = Cl, Br, I) in solvent mixtures of dichloromethane and acetonitrile at r. t. by slow diffusion reactions (Scheme 1). They are stable under dinitrogen, and the crystals of **2**–**5** are insoluble in common solvents, whereas **6** dissolves under decomposition in 1 : 1 mixtures of CH_2Cl_2 and CH_3CN. The products **2**, **3** and **4** can be obtained by reacting the hexaphosphaferrocene and the copper halide in a 1 : 1 stoichiometric ratio. They consist of one-dimensional, polymeric (CuX)$_n$ ladder structures, coordinated by the hexaphosphaferrocene molecules **1**, which act as chelating ligands in the already known 1,1′-coordination mode. Double-strand (CuX)$_n$ staircase structures are well known in literature [11], but in this case, the 1D polymeric (CuX)$_n$ ladder shows a unique sinusoidal form, due to the steric influence of the two *tert*-butyl groups on the carbon atoms in the phospholyl ligand. In the 1 : 1 stoichiometric reaction of **1** with CuCl and CuBr, the polymeric compounds **2** and **3** are formed exclusively, whereas in the reaction with CuI an additional product (**5**) is formed. The molecular structure of **5** displays an irregular (CuI)$_n$ chain, which is coordinated by the hexaphosphaferrocenes. The CuI chain consists of (Cu_4I_4) stairs, which are interconnected by {(LCu)$_2I_2$} four-membered rings (L = CH_3CN). In compound **5**, the hexaphosphaferrocenes again act as chelating ligands, but in a new 1,2,1′-coordination mode. When reacting **1** with CuX (X = Cl, Br, I) in a 1 : 2 stoichiometric ratio, only in the case of X = Cl a new oligomeric compound (**6**) was obtained, whereas in the cases of X = Br, I compounds **3** and **5** were formed. The molecular structure of **6** consists of a (Cu_4Cl_4) stair, which is coordinated by two hexaphosphaferrocenes in a 1,1′-coordination mode and by two acetonitrile ligands. The



Scheme 1. Formation of coordination polymers and oligomers from **1** upon reaction with CuX (X = Cl, Br, I) and Ag[Al{OC(CF_3)$_3$}$_4$]. (1) + CuX (X = Cl, Br, I), 1 : 1 stoichiometry, CH_2Cl_2/CH_3CN; (2) + CuI, 1 : 1 stoichiometry, CH_2Cl_2/CH_3CN; (3) + CuCl, 1 : 2 stoichiometry, CH_2Cl_2/CH_3CN; (4) + Ag[Al{OC(CF_3)$_3$}$_4$], 1 : 1 stoichiometry, CH_2Cl_2.

formation of Cu_4X_4 stairs (X = Cl, Br, I) and of (CuI)$_2$ four-membered rings as observed in **5** is well known in the literature [11, 12].

Crystals of **7** are formed in the reaction of **1** with Ag[Al{OC(CF_3)$_3$}$_4$] in a 1 : 1 stoichiometric ratio. Although the determination of the molecular structure of **7** was hampered, because all crystals of **7** from several independent reactions were pseudo-merohedrically twinned, the refinement indicated that the silver cation is coordinated by two hexaphosphaferrocenes (**1**), resulting in a dimeric monocationic compound (Scheme 1), in which **1** shows most likely the known 1,1′ coordination mode. In contrast to the obtained polymeric compounds **2**–**5**, **7** is soluble in CH_2Cl_2 and shows a dynamic behaviour in solution.

*The reaction of **1** with CuX (X = Cl, Br, I) in a 1 : 1 stoichiometric ratio*

The 1D-polymeric compounds [{Cu(μ_3-Cl)}$_4$-{Fe(μ,η^5:η^1-$P_3C_2t$$Bu_2$)$_2$}$_2$]$_n$ (**2**), [{Cu(μ_3-Br)}$_4$-{Fe(μ,η^5:η^1-$P_3C_2t$$Bu_2$)$_2$}$_2$]$_n$ (**3**) and [{Cu(μ_3-I)}$_4$-{Fe(μ,η^5:η^1-$P_3C_2t$$Bu_2$)$_2$}$_2$]$_n$ (**4**) are isostructural. A section of their molecular structure is exemplified in Fig. 1, whereas Fig. 2 shows the unique sinusoidal form of the Cu-halide ladder structure of **2**.

2 is obtained only in low yield, whereas **3** and **4** can be isolated in moderate yield. The polymeric compounds **2**–**4** consist of a one-dimensional (CuX)$_n$ (X = Cl, Br, I) double-strand, which is coordinated from both sides by the hexaphosphaferrocene molecules **1**, which adopt a 1,1′-chelating coordination mode. One of the two neighbouring phosphorus atoms from each tri-phospholyl ligand coordinates to the copper atoms. The unique phosphorus atoms of the tri-phospholyl ligands do not coordinate due to their sterical hindrance caused by the neighbouring carbon atoms, carrying *tert*-butyl substituents. These bulky substituents do not only hamper the coordination of the single P atoms, but they also cause a sinusoidal form of the copper halide ladder structure. To the best of our knowledge, these

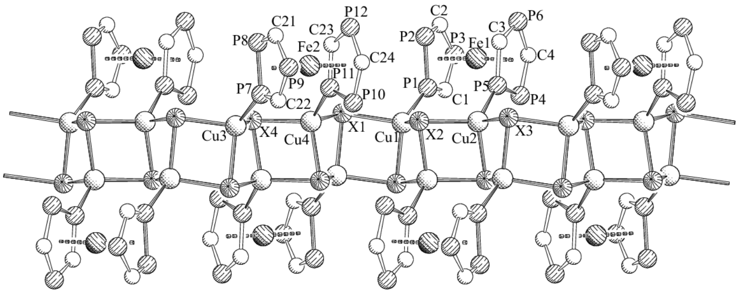


Fig. 1. Section of the 1D ladder structure of $[\{Cu(\mu_3\text{-}X)\}_4\{Fe(\mu,\eta^5{:}\eta^1\text{-}P_3C_2tBu_2)_2\}_2]_n$ (X = Cl (**2**); X = Br (**3**); X = I (**4**)). *tert*-Butyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **2**: Cu(1)–Cl(1) 2.437(3), Cu(2)–Cl(3) 2.390(3), Cu(1)–P(1) 2.173(4), Cu(2)–P(5) 2.188(4), P(1)–P(2) 2.109(5), P(4)–P(5) 2.118(5); Cl(2)–Cu(1)–P(1) 122.1(1), P(5)–Cu(2)–Cl(3) 114.6(1); for **3**: Cu(1)–Br(1) 2.520(1), Cu(2)–Br(3) 2.513(1), Cu(1)–P(1) 2.220(1), Cu(2)–P(5) 2.203(1), P(1)–P(2) 2.127(1), P(4)–P(5) 2.115(1); Br(2)–Cu(1)–P(1) 115.4(2), P(5)–Cu(2)–Br(3) 109.1(2); for **4**: Cu(1)–I(1) 2.664(1), Cu(2)–I(3) 2.657(1), Cu(1)–P(1) 2.248(3), Cu(2)–P(5) 2.250(3), P(1)–P(2) 2.124(3), P(4)–P(5) 2.119(3); I(2)–Cu(1)–P(1) 116.91(8), P(5)–Cu(2)–I(3) 106.99(8).

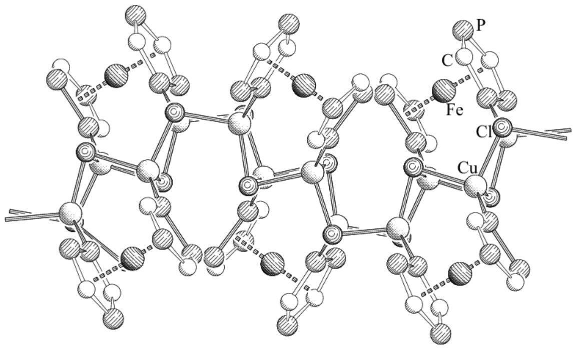


Fig. 2. View of the sinusoidal ladder structure of **2**. *Tert*-butyl groups are omitted for clarity.

are the first examples of sinusoidal copper halide ladder structures.

In comparison with **2**–**4** the 1D-polymeric compound $[\{Cu_3(\mu\text{-}I)(\mu_3\text{-}I)_2\}(CH_3CN)\{Fe(\mu,\eta^5{:}\eta^1\text{-}P_3C_2tBu_2)(\mu_3,\eta^5{:}\eta^1\text{-}P_3C_2tBu_2)\}]_n$ (**5**) shows a structurally different 1D-polymeric CuI strand. A section of the molecular structure is depicted in Fig. 3. It consists of (Cu_4I_4) stairs, which are connected *via* $[(LCu)_2I_2]$ four-membered rings (L = CH_3CN). The (Cu_nI_n) backbone is coordinated by hexaphosphaferrocene molecules, which once again act as chelating ligands, however, in the new 1,2,1′-coordination mode, in which the chelating hexaphosphaferrocene molecules coordinate *via* the two neighbouring phosphorus atoms of one tri-phospholyl ligand and *via* one of the two adjacent phosphorus atoms of the second tri-phospholyl ligand. The unique phosphorus atoms are again sterically hindered because of the *tert*-butyl-groups on the neighbouring carbon atoms and do not coordinate. Each copper atom is tetrahedrally coordinated, either through the coordination of three iodine atoms and one phosphorus atom (copper atoms in the $(CuI)_4$ stairs) or *via* two iodine atoms, one phosphorus atom and one acetonitrile ligand (copper atoms in the $(CuI)_2$ ring). Even when the hexaphosphaferrocenes act as chelating ligands, the tri-phospholyl rings remain planar, and they become even more parallel (the tilt angles are 5.8 and 6.0° in **2**, 4.5 and 5.6° in **3**, 4.5 and 4.9 in **4** and 4.7° in **5**) than in the uncoordinated molecule **1** (8°) [9].

The Cu–X bond lengths [X = Cl: 2.336(1)–2.490(1) Å (**2**); X = Br: 2.458(1)–2.532(1) Å (**3**);

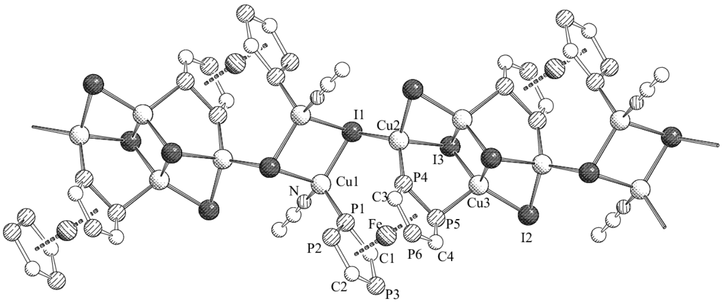


Fig. 3. Section of the 1D-polymeric structure of **5**. *tert*-Butyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)–I(1) 2.645(1), Cu(2)–I(1) 2.623(1), Cu(2)–I(3) 2.796(1), Cu(3)–I(3) 2.604(1), Cu(3)–I(2) 2.564(1), Cu(2)–I(2) 2.620(1), Cu(1)–P(1) 2.255(1), Cu(2)–P(4) 2.254(1), Cu(3)–P(5) 2.423(1), P(1)–P(2) 2.115(1), P(4)–P(5) 2.113(1); I(1)–Cu(1)–N 104.6(3), N–Cu(1) –P(1) 108.5(4), I(3)–Cu(3)–P(5) 101.64(9), I(1)–Cu(2)–P(4) 121.8(1).

X = I: 2.611(1) – 2.702(1) Å (**4**), X = I: 2.564(1) – 2.796(1) Å (**5**)] are within the expected range [13, 14]. The Cu–P distances are between 2.173(1) and 2.190(1) Å in **2**, 2.203(1) and 2.229(1) Å in **3**, 2.248(3) and 2.252(3) Å in **4**, and 2.254(1) Å and 2.423(1) Å in **5**. The bond lengths between the two neighbouring phosphorus atoms in the coordinated hexaphosphaferrocenes [2.109(1) – 2.118(1) Å in **2**, 2.103(1) – 2.137(1) Å in **3**, 2.119(3) – 2.126(3) Å in **4**, and 2.115(1) – 2.113(1) Å in **5**] are comparable to those in uncoordinated **1** (2.112(5) Å) [9]. Interestingly, the chelating coordination has a small influence on the distances between the iron atom and the P and C ring atoms of **1** [Fe–P: 2.333(1) – 2.387(1) Å in **2**, 2.332(1) – 2.380(1) Å in **3**, 2.328(3) – 2.388(3) Å in **4**, 2.333(1) – 2.399(1) Å in **5**; Fe–C: 2.174(1) – 2.256(1) Å in **2**, 2.161(1) – 2.252(1) Å in **3**, 2.193(10) – 2.219(9) Å in **4**, and 2.184(1) – 2.253(1) Å in **5**] in comparison to the uncoordinated sandwich complex **1** [Fe–P: 2.330(3) – 2.359(3); Fe–C: 2.197(11), 2.222(12)]. The average Fe–P distance becomes slightly longer upon coordination, whereas the Fe–C distances are partly elongated, but partly also shortened compared to those in **1**.

*The reaction of **1** with CuX (X = Cl, Br, I) in a 1 : 2 stoichiometric ratio*

The applied 1 : 2 stoichiometric ratio between the hexaphosphaferrocene **1** and CuX (X = Cl, Br, I) results in the formation of the already described compounds **3** and **5** for X = Br, I, however, in case of X = Cl green, parallelepiped-shaped crystals of the poorly soluble oligomeric compound [{Cu(μ_3-Cl)}$_4$(CH_3CN)$_2${Fe(μ,η^5:η^1-P_3C_2tBu$_2$)$_2$}$_2$] (**6**) were isolated. The best solubility was observed in mixtures of CH_2Cl_2 and CH_3CN (1 : 1), but according to the NMR data, **6** dissolves under decomposition. The ^{31}P{^{1}H} NMR spectra of dissolved crystals of **6** show three signals at 67.8 (pseudo-triplet), 52.9 (multiplet) and 31.2 ppm (multiplet) with relative intensities of 1 : 1 : 1, which resembles the spectrum of the starting material **1** (also with similar coupling constants), whereas the resonances of **6** are partly shifted to higher field (*cf.* ^{31}P{^{1}H} NMR spectra of **1**: 79.0, 71.0 and 32.0 ppm). The molecular structure of **6** consists of a (Cu_4Cl_4) stair, which is coordinated by two hexaphosphaferrocene molecules. The hexaphosphaferrocenes act once again as chelating ligands in a 1,1′ coordination mode. Two copper atoms are additionally coordinated by two acetonitrile ligands. The molecular structure of **6** is shown in Fig. 4.

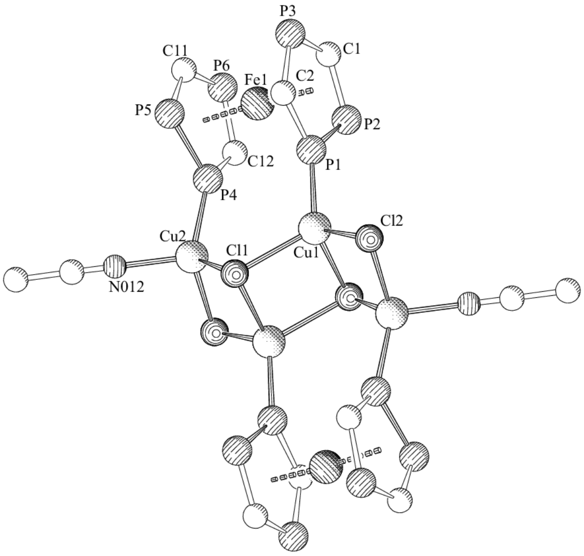
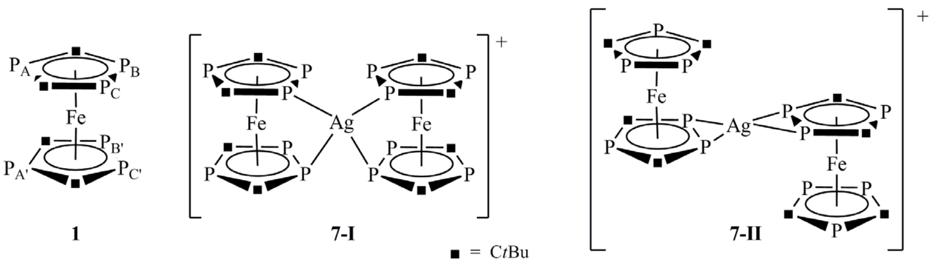


Fig. 4. Molecular structure of the oligomeric compound **6**. *tert*-Butyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)–Cl(1) 2.419(1), Cu(2)–Cl(2) 2.338(1), Cu(2)–Cl(1) 2.390(1), Cu(1)–Cl(2) 2.323(1), Cu(1)–P(1) 2.183(1), Cu(2)–P(4) 2.203(1), Cu(2)–N(012) 2.022(1), P(1)–P(2) 2.116(2), P(4)–P(5) 2.113(2); Cl(2)–Cu(1)–Cl(1) 109.80(1), Cu(1)–Cl(1)–Cu(2) 99.70(1), P(1)–Cu(1)–Cl(1) 118.35(1), P(4)–Cu(2)–Cl(1) 112.58(1).

The hexaphosphaferrocene molecules coordinate with one of the two neighbouring phosphorus atoms to the copper atoms of the CuCl stair-like structure. The sterically hindered phosphorus atoms do not take part in the coordination. Each copper atom is in a tetrahedral coordination sphere. The Cu–Cl bond lengths are between 2.323(1) and 2.419(1) Å and are therefore in good agreement with the Cu–Cl bond lengths in **2**. The Cu–P distances range from 2.183(1) to 2.203(1) Å and thus are slightly longer than those in **2** (2.173(1) – 2.190(1) Å), but slightly shorter than those in **3** (2.203(1) – 2.229(1) Å) and considerably shorter than those observed in **4** (2.248(3) – 2.252(3) Å) and **5** (2.254(1) – 2.423(1) Å). The P–P bond lengths (P1–P2: 2.116(1), P4–P5: 2.113(1) Å) are in a very good agreement with those in **1** (2.112(5) Å), **2** (2.109(1) – 2.118(1) Å), **3** (2.103(1) – 2.137(1) Å), **4** (2.119(3) – 2.126(3) Å) and **5** (2.115(1) Å, 2.113(1) Å). Finally, the distances between the central iron atom and the tri-phospholyl ligands are again only slightly changed in comparison those in **2**, **3**, **4** and **5**,



Scheme 2. Proposed molecular structures of the cation of **7**.

and in a good agreement with the bond lengths observed in **1**. In **6**, the Fe–P distances are between 2.340(1) and 2.369(1) Å and the Fe–C distances between 2.199(1) and 2.234(1) Å. Again, the triphospholyl ligands are planar and approximately parallel with an angle between the planes of 5.7°.

*The reaction of **1** with Ag[Al{OC(CF$_3$)$_3$}$_4$] in a 1 : 1 stoichiometric ratio*

The reaction of **1** with Ag[Al{OC(CF$_3$)$_3$}$_4$] in a 1 : 1 stoichiometric ratio in CH_2Cl_2 results in the formation of yellow-brown needles of **7**. The crystal structure analysis was not completely successful [15], because the crystals were pseudo-merohedrically twinned. However, the structure refinement indicates that one silver cation is coordinated by two hexaphosphaferrocene molecules **1**, resulting in compound **7** (Scheme 2). The elemental analysis of the isolated crystals was in agreement with the suggested molecular composition. Moreover, the proposed composition derived from the X-ray crystal structure analysis was confirmed by the ESI mass spectra through the observation of the molecular cation at *m/z* = 1143. Interestingly, the base peak most likely corresponds to the tripledecker complex [{(η^5-$P_3C_2t Bu_2$)Fe}$_2$(μ,η^4-P_4)] (*m/z* = 698), which is unknown so far. Its formation is reasonable, however, since a polymeric compound, which contains a similar tripledecker complex [Cp‴Fe$_2$(μ,η^4-P_4)] (Cp‴ = η^5-$C_5H_2t Bu_3$) is formed in the reaction of [Cp‴Fe(η^5-$P_3C_2t Bu_2$)] with CuCl in a 1 : 2 stoichiometric ratio [8]. The X-ray crystallographic data established the position of the heavier atoms and gives evidence for the molecular structure **7-I** (Scheme 2). However, it is uncertain if a square-planar arrangement or a spiro-type coordination is adopted. The only compound, in which a silver cation is distorted tetrahedrally coordinated by the chelating 1,1′-diphosphaferrocene [Fe(η^5-PC_4Me_4)$_2$], was described by Cowley and coworkers in 1993 [16].

The ^{31}P{^{1}H} NMR spectrum of **7** in CD_2Cl_2 at r. t. displays three broad signals at 82.3, 60.6 and −37.7 ppm (starting material **1** [9]: 79.0 (P_A), 71.0 (P_B) and 32.0 (P_C) ppm, Scheme 2) without any detectable coupling to the $^{107/109}$Ag nuclei and an integration ratio of approximately 1 : 1 : 1. The signal at 60.6 ppm (broad doublet) shows a splitting of 393 Hz, which also appears in the signal at −37.7 ppm (broad doublet). The shift to higher field of these two signals (probably belonging to the phosphorus atoms P_B and P_C) compared to those of uncoordinated **1** indicates a coordination of the adjacent phosphorus atoms to Ag^+. The room-temperature ^{1}H NMR spectrum of **7** displays two singlets at 1.66 and 1.55 ppm, whereas only one signal for the chemically equivalent *tert*-butyl groups in **7-I** would be expected. According to these results, it is more likely that structure **7-II** (Scheme 2), in which the hexaphosphaferrocene **1** shows a dynamic π coordination, is present in solution. This is in accord with compounds containing Ag^+ as the connecting metal ion, which are known to undergo rearrangement in solution [7]. Variable-temperature ^{31}P{^{1}H} and ^{1}H NMR spectra were recorded. When the temperature is reduced, the signals become very broad (in both the ^{31}P{^{1}H} and ^{1}H NMR spectrum), whereas new, broad signals appear (^{31}P{^{1}H} NMR at 92 ppm, ^{1}H NMR at 0.05 ppm). However, it is doubtful that the variable-temperature NMR data show the conversion of **7-II** to the solid-state structure **7-I**.

The results have shown that the hexaphosphaferrocene **1** is a promising and useful ligand for Cu(I) and Ag(I). It acts as a chelating ligand and shows in addition to the favoured 1,1′-ligation also the new 1,2,1′-coordination mode. The coordination compounds obtained starting from CuX [X= Cl (**2**), Br (**3**), I (**4**, **5**)] are either insoluble 1D-polymeric compounds or the oligomeric compound **6**, which dissolves under decomposition. With Ag[Al{OC(CF$_3$)$_3$}$_4$] the monocationic coordination compound **7** was obtained, which undergoes rearrangement in solution.

The ready attachment of **1** to polymeric CuX units poses the interesting question whether these systems could behave as “supported catalysts” in view of the availability of several “unused” phosphorus lone pairs on the coordinated $P_3C_2tBu_2$ rings and their potential to interact with rhodium or palladium metal centres.

Experimental Section

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk techniques. All solvents were dried using standard procedures and distilled freshly before use. $[Fe(\eta^5\text{-}P_3C_2tBu_2)_2]$ (**1**) [9] and $Ag[Al\{OC(CF_3)_3\}_4]$ [17] were prepared according to the literature.

Synthesis of $[\{Cu(\mu_3\text{-}Cl)\}_4\{Fe(\mu,\eta^5{:}\eta^1\text{-}P_3C_2tBu_2)_2\}_2]_n$ *(2)*

A solution of CuCl (16 mg, 0.16 mmol) in 10 mL of CH_3CN was layered onto a solution of $[Fe(\eta^5\text{-}P_3C_2tBu_2)_2]$ (**1**) (85 mg, 0.16 mmol) in 10 mL of CH_2Cl_2 at r. t. After complete diffusion of the phases, the solution was filtered and reduced to half the volume. After some weeks bright-green, very thin needles of **2** were formed. The mother liquor was decanted, and the crystals were washed with pentane and dried under vacuum. Yield: 5 mg (0.003 mmol, 4 %). Due to the low yield no other analytical data besides the crystal structure analysis were collected.

Synthesis of $[\{Cu(\mu_3\text{-}Br)\}_4\{Fe(\mu,\eta^5{:}\eta^1\text{-}P_3C_2tBu_2)_2\}_2]_n$ *(3)*

A solution of CuBr (23 mg, 0.16 mmol) in 10 mL of CH_3CN was layered onto a solution of $[Fe(\eta^5\text{-}P_3C_2tBu_2)_2]$ (**1**) (85 mg, 0.16 mmol) in 10 mL of CH_2Cl_2 at r. t. After complete diffusion of the phases, the solution was filtered and reduced to half the volume. After a few weeks dark-green needles of **3** were formed. The mother liquor was decanted, and the crystals were washed with pentane and dried under vacuum. Yield: 25 mg (0.02 mmol, 20 %). – Anal. for $C_{41}H_{74}Br_4Cl_2Cu_4Fe_2P_{12}$: calcd. C 29.07, H 4.40; found C 29.08, H 4.60.

Synthesis of $[\{Cu(\mu_3\text{-}I)\}_4\{Fe(\mu,\eta^5{:}\eta^1\text{-}P_3C_2tBu_2)_2\}_2]_n$ *(4) and* $[\{Cu_3(\mu\text{-}I)(\mu_3\text{-}I)_2\}(CH_3CN)\{Fe(\mu,\eta^5{:}\eta^1\text{-}P_3C_2tBu_2)(\mu_3,\eta^5{:}\eta^1\text{-}P_3C_2tBu_2)\}]_n$ *(5)*

A solution of CuI (31 mg, 0.16 mmol) in 10 mL of CH_3CN was layered onto a solution of $[Fe(\eta^5\text{-}P_3C_2tBu_2)_2]$ (**1**) (85 mg, 0.16 mmol) in 10 mL of CH_2Cl_2 at r. t. After complete diffusion of the phases brown rod-shaped crystals of **4** and brown cuboidal crystals of **5** were formed. The mother liquor was decanted and the crystals were washed with pentane and dried under vacuum. Yield: 31 mg (0.026 mmol, 47 %). – Anal. for $C_{23}H_{41}Cu_3FeI_3NP_6Cl_2$ (**5**): calcd. C 22.72, H 3.40, N 1.15; found C 22.65, H 3.44, N 1.16.

Synthesis of $[\{Cu(\mu_3\text{-}Cl)\}_4(CH_3CN)_2\{Fe(\mu,\eta^5{:}\eta^1\text{-}P_3C_2tBu_2)_2\}_2]$ *(6)*

A solution of CuCl (24 mg, 0.24 mmol) in 5 mL of CH_3CN was layered onto a solution of $[Fe(\eta^5\text{-}P_3C_2tBu_2)_2]$ (**1**) (62 mg, 0.12 mmol) in 5 mL of CH_2Cl_2 at r. t. After complete diffusion of the phases, the reaction mixture was filtered and layered with Et_2O. Green parallelepiped-shaped crystals of **6** were formed within three weeks. The mother liquor was decanted, and the crystals were washed with hexane and dried under vacuum. Yield: 47 mg (0.031 mmol, 52 %). – Anal. for $C_{44}H_{78}Cl_4Cu_4Fe_2P_{12}N_2$: calcd. C 33.78, H 5.00, N 1.75; found C 33.52, H 5.09, N 1.28. – $^{31}P\{^1H\}$ NMR (400 MHz, 298 K, CD_2Cl_2/CH_3CN): δ = 67.9 (m), 52.9 (m) and 32.2 ppm (m).

Synthesis of $[Ag\{Fe(\mu,\eta^5{:}\eta^1\text{-}P_3C_2{}^tBu_2)_2\}_2][Al\{OC(CF_3)_3\}_4]$ *(7)*

A solution of $Ag[Al\{OC(CF_3)_3\}_4]$ (184 mg, 0.16 mmol) in 10 mL of CH_2Cl_2 was mixed with a solution of $[Fe(\eta^5\text{-}P_3C_2tBu_2)_2]$ (**1**) (85 mg, 0.16 mmol) in 10 mL of CH_2Cl_2 at r. t. A small amount of a brown precipitate was filtered off, and the clear green solution was kept at 8 °C for one week, during which time yellow-brown needles of **7** formed. The mother liquor was decanted, and the crystals were washed with hexane and dried under vacuum. Yield: 59 mg (0.028 mmol, 34 %). – Anal. for $C_{56}H_{72}P_{12}Fe_2AgAlO_4F_{36}$: calcd. C 31.8, H 3.4; found C 31.97, H 3.51. – ^1H NMR (400 MHz, 298 K, CD_2Cl_2): δ = 1.55 (s, *t*Bu), 1.66 ppm (s, *t*Bu). – ^1H NMR (400 MHz, 193 K, CD_2Cl_2): δ = 0.05 ppm (s, broad). – $^{31}P\{^1H\}$ NMR (400 MHz, 298 K, CD_2Cl_2): δ = 82.3 (m), 60.6 (m) and −37.7 ppm (m). – $^{31}P\{^1H\}$ NMR (400 MHz, 193 K, CD_2Cl_2): δ = 92 ppm (very broad). – ^{19}F NMR (300 MHz, 298 K, CD_2Cl_2): δ = −75.6 ppm (s, $[Al\{OC(CF_3)_3\}_4]^-$). – MS (ESI): cations: *m/z* (%) = 1143.2 (6) $[M]^+$, 698.3 (100) $[(P_3C_2tBu_2)Fe(\mu,\eta^4\text{-}P_4)Fe(P_3C_2tBu_2)]^+$; anions: *m/z* (%) = 967.2 (100) $[Al\{OC(CF_3)_3\}_4]^-$.

Crystal structure determinations

Details of the crystal structure determination are listed in Table 1. The crystal structure measurements of compounds **2** – **7** were carried out on an Oxford Diffraction Gemini R Ultra CCD diffractometer with CuK_α radiation (λ = 1.54180 Å). The structures were solved using either SIR-

Table 1. Crystallographic data of the polymeric and oligomeric compounds **2**–**6**.

Crystallographic data	**2** · CH_3CN	**3** · $2CH_2Cl_2$	**4** · $2CH_2Cl_2$	**5** · CH_2Cl_2	**6**
Empirical formula	$C_{42}H_{75}Cl_4Cu_4$-$Fe_2P_{12}N$	$C_{42}H_{76}Br_4Cl_4Cu_4$-Fe_2P_{12}	$C_{42}H_{76}Cl_4Cu_4$-$Fe_2I_4P_{12}$	$C_{23}H_{41}Cu_3$-$FeI_3NP_6Cl_2$	$C_{44}H_{78}Cl_4Cu_4$-$Fe_2P_{12}N_2$
M_r	1473.37	1779.97	1967.97	1215.49	1514.42
Crystal size, mm^3	0.323×0.020×0.017	0.15×0.04×0.02	0.3820×0.0934×0.0443	0.32×0.11×0.08	0.18×0.10×0.06
T, K	150(1)	150(1)	123(1)	123(1)	123(1)
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	12.181(1)	13.656(3)	14.0754(6)	11.1717(15)	11.1315(7)
b, Å	16.557(2)	15.084(2)	15.2164(8)	13.4627(16)	11.4506(7)
c, Å	16.816(2)	16.387(3)	16.4891(9)	13.8104(17)	15.6164(9)
α, deg	102.32(1)	96.499(12)	97.484(4)	88.261(10)	96.948(5)
β, deg	127.02(1)(2)	105.397(17)	106.520(4)	66.465(13)	95.840(5)
γ, deg	92.59(1)	91.813(15)	93.736(4)	84.304(11)	118.448(6)
V, Å^3	3090.7(5)	3226.7(11)	3337.5(3)	1894.8(5)	1708.1(2)
Z	2	2	2	2	1
ρ_{calcd}, g cm^{-3}	1.58	1.83	1.96	2.13	1.47
μ, mm^{-1}	9.9	12.4	23.7	27.9	9.0
$F(000)$, e	1500	1768	1912	1164	772
hkl range	±12, ±16, ±16	$-14 \leq h \leq 15$ $-17 \leq k \leq 17$ $-18 \leq l \leq 18$	$-16 \leq h \leq 8$ $-17 \leq k \leq 17$ $-18 \leq h \leq 19$	±12, ±15, ±15	$-12 \leq h \leq 12$ $-12 \leq k \leq 13$ $-17 \leq l \leq 17$
Refl. measd. / unique	12577 / 12577	23838 / 10078	20936 / 11116	23978 / 5219	30315 / 5346
R_{int}	[a]	0.0594	0.0548	0.0492	0.0759
Param. refined	397	637	637	366	320
$R(F)/wR(F^2)$[b] (all refl.)	0.0817 / 0.2295	0.0478 / 0.1108	0.0646 / 0.1788	0.0335 / 0.0858	0.0359 / 0.0927
GoF (F^2)[c]	0.988	0.879	0.999	0.974	0.997
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	1.001 / −0.522	0.920 / −1.051	3.088 / −1.834	1.719 / −0.838	0.838 / −0.631

[a] The measured crystal was a two-domain non-merohedral twin, the twin law is a twofold rotation about the axis [0 0 1]. The intensities were integrated separately for both orientation matrices and then combined to a SHELXL HKLF5-format file considering an overlap threshold. This special format does not allow further merging of equivalent reflections in SHELXL, no R_{int} can be given. Due to the crucial question of determining the intensities of partially overlapped reflections correctly, all final R values are slightly enlarged; [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$; [c] GoF $= [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

97 [18] or SHELXS-97 [19] and refined using SHELXL-97 [20] with anisotropic displacements for non-hydrogen atoms. Hydrogen atoms were located in idealised positions and refined isotropically according to the riding model. Only a moderate data set could be collected for compound **7**, since the obtained crystals were twinned.

CCDC 749554 (**2**), 749555 (**3**), 749556 (**4**), 749557 (**5**) and 749558 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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