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Remarkable Differences in the Coordination Chemistry of Structurally Related 1,2,4-Triphosphaferrocenes with Copper(I) Halides and Silver(I) Salts

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Dedicated to Professor Wolfgang Kaim on the occasion of his 60th birthday

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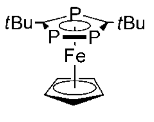
The coordination behavior of 1,2,4-triphosphaferrocenes [FeCp^R(η^5-P$_3$C$_2t$Bu$_2$)] [Cp^R = Cp (**1**), Cp''' = η^5-C$_5$H$_2t$Bu$_3$ (**3**)] towards Cu^I halides is significantly influenced by the substitution pattern of the cyclopentadienyl ring attached to the iron atom. The reaction of the Cp derivative **1** with CuBr in a 1:1 stoichiometry leads to the dimeric complex [{FeCp(η^5:η^1:η^1-P$_3$C$_2t$Bu$_2$)}{μ-CuBr(MeCN)}]$_2$ (**5b**), in which two 1,2,4-triphosphaferrocenes are linked by two CuBr units. By using a 1:2 stoichiometry, the 1D polymeric compound [{FeCp(η^5:η^1:η^1:η^1-P$_3$C$_2t$Bu$_2$)}μ-{(CuBr)$_3$(MeCN)$_2$}]$_n$ (**6**) is formed in which the triphosphaferrocenes are bridged by (CuBr)$_2${CuBr(MeCN)$_2$} units. Starting from CuI, independent of the stoichiometry, the cage compound [{FeCp(η^5:η^1:η^1-P$_3$C$_2t$Bu$_2$)}$_3${Cu(μ-I)}$_3${Cu(μ_3-I)}$_3${Cu(NCMe)}(μ_6-I)] (**7**) is formed. However, if the bulky Cp''' derivative **3** is used already in a 1:1 stoichiometry with CuBr, a transformation of the initially five-membered 1,2,4-triphospholyl ring into a four-membered 1,2-diphosphete ligand is observed, which is linked by CuBr moieties forming the dimeric paramagnetic complex [{FeCp'''(η^4:η^1:η^1-P$_2$C$_2t$Bu$_2$)}(μ-CuBr)]$_2$ (**9**). Furthermore, applying a 1:2 stoichiometry between **3** and CuX (X = Br, I) the complete fragmentation of the 1,2,4-triphospholyl ring under mild conditions into a tetraphosphabutadiene ligand is observed. In the formed 1D polymeric complexes [{(FeCp''')$_2$(μ,η^4:η^1:η^1-P$_4$)}{(μ-CuX)$_2$(MeCN)}]$_n$ [X = Br (**10a**), I (**10b**)] this ligand represents now the middle deck of the triple-decker sandwich complexes linked by four-membered [(CuX)$_2$(CH$_3$CN)] moieties. Moreover, the reaction of the Cp derivative **1** with the Ag salt of the weakly coordinating anion [Al{OC(CF$_3$)$_3$}]$_4^-$ leads to the dimeric Ag(CH$_3$CN)-bridged dicationic product [{FeCp(η^5-P$_3$C$_2t$Bu$_2$)}Ag(MeCN)]$_2$[Al{OC(CF$_3$)$_3$}$_4$]$_2$ (**11**).

Introduction

The use of E$_n$ ligand complexes of group 15 elements (E = P, As) as additional ligands for coordinatively unsaturated metal ions proved to be a milestone in the synthesis of inorganic, phosphorus-based polymers and oligomers.[1] This approach is in contrast to contemporary concepts in supramolecular chemistry using N- and O-donor ligand moieties to connect different metal centers together.[2] The most commonly used P$_n$ ligand complex as a building block is [FeCp*(η^5-P$_5$)] (Cp* = C$_5$Me$_5$) which is able to form one-dimensional and two-dimensional polymeric structures with Cu^I,[3] Ag^I,[4] and Tl^I[5] salts. A highlight of the coordination chemistry of [FeCp*(η^5-P$_5$)] was achieved in the reaction with Cu^I halides by careful use of the reaction conditions and stoichiometry when fullerene-like aggregates containing an inorganic core could be isolated.[6] Furthermore, these systems are able to encapsulate smaller guest molecules such as C$_{60}$ or even *o*-carborane[6c,6d] or form organometallic-based nanosized capsules attracted by only weak interactions.[6a] The ability to form polymeric or oligomeric structures is not limited to [FeCp*(η^5-P$_5$)]. The P$_n$ ligand complexes [{MCp(CO)$_2$}$_2$][(μ,η^2-P$_2$)] (M = Cr, Mo),[5,7] and [(MoCp*)$_2$(μ,η^3-P$_3$)(μ,η^2-PS)][8] form oligomeric or polymeric aggregates whereas [TaCp''(CO)$_2$(η^4-P$_4$)][9] forms spherical clusters.

We have previously investigated the coordination behavior of the isolobal 1,2,4-triphosphaferrocene derivatives [FeCp^R(P$_3$C$_2t$Bu$_2$)] [Cp^R = Cp (**1**), Cp* = C$_5$Me$_5$ (**2**), Cp'''



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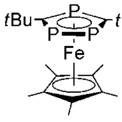

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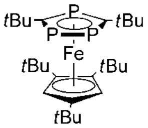

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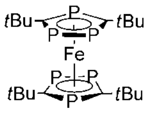

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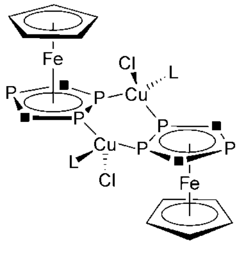
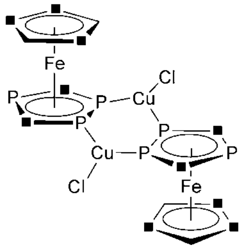


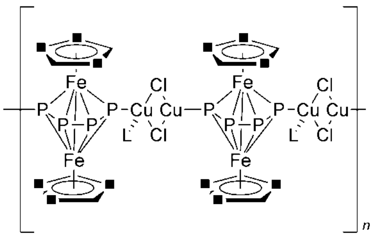
■ = C*t*Bu

A



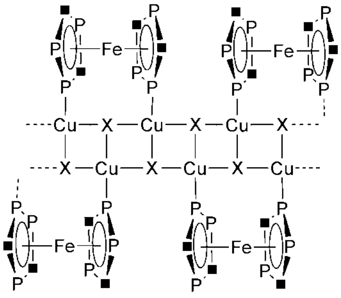
■ = C*t*Bu

B



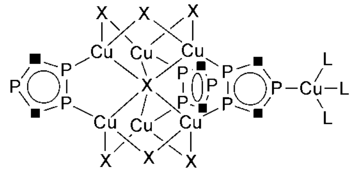
■ = C*t*Bu
L = CH_3CN

C



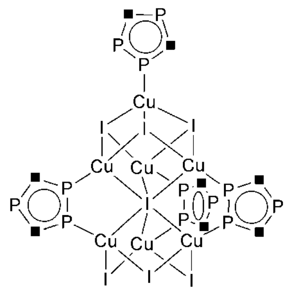
■ = C*t*Bu
X = Cl, Br, I

D



X = Cl, Br
L = CH_3CN

E



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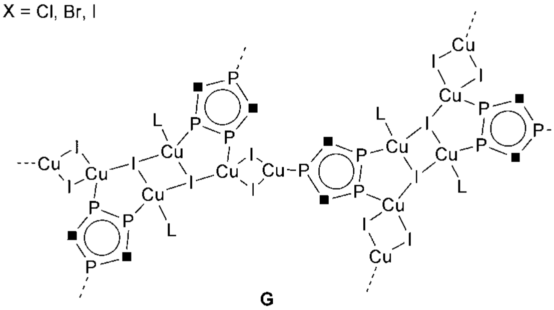

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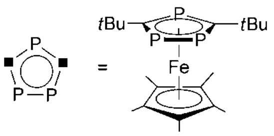
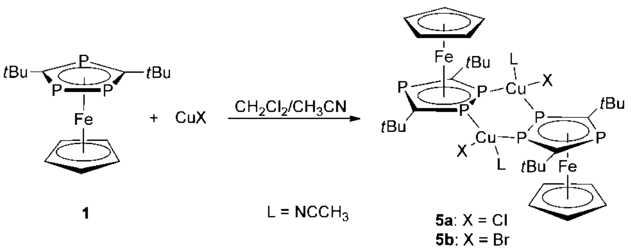


= $C_5H_2tBu_3$ (**3**)][10] and the hexaphosphaferrocene [Fe(η^5-$P_3C_2tBu_2$)$_2$] (**4**)[11] towards Cu^I halides to examine the effect of the nature and bulkiness of the Cp^R group on the resulting complexes. A variety of unusual structures are summarized in **A**–**G** shown above. Structure **A** results from **1**, structures **B** and **C** arise from **3** while motifs **D** result from **4**. Very recently we reported solely on the complexes **E**–**G** involving the Cp*-substituted ferrocene **2**.[11] Herein we report in greater detail further unexpected chemical behavior of [FeCp^R(η^5-$P_3C_2tBu_2$)] [Cp^R = Cp (**1**) Cp′′′ = $C_5H_2tBu_3$ (**3**)] towards copper halides and silver(I) salts.

Results and Discussion

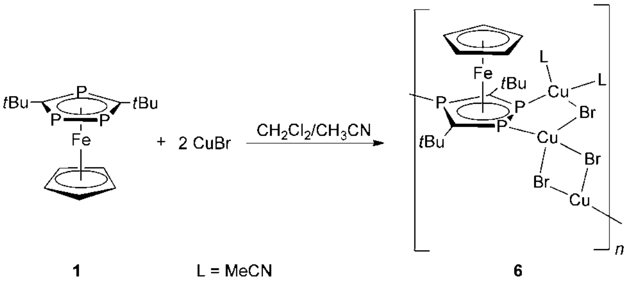
In a preliminary communication we have shown that the reaction of [CpFe(η^5-$P_3C_2tBu_2$)] (**1**) with CuCl in a 1:1 stoichiometry leads to the formation of the dimeric complex [{CpFe(η^5:η^1:η^1-$P_3C_2tBu_2$)}{μ-CuCl(MeCN)}]$_2$ (**5a**) in which the two 1,2,4-triphosphaferrocene units are bridged via two Cu(Cl)NCMe units by coordination to both adjacent ring phosphorus atoms.[10] The presence of an additional uncoordinated phosphorus atom in **5a** suggests the possibility of further coordination to a cooper cation leading to the formation of a polymeric chain. However, when a solution of CuCl in acetonitrile is carefully layered over a solution of **1** in CH_2Cl_2 in a stoichiometric ratio of 1:2, only the formation of red crystals of **5a** was observed [Equation (1)].



(1)

Performing the reaction of **1** with CuBr under similar conditions as for **5a** in a stoichiometry of 1:1 readily affords a red solid **5b** which is sparingly soluble in MeCN. Unfortunately, no X-ray crystallographic-quality crystals could be obtained. On the basis of the spectroscopic data, which were derived from the mother liquor, we tentatively assign the structure as [{FeCp(η^5:η^1:η^1-$P_3C_2t$$Bu_2$)}{μ-CuBr(MeCN)}]$_2$ (**5b**), which should be isostructural with **5a**.

The ESI-MS spectrum in MeCN reveals peaks attributed to the cations of [{FeCp($P_3C_2t$$Bu_2$)}$_2$$Cu_2$Br(MeCN)]$^+$, [{FeCp($P_3C_2t$$Bu_2$)}$_2$Cu]$^+$, and [{FeCp($P_3C_2t$$Bu_2$)}$Cu_2$Br(MeCN)$_2$]$^+$, suggesting the presence of a dimeric copper complex in the reaction solution. The $^{31}P\{^1H\}$ NMR spectrum shows an AM_2 spin system exhibiting a triplet (δ = 33.5 ppm) and a broadened doublet (δ = 14.6 ppm). These chemical shifts are almost identical with those found for **5a** (triplet at δ = 33.1 ppm and a broad doublet at δ = 15.3 ppm), the latter being shifted 25 ppm upfield compared to that of the starting material. The spectroscopic data support the existence of a dimeric copper complex **5b** similar to **5a** in the mother liquor.



1 L = MeCN **6**

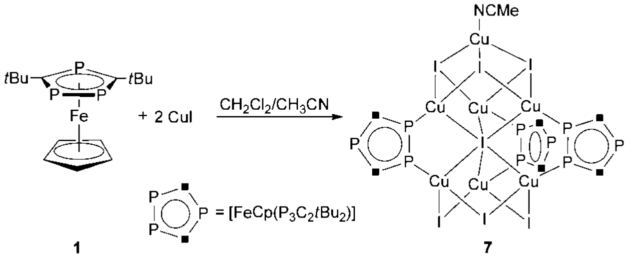
(2)

In contrast to the CuCl reactions, when a solution of **1** in CH_2Cl_2 was layered with a solution of CuBr in MeCN in a stoichiometric ratio of 1:2 the formation of the 1D polymer [{FeCp(η^5:η^1:η^1:η^1-$P_3C_2t$$Bu_2$)}{CuBr}$_3$(MeCN)$_2$]$_n$ (**6**) was observed [Equation (2)]. The brown crystalline solid is moderately soluble in MeCN. It can be stored under an inert atmosphere at ambient conditions.

In the ^{31}P NMR spectrum of **6** a triplet was observed at δ = 33.8 ppm with a coupling constant of 44.6 Hz and a broad doublet at δ = 14.9 ppm ($\omega_{1/2}$ = 115 Hz). The broad signal suggests a dynamic behavior in solution, which unfortunately could not be studied due to the low solubility of **6**. It is probable that an equilibrium exists in MeCN solution between different aggregates with a structure similar to **5b**. This is also suggested by the almost identical chemical shifts of **5b** and **6**.

The molecular structure of **6** was determined by a single-crystal X-ray diffraction study and is depicted in Figure 1.

Interestingly **6** differs from its chloro analogue **5a**, in that it involves three different types of Cu atoms linking the two triphosphaferrocene moieties. Two copper atoms are tetrahedrally coordinated, one by two MeCN ligands, a phosphorus atom and a bromine atom, the second one by three bromine atoms and one phosphorus atom. The third copper atom is trigonal planar coordinated by two bromine and one phosphorus atom. In **6** all P atoms of the 1,2,4-triphospholyl ring are now involved into the coordination towards Cu.



1 **7**

(3)

However, when **1** is reacted with CuI in a similar procedure, using a stoichiometric ratio of the reactants of 1:1 or even 1:2, the cage compound [{FeCp(η^5:η^1:η^1-$P_3C_2t$$Bu_2$)}$_3$\{Cu(μ-I)\}$_3$\{Cu($\mu_3$-I)\}$_3$\{Cu(NCMe)\}($\mu_6$-I)] (**7**) is formed [Equation (3)]. Compound **7** is an air-sensitive red crystalline compound that can be stored under an inert atmosphere at ambient conditions and is moderately soluble in CH_2Cl_2, MeCN, but sparingly so in THF and insoluble in nonpolar solvents such as alkanes.

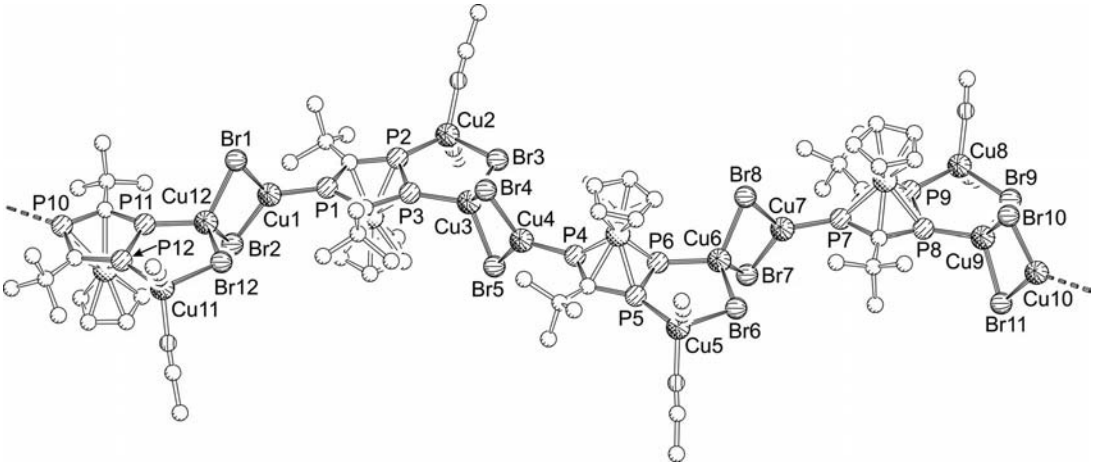


Figure 1. Section of the 1D polymeric structure of [{FeCp(η^5:η^1:η^1:η^1-$P_3C_2t$$Bu_2$)}{CuBr}$_3$(MeCN)$_2$]$_n$ (**6**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1–P1 2.174(5), Cu2–P2 2.246(5), Cu3–P3 2.213(5), Cu4–P4 2.171(5), Br3–Cu2 2.502(3), Br3–Cu3 2.457(3), Br4–Cu3 2.476(3), Br4–Cu4 2.366(3), Br5–Cu3 2.519(3), Br5–Cu4 2.369(3), P2–P3 2.105(5); Cu1–P1–C1 131.5(5), Cu1–P1–C6 126.7(5), Cu2–P2–P3 114.0(2), Cu3–P3–P2 116.2(2), Br3–Cu2–P2 100.74(13), Br3–Cu3–P3 101.18(13), Br1–Cu1–P1 125.61(15), Br2–Cu1–P1 123.15(15).

In the EI-MS spectrum of **7**, $[\{FeCp(P_3C_2tBu_2)\}_3Cu_7I_6]^+$ and other cations were detected arising from the fragmentation of **7** through successive loss of copper and iodine atoms under electron impact.

The ^1H NMR spectrum of **7** shows three signals: two multiplets at $\delta = 0.80$ and 1.22 ppm corresponding to the chemically and magnetically inequivalent *t*Bu groups of the P_3C_2 ring as well as a singlet at $\delta = 3.56$ ppm corresponding to the protons on the cyclopentadienyl ring. In the $^{31}P\{^1H\}$ NMR spectrum of **7** there are two broad signals centered at $\delta = 8.2$ and 34.9 ppm, respectively. In comparison with the corresponding chemical shifts of **1** [$\delta(P_B) = 39.6$ ppm (d) and $\delta(P_A) = 40.2$ ppm (t)],[12] a significant upfield shift of the resonance corresponding to the adjacent phosphorus atoms in the P_3C_2 ring is observed.

The molecular structure of **7** was determined by a single-crystal X-ray diffraction study and is depicted in Figure 2. It is strikingly similar to the Cp*-derivative **F**,[11] the only difference being the coordination of a MeCN ligand to one Cu centre instead of the η^1-bonded triphosphaferrocene **1**. In the crystal structure the molecule of **7** lies in a crystallographic symmetry plane that leads to a disordering of one CpFe fragment (Fe2) over two positions with 50% occupancy. Additionally, the copper atom Cu1 and the MeCN ligand are disordered over two positions with 50% occupancy.

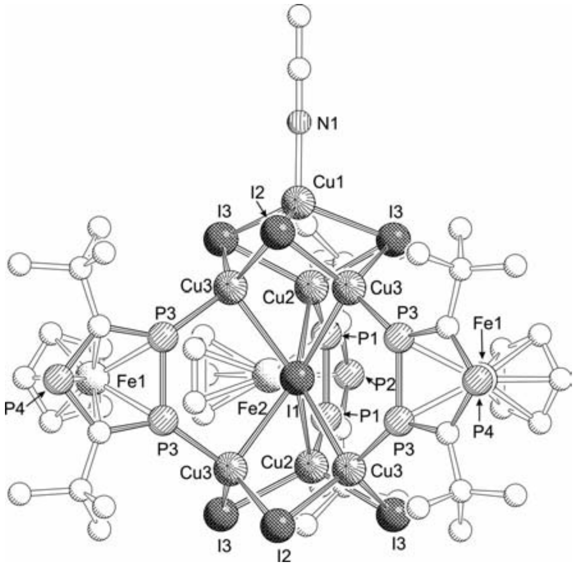


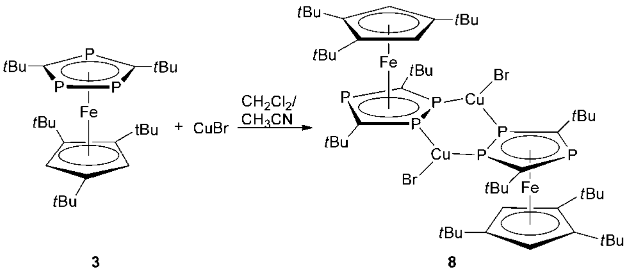
Figure 2. Molecular structure of $[\{FeCp(\eta^5:\eta^1:\eta^1-P_3C_2tBu_2)\}_3\{Cu(\mu-I)\}_3\{Cu(\mu_3-I)\}_3\{Cu(NCMe)\}(\mu_6-I)]$ (**7**) in the crystal (H atoms are omitted for clarity). Only one set from the disordered atoms are depicted. Selected bond lengths [Å] and angles [°]: P1–P1 2.102(2), P3–P3 2.110(2), P1–Cu2 2.241(2), P3–Cu3 2.2385(16), Cu1–I2 2.715(3), Cu1–I3 2.6673(15), Cu2–I1 2.8951(13), Cu2–I3 2.5889(8), Cu3–I1 2.9084(10), Cu3–I2 2.5835(10), Cu3–I3 2.5993(10), Cu3–P3–P3 123.44(7), Cu2–P1–P1 122.60(9), Cu2–I1–Cu2 102.54(3), Cu3–I1–Cu3 63.47(2)–142.36(3), Cu2–I1–Cu3 65.66(2)–144.66(2).

The average Cu–I bond length (2.708 Å) in the $(CuI)_4$ unit is slightly longer than those in the complexes $[Cu_4I_4(PPh_2Me)_4]$ (2.698 Å) and $[Cu_4I_4(PPh_3)_4]$ (2.691 Å).[13] The average Cu–P bond length (2.238 Å) in the $(CuI)_4$ unit is almost the same as that in $[\{FeCp^*(\eta^5:\eta^1:\eta^1-P_3C_2tBu_2)\}_4(CuI)_7]$ (**F**) (2.237 Å) but slightly shorter than those found in $[Cu_4I_4(PPh_2Me)_4]$ (2.250 Å) and $[Cu_4I_4(PPh_3)_4]$ (2.252 Å). In the 1D polymer $[Cu(\mu-I)\{Cp_2Mo_2(CO)_4(\mu,\eta^2:\eta^1:\eta^1-P_2)\}]_n$ the Cu–P distance is 2.312(1) Å and thus slightly longer than in **7**.

The iodine atom (I1) in the core connected to six copper atoms has a relatively longer average distance (2.902 Å) in comparison to the rest of the Cu–I bond lengths (2.631 Å) and is shorter than that in $[\{FeCp^*(\eta^5:\eta^1:\eta^1-P_3C_2tBu_2)\}_4(CuI)_7]$ (**F**) (2.941 Å) (*vide infra*). One copper atom of the $(CuI)_4$ unit and one of the $(CuI)_3$ unit are bridged by the two adjacent phosphorus atoms of the *cyclo*-P_3C_2 ring of the triphosphaferrocene moiety.

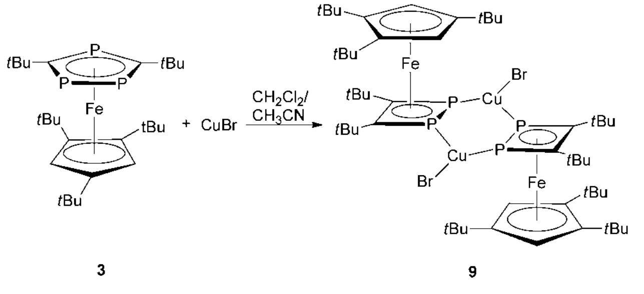
In all of the above systems involving Cp and Cp*[11] rings attached to iron, although the structures of the resulting complexes with copper halides differ the $P_3C_2tBu_2$ ring remains intact. However, unexpectedly using bulky substituents on the cyclopentadienyl ring led to fragmentation of the $P_3C_2tBu_2$ ring. This was first observed by us[10] in the reaction of $[FeCp'''(\eta^5-P_3C_2tBu_2)]$ (**3**) with CuCl, but appears to be more general.

After layering an acetonitrile solution of CuBr onto a red CH_2Cl_2 solution of $[FeCp'''(\eta^5-P_3C_2tBu_2)]$ (**3**) in a ratio of 1:1, the reaction mixture was kept at room temperature, and a brown solution was formed. The $^{31}P\{^1H\}$ NMR spectrum of this solution shows a triplet at $\delta = 51.6$ ppm and a broad doublet at $\delta = 28.4$ ppm, which are similar to those of **B**, indicating the likelihood of the presence of the dimeric complex **8** in the reaction mixture [Equation (4)].



(4)

The ESI-MS spectrum of **8** in MeCN at room temperature shows the expected fragments $[\{FeCp'''(P_3C_2tBu_2)\}_2\{Cu(MeCN)\}_2]^+$, $[\{FeCp'''(P_3C_2tBu_2)\}_2Cu]^+$, and $[\{FeCp'''(P_3C_2tBu_2)\}Cu]^+$. The detected ions compare well to those found for **5b**, indicating the presence of a dimeric complex. Since no single crystals suitable for X-ray diffraction could be obtained, another experiment was carried out in which a solution of CuBr in CH_3CN was layered onto **3** in CH_2Cl_2 in the ratio of 1:1. However now, when the two reactants had diffused completely, the reaction mixture was concentrated and kept at –28 °C for two weeks to afford dark-brown plates of complex **9** [Equation (5)].



(5)

The molecular structure of **9** (determined by a single-crystal X-ray diffraction study *vide infra*) is remarkable since the $P_3C_2tBu_2$ ring in the starting material **3** has unexpectedly been fragmented with formal elimination of one phosphorus atom resulting in a 1,2-diphospha-3,4-di-*tert*-butyl cyclobutadiene ring. The two $[FeCp'''(\eta^4\text{-}P_2C_2tBu_2)]$ fragments are now linked by two CuBr units to form a novel dimeric complex $[\{FeCp'''(\eta^4:\eta^1:\eta^1\text{-}P_2C_2tBu_2)\}(\mu\text{-}CuBr)]_2$ (**9**).

Complex **9** crystallizes in the triclinic space group $P\bar{1}$ and the structure illustrated in Figure 3, reveals that two copper centers are bridged by two 1,2-*cyclo*-$P_2C_2tBu_2$ rings, thereby forming a planar six-membered ring. This P_4Cu_2 ring together with the two joined P_2C_2 rings adopts a chair conformation. The copper atoms exhibit a trigonal planar coordination mode involving two phosphorus atoms and one bromine atom (average P–Cu–Br angle of 130.1°). The P1–Cu1 bond length is 2.256(6) Å whereas the P2–Cu1 distance is 2.229(5) Å. The P–P bond length in **9** [2.147(7) Å] is longer than that of the starting material **3** [2.121(3) Å] presumably because of the greater ring strain of the four-membered ring compared to the five-membered ring. This P–P bond length is almost the same as that in the complex [1,2-μ-{(3,4-di-*tert*-butyl-η^4-1,2-diphosphete)-$Fe(CO)_3$}$(Cr(CO)_5)_2$] [2.147(2) Å][14] synthesized by Zenneck and co-workers and both P–P bond lengths are shorter than that in the complex [(3,4-di-*tert*-butyl-η^4-1,2-diphosphete)(η^8-COT)-Ti] [2.175(1) Å][15] reported by Binger et al. This presumably arises because the lone pairs of the two phosphorus atoms of the P_2C_2 ring participate in η^1-bonding to the metal atoms. The average P–C bond lengths within the P_2C_2 ring in complex **9** [P1–C2 1.866(17) Å and P2–C1 1.805(18) Å] are similar to that in the two 1,2-diphosphete complexes $[1,2\text{-}\mu\text{-}\{(\eta^4\text{-}P_2C_2tBu_2)Fe(CO)_3\}\{Cr(CO)_5\}_2]$ and $[(\eta^4\text{-}P_2C_2tBu_2)Ti(\eta^8\text{-}COT)]$ (COT = cyclooctatetraene) [1.816, 1.811 Å (av.)].

The $[\{FeCp'''(\eta^4\text{-}P_2C_2tBu_2)\}]$ fragment is a 17-electron system and therefore is paramagnetic. In the ESR spectrum of **9** a signal at $g_1 = 2.026$ shows a hyperfine splitting with $a = 10$ mT, suggesting that there are unpaired electrons delocalized over the whole plane of the two four-membered P_2C_2 rings and the six-membered P_4Cu_2 ring. The half-field signal for an antiferromagnetic coupling of $g_2 = 5.3$ indicates the existence of two unpaired electrons in this compound. The g_1 factor for the ferrocenium cation, implies 17 valence electrons for the two iron atoms. Since this work was completed Lammertsma et al. have described the 17-valence-electron complex $[Fe(\eta^4\text{-}P_2C_2tBu_2)_2]^-$ involving a 1,3-diphosphete which also is paramagnetic as well as a neutral 16-electron complex.[16]

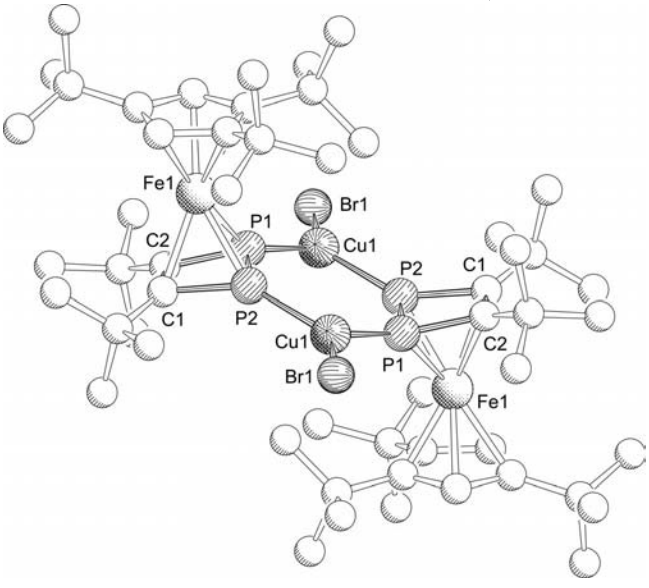


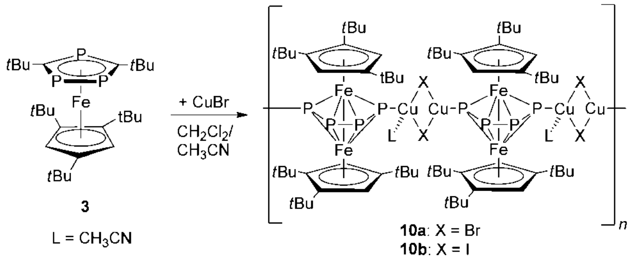
Figure 3. Molecular structure of $[\{FeCp'''(\eta^4:\eta^1:\eta^1\text{-}P_2C_2tBu_2)\}_2(CuBr)_2]$ (**9**) in the crystal (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–P2 2.147(7), P1–C2 1.866(17), P2–C1 1.805(18), C1–C2 1.41(3), P1–Cu1 2.250(6), P2–Cu1 2.229(5), Cu1–Br1 2.286(4), P1–Fe1 2.258(6), P2–Fe1 2.278(5), C2–Fe1 2.179(18), C1–Fe1 2.156(18), P1–Cu1–P2 100.0(2), Cu1–P2–P1 133.1(3), Cu1–P1–P2 126.9(2), C1–P2–P1 78.0(6), P2–P1–C2 78.8(6), P2–C1–C2 104.7(12), C1–C2–P1 98.6(12).

Interestingly it was found that the *cyclo*-P_3C_2 ring can also be fragmented when $[FeCp'''(\eta^5\text{-}P_3C_2tBu_2)]$ (**3**) is treated with two equivalents of CuCl or one equivalent of CuBr. It is assumed that in addition to the coordination of the Cu^I center, the size of the halide also affects the ring fragmentation. In order to gain further insight into the coordination behavior of the sterically bulky triphosphaferrocene **3** with other copper halides, similar procedures to those applied for **1** were carried out.

When two equivalents of CuX (X = Br, I), respectively, in acetonitrile were layered onto a CH_2Cl_2 solution of **3**, the air-sensitive dark-brown crystalline compounds $[\{(FeCp''')_2(\mu,\eta^4:\eta^1:\eta^1\text{-}P_4)\}\{(\mu\text{-}CuX)_2(MeCN)\}]_n$ [X = Br (**10a**), I (**10b**)] were formed. Even using one equivalent of CuI, compound **10b** was obtained. As observed with complex **9**, the P_3C_2 ring of the starting material **3** was fragmented and rearranged now to form a new triple-decker $[\{(FeCp''')_2(\eta^4\text{-}P_4)\}]$ unit during the reaction [Equation (6)].

The polymeric compounds **10a**,**b** can be stored under an inert atmosphere and are sparingly soluble in DMF but are insoluble in CH_2Cl_2, toluene or THF.

The ESI-MS of **10a** at room temperature displays peaks corresponding to the cations of $[\{(FeCp''')_2(P_4)\}_2Cu]^+$,



(6)

$[\{(\mathrm{FeCp'''})_2(\mathrm{P}_4)\}\mathrm{Cu}]^+$ and $[(\mathrm{FeCp'''})_2(\mathrm{P}_4)]^+$ while in **10b** peaks attributed to $[\{(\mathrm{FeCp'''})_2(\mathrm{P}_4)\}\mathrm{Cu}_2\mathrm{I}]^+$, $[\{(\mathrm{FeCp'''})_2(\mathrm{P}_4)\}\mathrm{Cu}_2]^{2+}$ and $[\{(\mathrm{FeCp'''})_2(\mathrm{P}_4)\}]^+$ were also detected.

Because of the poor solubility of the coordination polymers in common solvents, only the reaction solutions of **10a** could be studied by NMR spectroscopy. Two broad signals in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of the reaction solution of **10a** at δ = 76.2 ppm ($\omega_{1/2}$ = 520 Hz) and δ = 120.6 ppm ($\omega_{1/2}$ = 490 Hz), respectively are assigned to the two types of phosphorus atoms of the P_4 skeleton. Likewise in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of the reaction solution of **10b**: the signal at δ = 72.9 ppm ($\omega_{1/2}$ = 1300 Hz) and δ = 118.4 ppm ($\omega_{1/2}$ = 650 Hz), are similarly assigned. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of **10a** reveal two inequivalent phosphorus atoms suggesting that the solid-state coordination environment is probably present in solution.

As in the case of **5**, the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of the reaction solutions of **10** show two additional signals (**10a**: 52.8 and 41.4 ppm, **10b**: 51.8 and 39.1 ppm), which are only marginally different to those of the starting material suggesting there are weak interactions between the Cu^{I} species and unreacted starting materials.

Since both triple-decker copper polymers dissolve sparingly in DMF, the $^{31}\mathrm{P}$ NMR spectra of these solutions were recorded exhibiting at room temperature one broadened signal similar to that of $[\{(\mathrm{FeCp^R})_2(\mu,\eta^4\text{-}\mathrm{P}_4)\}]$ [$\mathrm{Cp^R}$ = 1,3-$(\mathrm{Me_3Si})_2\mathrm{C_5H_3}$ and 1,3,4-$(\mathrm{Me_3Si})_3\mathrm{C_5H_2}$][17] indicating that in solution the polymer chain may be depolymerizing to $[(\mathrm{FeCp'''})_2(\mu,\eta^4\text{-}\mathrm{P}_4)]$ moieties which undergo a dynamic process.[18] Considering the somewhat different chemical shifts in these spectra, there may be a weak interaction between the triple-decker $[(\mathrm{FeCp'''})_2(\mu,\eta^4\text{-}\mathrm{P}_4)]$ unit and the copper halides.

Solid-state structures of **10a**,**b** have been established by X-ray crystallography and are shown in Figure 4. In both complexes two phosphorus atoms at the end of the "tetraphosphabutadiene" fragment in the triple-decker complex are bound to two copper atoms in the $[(\mu\text{-CuX})_2(\mathrm{MeCN})]$ unit to form a one-dimensional polymer. As in complex **C**, the coordination geometry of one copper atom (Cu2) is tetrahedral with a Cu2–P4 bond length of 2.160(5) Å for **10a** and 2.2498(17) Å for **10b** and X–Cu2–P4 bond angles averaging 125.6(2)° for **10a** and 117.64(6)° for **10b**. The other copper atom (Cu1) coordinates in a trigonal planar fashion to one phosphorus atom and two chlorine atoms with Cu1–P1 bond lengths equal to 2.183(6) Å for **10a** and 2.1991(14) Å for **10b** and X–Cu1–P1 bond angles averaging 127.4° for **10a** and 126.3° for **10b**. In parallel with the case of the complex $[(\mathrm{FeCp'''})_2(\mu,\eta^4\text{-}\mathrm{P}_4)]$,[18] three P–P bonds in the P_4 skeleton show inequality, two short bonds [P1–P2 2.093(6) Å and P3–P4 2.121(6) Å in **10a** and P1–P2 2.104(2) Å and P3–P4 2.105(2) Å in **10b**] and one long bond [P2–P3 2.303(7) Å in **10a** and 2.338(2) Å in **10b**]. The P–Fe bond lengths of these tetraphosphabutadiene moieties also fall into two groups: short Fe1–P1 [**10a**: 2.234(6) Å, **10b**: 2.2418(15) Å] and Fe2–P4 [**10a**: 2.250(5) Å, **10b**: 2.2576(14) Å] bonds; and longer Fe1–P2 [**10a**: 2.348(5), **10b**: 2.3513(13) Å] and Fe2–P3 [**10a**: 2.348(6), **10b**: 2.3498(15) Å] bonds.

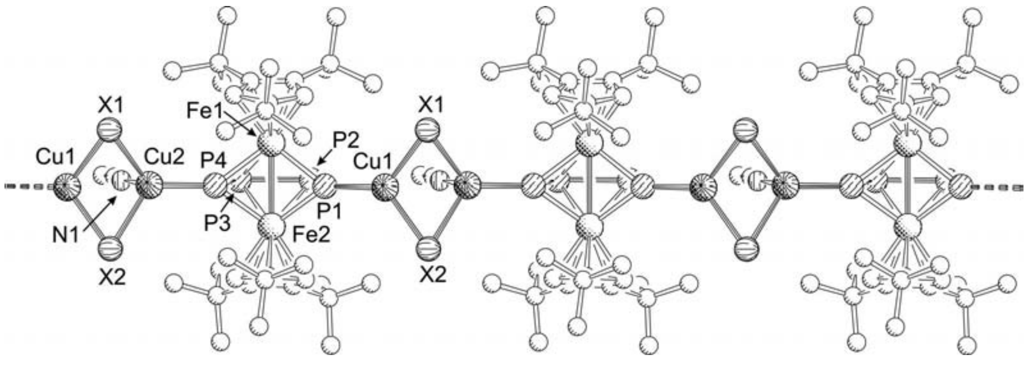
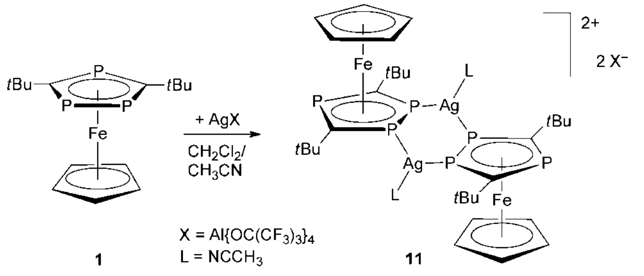


Figure 4. Section of the structures of $[\{(\mathrm{FeCp'''})_2(\mu,\eta^4{:}\eta^4\text{-}\mathrm{P}_4)\}\{(\mathrm{CuX})_2\mathrm{MeCN}\}]$ [X = Br (**10a**), I (**10b**)] in the crystal (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°] for **10a** (X = Br): P1–P2 2.093(6), P2–P3 2.303(7), P3–P4 2.121(6), Fe1–Fe2 2.647(3), P4–Cu2 2.160(5), P1–Cu1 2.183(6), P1–Fe1 2.234(6), P2–Fe1 2.348(5), P3–Fe1 2.348(5), P4–Fe1 2.245(5), P1–Fe2 2.237(6), P2–Fe2 2.344(5), P3–Fe2 2.348(6), P4–Fe2 2.250(5), Cu1–Br1 2.388(3), Cu1–Br2 2.402(3), Cu2–Br1 2.437(5), Cu2–Br2 2.449(4), Cu1–P1–P2 129.8(3), P1–P2–P3 106.6(3), P2–P3–P4 106.4(3), P3–P4–Cu2 124.2(3), Br1–Cu1–Br2 104.64(13), Br1–Cu1–P1 129.43(19), Br2–Cu1–P1 125.24(18), Br1–Cu2–Br2 101.79(14), Br1–Cu2–P4 128.1(2), Br2–Cu2–P4 123.1(2). Selected bond lengths [Å] and angles [°] for **10b** (X = I): P1–P2 2.1037(17), P2–P3 2.338(2), P3–P4 2.1050(17), Fe1–Fe2 2.6453(9), P4–Cu2 2.2498(17), P1–Cu1 2.1991(14), P1–Fe1 2.2418(15), P2–Fe1 2.3513(13), P3–Fe1 2.3550(13), P4–Fe1 2.2489(15), P1–Fe2 2.2474(14), P2–Fe2 2.3503(16), P3–Fe2 2.3498(15), P4–Fe2 2.2576(14), Cu1–I1 2.5637(9), Cu1–I2 2.5662(9), Cu2–I1 2.7323(13), Cu2–I2 2.7143(12), Cu1–P1–P2 129.86(7), P1–P2–P3 106.16(7), P2–P3–P4 106.38(7), P3–P4–Cu2 114.31(7), I1–Cu1–I2 107.18(2), I1–Cu1–P1 124.47(4), I2–Cu1–P1 128.13(4), I1–Cu2–I2 98.58(3), I1–Cu2–P4 115.07(5), I2–Cu2–P4 118.75(5).

In view of the variety of ligating modes discussed above it was of interest to consider the complexation behavior of [FeCp(η^5-P_3C_2tBu$_2$)] (**1**) towards silver(I) salts. Preliminary experiments using different silver salt solutions such as $AgCF_3SO_3$, $AgCF_3CO_2$ and Ag[Al{OC(CF_3)$_3$}$_4$] layered onto the [FeCp(η^5-P_3C_2tBu$_2$)] solution only resulted in precipitation of silver on the walls of the Schlenk tubes after a few days. However, direct mixing of the reactants and the use of a very weakly coordinating anion [Al{OC(CF_3)$_3$}$_4$]$^-$[19] proved to be more successful.[20] Thus, when a 1:1 mixture of [FeCp(η^5-P_3C_2tBu$_2$)] (**1**) with Ag[Al{OC(CF_3)$_3$}$_4$] in CH_2Cl_2 and MeCN was stirred at room temperature for one hour, after filtration of the resulting black powder the filtrate was kept at about 4 °C until the air- and light-sensitive red orange crystalline compound **11** was deposited [Equation (7)].



(7)

Compound **11** dissolves in THF, MeCN, and sparingly in CH_2Cl_2 but is insoluble in nonpolar solvents such as alkanes. It can be stored under an inert atmosphere at low temperature.

In the negative ESI-MS spectrum of **11** in MeCN at room temperature the most abundant peak corresponded to the [Al{OC(CF_3)$_3$}$_4$]$^-$ anion. The positive ESI-MS spectrum reveals a peak with the highest relative abundance corresponding to the [{FeCp(η^5-P_3C_2tBu$_2$)}$_2$Ag]$^+$ cation indicating that this dimeric silver species is most likely present in solution. A peak attributed to the [{FeCp(η^5-P_3C_2tBu$_2$)}Ag(MeCN)]$^+$ cation was also detected.

The ^{1}H NMR spectrum of **11** shows the expected two signals. A singlet at δ = 1.43 ppm represents the *t*Bu groups of the P_3C_2 ring and the singlet at δ = 3.57 ppm is assigned to the cyclopentadienyl ring. In the ^{31}P{^{1}H} NMR spectrum of **11** there are two signals, one triplet at δ = 34.3 ppm for the unique phosphorus and one broad doublet at δ = 12.7 ppm for the two adjacent phosphorus atoms of the P_3C_2 ring. The corresponding chemical shifts of **11** are shifted upfield in comparison to those in the free complex [FeCp(η^5-P_3C_2tBu$_2$)] [δ(P_M) = 39.6 ppm and δ(P_A) = 40.2 ppm].

Confirmation of the molecular structure of **11** came from a single-crystal X-ray diffraction study and the cation shown in Figure 5 has a structure very similar to that previously discussed for the dimeric copper complexes **5** and **8**. The cation in **11** consists of two triphosphaferrocene units doubly bridged to two silver centers via the two adjacent phosphorus atoms of the P_3C_2tBu$_2$ ring system forming a six-membered ring [Figure 5]. The two silver atoms lie above and below the plane defined by the phosphorus atoms P2, P3, P2′ and P3′ [deviation of silver atoms from the P2P3P2′P3′ plane = 0.424(1) Å] and are triply coordinated by two phosphorus atoms of two different P_3C_2 rings and one nitrogen atom of an acetonitrile molecule, creating a P2–Ag1–P3 angle of 116.23(8)°. Two slightly different Ag–P bond lengths are observed [2.432(2), 2.460(2) Å] in **11**. The P2–P3 bond length [2.105(3) Å] in **11** is slightly longer than that in **5** [2.072(2) Å][10] and the free complex [Fe(η^5-P_3C_2tBu$_2$)$_2$] [2.114(1) Å].[12]

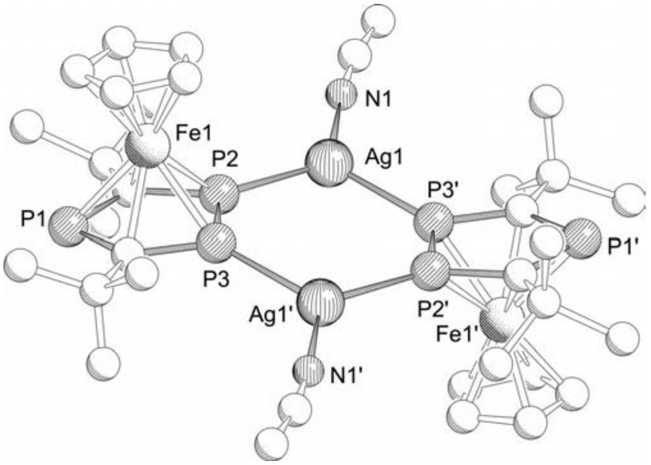


Figure 5. Structure of the dicationic part of complex [{FeCp(η^5-P_3C_2tBu$_2$)}Ag(MeCN)]$_2$[Al{OC(CF_3)$_3$}$_4$]$_2$ (**11**) (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P2–P3 2.105(3), Ag1–P2 2.432(2), Ag1–P3 2.460(2), Ag1–P2–P3 121.50(11), Ag1–P3–P2 119.39(11), P2–Ag1–P3 116.23(8).

Conclusions

The results have shown that the reaction behavior of the 1,2,4-triphospholyl ring in the triphosphaferrocenes is very sensitive towards the sterics of the adjacent Cp^R ligand and the halogen substituent used. Whereas for the Cp ligand the formation of similar dimeric compounds [{FeCp(η^5:η^1:η^1-P_3C_2tBu$_2$)}{μ-CuX(MeCN)}]$_2$ (X = Cl, Br) (**5a,b**) with coordination number 4 at the Cu atom were observed, using bulkier Cp′′′ ligands leads to the dimeric compound [{FeCp′′′(P_3C_2tBu$_2$)}$_2${(μ-CuBr)}$_2$] (**8**) with coordination number 3 at the copper atoms. In addition to dimer **8**, a fragmentation of the 1,2,4-triphospholyl ring of Cp′′′ derivative **3** into an unexpected and very rare 1,2-diphosphete moiety was observed, and the paramagnetic complex [{FeCp′′′(η^4:η^1:η^1-P_2C_2tBu$_2$)}(μ-CuBr)]$_2$ (**9**) was isolated. This tendency is already partially expressed in the reaction with CuBr and Cp derivative **1**, since in the 1D polymer **6** a [(CuBr)$_3$(CH_3CN)$_2$] moiety interconnects the triphosphaferrocenes. In contrast, the reaction of Cu^I iodide with Cp derivative **1** leads to the (CuI)$_7$ cage compound **7** regardless of the used stoichiometry, revealing an extended iodide-centered (CuI)$_7$ cage surrounded by three 1,2,4-triphosphaferrocenes. The mentioned behavior is also observed for a 1:2 stoichiometry in these reactions. However, by applying a 1:2 stoichiometry between Cp derivative **1** and CuBr, the 1D polymer **6** is formed in which $[(CuBr)_3(CH_3CN)_2]$ moieties bridge the triphosphaferrocenes, instead of dimer **5b**, which is found for the 1:1 reaction ratio. In contrast to the products **5a**,**b**, **7**, and **8** obtained before, in which only the two neighboring phosphorus atoms are involved in the coordination to the Cu^I halides, in compound **6**, all of the P atoms of the triphosphole ring are linked to Cu moieties. Furthermore, similarly applying a 1:2 stoichiometry but using the bulky Cp′′′ ligand in **3** leads to a complete fragmentation of the 1,2,4-triphosphaferrocene ring into a tetraphosphabutadiene moiety revealing the decisive steric influence of the adjacent Cp^R ligand. The formed tetraphosphabutadiene moiety is stabilized as a middle deck in triple-decker sandwich complexes, which are linked by $[(CuX)_2CH_3CN]$ moieties into the 1D polymeric structure of product **10**. Interestingly, for CuI with the Cp′′′ derivative **3** the exclusive formation of 1D polymer **10b** is seen, independent of the used stoichiometry. This fragmentation is not observed for Cp or Cp* derivatives **1** and **2** of the 1,2,4-triphosphaferrocenes. However, here the excess of CuX and the 1:2 stoichiometry leads to the formation of CuX networks leading for Cp derivative **1** with CuBr to the 1D polymer **6** instead of the dimeric molecular compound **8**, which was seen when a 1:1 ratio was used. Using CuI and Cp derivative **1** the formation of $(CuI)_n$ cages is observed independently of the used stoichiometry. The same behaviour of cage product formation **E** and **F** is generally found by using the Cp* derivative **2** in the reaction with Cu^I halides. Moreover, Cp derivative **1** in combination with silver(I) salts carrying the weakly coordinating counter anion $[Al\{OC(CF_3)_3\}_4]^-$ led to successful isolation of the dimeric dicationic silver complex $[\{FeCp(\mu,\eta^5{:}\eta^1{:}\eta^1\text{-}P_3C_2tBu_2)\}\{Ag(MeCN)\}]_2[Al\{OC(CF_3)_3\}_4]_2$ (**11**).

By generalizing the reactions of the three triphosphaferrocenes **1**, **2** and **3** with Cu^I halides it can be assessed that the reaction of the, sterically speaking small triphosphaferrocenes $[FeCp(\eta^5\text{-}P_3C_2tBu_2)]$ (**1**) and $[FeCp^*(\eta^5\text{-}P_3C_2tBu_2)]$ (**2**) with CuX (X = Cl, Br and I) leads to the formation of oligomeric or polymeric complexes, whereas the sterically more crowded triphosphaferrocene $[FeCp'''(\eta^5\text{-}P_3C_2tBu_2)]$ (**3**) reacts with copper halides through the fragmentation of the triphospholyl unit in **3**. An exception is the reaction of **3** with CuCl in a 1:1 stoichiometry.

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. $[FeCp(\eta^5\text{-}P_3C_2tBu_2)]$ (**1**),[12] $[FeCp'''(\eta^5\text{-}P_3C_2tBu_2)]$ (**3**),[21] and $Ag[Al\{OC(CF_3)_3\}_4]$[19] were prepared according to literature procedures.

Crystal Structure Determination: The crystal structure analyses were performed with an Oxford Diffraction Gemini R Ultra CCD (**6**, **7**, **9**, **10a**, **11**) using Cu radiation (λ = 1.54178 Å) and with a Bruker Smart APEX employing Mo radiation (λ = 0.71073 Å), respectively (**10b**). Semi-empirical absorption corrections from equivalents (multi-scan) were applied.[22] The structures were solved by direct methods with the program SIR-97,[23] and full-matrix least-square refinement on F^2 in SHELXL-97[24] was performed. Hydrogen atoms were calculated from geometry considerations and refined isotropically, applying the riding model. The strategy for **6** was erroneously computed for *mmm* Laue class, due to a β-angle close to 90°. Thus, only a completeness of 83% could be achieved. Hence all carbon and nitrogen atoms were refined isotropically. In **7** parts of the structure are disordered and were refined using least-square restraints. A further two severely disordered CH_2Cl_2 molecules were treated with SQUEEZE.[25] Only low-quality crystals were available for **9** and **10a**. For this reason restraints were applied (**9**) and atoms were partially kept isotropic (**10a**), resulting in increased quality factors. The very small crystals of **11** undergo a first-order phase transition at about 140 K. Hence the crystal was processed at 150 K. This high temperature leads to an extreme disorder of the aluminate anion. Together with the weak data owing to the size of the crystal, the counterion $[Al\{OC(CF_3)_3\}_4]^-$ could not be modeled. For these reasons the only opportunity was to use SQUEEZE.[25] The Flack parameters of **10a** and **10b** are 0.493(17) and 0.466(15), respectively. However, PLATON detects no additional symmetry.[26] Hence, the most likely explanation is inversion twinning. Residual density is located close to the heavy atoms. Further crystallographic details are summarized in Table 1. CCDC-815415 (for **6**), -815416 (for **7**), -815417 (for **9**), -815412 (for **10a**), -815414 (for **10b**), and -815414 (for **11**) 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.

$[\{FeCp(\eta^5{:}\eta^1{:}\eta^1{:}\eta^1\text{-}P_3C_2tBu_2)\}\{CuBr\}_2]_n$ (5b): CuBr (9 mg, 0.058 mmol) in CH_3CN (5 mL) was layered onto a solution of $[FeCp(\eta^5\text{-}P_3C_2tBu_2)]$ (20 mg, 0.056 mmol) in CH_2Cl_2 (5 mL). After the reaction mixture diffused completely, the solution was concentrated to ca. 5 mL and kept in the refrigerator for one week. Red crystals of **5b** were formed on the wall of the Schlenk tube. Yield: 11 mg (38%). The mother liquor was used for the following NMR and mass spectroscopic measurements. ^1H NMR (C_6D_6/MeCN, 27 °C, 400.13 MHz): δ = 4.71 (s, 5 H), 1.26 (s, 18 H) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6/MeCN, 27 °C, 161.98 MHz, AM_2 spin system): $\delta(P_A)$ = 33.5 (t, 1 P), $\delta(P_M)$ = 14.6 (br., 2 P), $^2J(P_A,P_M)$ = 44.6 Hz ppm. Positive-ion ESI-MS (MeN, r.t.): *m*/*z* (%) = 456 (28) $[\{FeCp(P_3C_2tBu_2)\}CuMeCN]^+$, 599 (100) $[\{FeCp(P_3C_2tBu_2)\}Cu_2BrMeCN]^+$, 640 (78) $[\{FeCp(P_3C_2tBu_2)\}Cu_2Br_2MeCN]^+$, 767 (18) $[\{FeCp(P_3C_2tBu_2)\}_2Cu_2]^+$, 910 (17) $[\{FeCp(P_3C_2tBu_2)\}_2Cu_2Br]^+$, 951 (20) $[\{FeCp(P_3C_2tBu_2)\}_2Cu_2BrMeCN]^+$.

$[\{FeCp(\eta^5{:}\eta^1{:}\eta^1{:}\eta^1\text{-}P_3C_2tBu_2)\}_2\{CuBr\}_3(MeCN)_2]_n$ (6): A solution of CuBr (17 mg, 0.11 mmol) in CH_3CN (5 mL) was layered onto a solution of $[FeCp(\eta^5\text{-}P_3C_2tBu_2)]$ (20 mg, 0.056 mmol) in CH_2Cl_2 (5 mL) at room temperature. After the reaction mixture diffused completely, the solution was concentrated to ca. 5 mL and kept at about 0 °C for one week. A brown crystalline compound was obtained on the walls of the Schlenk tube. Yield: 10 mg (27%). ^1H NMR (CD_2Cl_2, 25 °C, 400.13 MHz): δ = 1.32 (s, 18 H), 4.80 (s, 5 H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 161.97 MHz) AM_2 spin system: $\delta(P_A)$ = 33.8 (t), $\delta(P_M)$ = 14.9 (br), $^2J(P,P)$ = 44.6 Hz ppm. Positive-ion EI-MS (MeN, r.t.): *m*/*z* (%) = 498 (2.5) $[\{FeCp(P_3C_2tBu_2)\}CuBr]^+$, 352 (13) $[\{FeCp(P_3C_2tBu_2)\}]^+$, 185 (58) $[\{Fe(P_3C_2tBu_2)\}]^+$.

$[\{FeCp(\eta^5{:}\eta^1{:}\eta^1\text{-}P_3C_2tBu_2)\}_3(CuI)_7MeCN]$ (7): A solution of CuI (21 mg, 0.11 mmol) in CH_3CN (6 mL) was layered onto a solution

Table 1. Crystallographic data and details of X-ray experiments of complexes **6**, **7**, **9**–**11**.

	6	**7**	**9**
*F*ormula	$C_{76}H_{116}Br_{12}Cu_{12}Fe_4N_8P_{12}$	$C_{93}H_{147}Cu_{14}Fe_6I_{14}NP_{18}$	$C_{56}H_{98}Br_2Cl_4Cu_2Fe_2P_4$
M_r	3458.22	4828.91	1435.62
Crystal size [mm]	0.10 × 0.05 × 0.05	0.08 × 0.02 × 0.02	0.09 × 0.02 × 0.02
T [K]	123(1)	105(1)	150(1)
Space group	*Cc*	*Cmcm*	$P\bar{1}$
Crystal system	monoclinic	orthorhombic	triclinic
a [Å]	37.4376(11)	15.592(3)	11.072(3)
b [Å]	21.6564(11)	26.504(3)	11.461(2)
c [Å]	27.8413(8)	21.542(3)	14.659(4)
a [°]	90	90	84.271(19)
β [°]	90.064(4)	90	75.60(2)
γ [°]	90	90	63.03(2)
V [Å^3]	22572.7(15)	8902(2)	1605.6(8)
Z	8	2	1
$\rho_{calcd.}$ [g cm^{-3}]	2.035	1.801	1.485
M [mm^{-1}]	13.258	26.350	8.478
Θ range [°]	2.84–62.25	3.33–65.01	4.33–51.65
Index range	$-42 \le h \le 42$	$-18 \le h \le 17$	$-11 \le h \le 10$
	$-22 \le k \le 18$	$-30 \le k \le 30$	$-10 \le k \le 11$
	$-24 \le l \le 31$	$-25 \le l \le 23$	$-14 \le l \le 14$
Data/restraints/parameters	32319/2/1390	37001/60/247	8205/30/331
Unique reflections $I > 2\sigma$ (R_{int})	17755 (0.0284)	3973 (0.0234)	3405 (0.990)
GOF in F^2	1.117	0.981	0.985
R_1/wR_2 [$I > 2\sigma(I)$]	0.0499, 0.1233	0.0323, 0.0889	0.0961, 0.2478
R_1/wR_2 (all data)	0.0528, 0.1245	0.0393, 0.0909	0.1774, 0.3045
Largest diff. [e Å^{-3}]	1.510, –0.744	1.632, –1.572	1.738, –2.243
	10a	**10b**	**11**
Formula	$C_{37}H_{63}Br_2Cl_2Cu_2Fe_2NP_4$	$C_{36.2}H_{61.8}Cl_2Cu_2Fe_2I_2N_{0.6}P_4$	$C_{68}H_{56}Ag_2Al_2Cl_4F_{72}Fe_2N_2O_8P_6$
M_r	1115.26	1192.85	3106.13
Crystal size [mm]	0.40 × 0.02 × 0.01	0.24 × 0.17 × 0.10	0.08 × 0.06 × 0.05
T [K]	150(1)	100(1)	150(1)
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
Crystal system	orthorhombic	orthorhombic	monoclinic
a [Å]	10.1451(3)	10.243(2)	10.7479(9)
b [Å]	13.4635(4)	13.351(3)	31.380(5)
c [Å]	33.2088(16)	33.422(7)	15.628(3)
a [°]	90	90	90
β [°]	90	90	97.782(11)
γ [°]	90	90	90
V [Å^3]	4535.9(3)	4570.6(17)	5222.3(14)
Z	4	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.633	1.734	1.975
M [mm^{-1}]	10.766	3.174	8.803
Θ range [°]	2.66–62.94	1.64–28.00	2.82–51.36
Index range	$-11 \le h \le 9$	$-12 \le h \le 13$	$-10 \le h \le 10$
	$-15 \le k \le 15$	$-17 \le k \le 12$	$-31 \le k \le 31$
	$-35 \le l \le 38$	$-40 \le l \le 42$	$-15 \le l \le 14$
Data/restraints/parameters	15442/0/269	20124/10/496	18263/6/242
Unique reflections $I > 2\sigma$ (R_{int})	6822 (0.0575)	10081 (0.0370)	2570
GOF in F^2	1.111	0.959	0.860
R_1/wR_2 [$I > 2\sigma(I)$]	0.0961, 0.2259	0.0396, 0.0798	0.0483, 0.1050
R_1/wR_2 (all data)	0.1199, 0.2374	0.0556, 0.0829	0.0823, 0.1083
Largest diff. [e Å^{-3}]	1.601, –1.354	1.513, –0977	0.409, –0.336

of [FeCp(η^5-$P_3C_2t Bu_2$)] (20 mg, 0.056 mmol) in CH_2Cl_2 (6 mL). After the reaction mixture diffused completely, the solution was concentrated to ca. 5 mL, layered with pentane (5 mL), and allowed to stand for one week. A red crystalline solid was obtained on the walls of the Schlenk tube. Yield: 20 mg (43.5 %). ^{1}H NMR (CD_2Cl_2, 27 °C, 400.13 MHz): δ = 3.56 (m, 5 H), 1.22 (m, 9 H), 0.8 (m, 9 H) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 27 °C, 161.98 MHz, AM_2 spin system): $\delta(P_A)$ = 34.9 (br., $\omega_{1/2}$ = 180 Hz), $\delta(P_M)$ = 8.2 (br., $\omega_{1/2}$ = 240 Hz) ppm. EI-MS (70 eV): *m*/*z* (%) = 2260 (22.5) [{FeCp($P_3C_2t Bu_2$)}$_3$Cu$_7$I$_6$]$^+$, 2133 (30) [{FeCp($P_3C_2t Bu_2$)}$_3$Cu$_5$I$_6$]$^+$, 1945 (29) [{FeCp($P_3C_2t Bu_2$)}$_3$Cu$_4$I$_5$]$^+$.

[{FeCp′′′(μ,η^5:η^1:η^1-$P_3C_2tBu_2$)}(CuBr)]$_2$ (8): A solution of CuBr (6 mg, 0.038 mmol) and CH_3CN (2 mL) was layered onto a solution of [FeCp′′′(η^5-$P_3C_2t Bu_2$)] (20 mg, 0.038 mmol) in CH_2Cl_2 (3 mL) at room temperature. After complete diffusion of the two phases, the red-brown reaction mixture was used for NMR and mass spectroscopic measurements. ^{31}P{^{1}H} NMR ([D$_8$]THF/

MeCN, 27 °C, 161.98 MHz, AM_2 spin system): $\delta(P_A) = 51.6$ (t), $\delta(P_M) = 28.4$ (br), $^2J(P_A,P_M) = 44.7$ Hz. Positive-ion ESI-MS (MeN, r.t.): m/z (%) = 1247 (1.0) $[\{FeCp'''(P_3C_2tBu_2)\}_2Cu_2Br]^+$, 1103 (1.7) $[\{FeCp'''(P_3C_2tBu_2)\}_2Cu]^+$, 832 (3.1) $[FeCp'''(P_3C_2tBu)Cu_3BrMeCN]^+$, 624 (22) $[FeCp'''(P_3C_2tBu)CuMeCN]^+$, 582 (82) $[FeCp'''(P_3C_2tBu)Cu]^+$.

$[\{FeCp'''(\mu,\eta^4{:}\eta^1{:}\eta^1\text{-}P_2C_2tBu_2)\}\{CuBr(MeCN)\}]_2$ (9): A solution of CuBr (3 mg, 0.019 mmol) in CH_3CN (2 mL) was layered onto a solution of $[FeCp'''(\eta^5\text{-}P_3C_2tBu_2)]$ (10 mg, 0.019 mmol) in CH_2Cl_2 (3 mL) at room temperature. After complete diffusion of the two phases, the reaction mixture was concentrated under reduced pressure to about one half of the original volume (2.5 mL) and stored at –28 °C. After 2 weeks the brown crystalline complex **9** was obtained on the walls of the Schlenk tube. Yield: 5 mg (38.8%). Positive-ion ESI-MS (MeN, r.t.): m/z (%) = 1103 (2.5) $[\{FeCp'''(P_2C_2tBu_2)\}_2Cu_2]^+$, 489 (4.2) $[FeCp'''(P_2C_2tBu_2)]^+$. ESR (r.t.): $g = 2.026$, $a_1 = 10$ mT, g (half field) = 5.3.

$[\{(FeCp''')_2(\mu,\eta^4{:}\eta^4\text{-}P_4)\}(CuBr)_2(MeCN)]_n$ (10a): A solution of CuBr (12 mg, 0.075 mmol) and CH_3CN (5 mL) was layered onto a solution of $[FeCp'''(\eta^5\text{-}P_3C_2tBu_2)]$ (20 mg, 0.0375 mmol) in CH_2Cl_2 (7 mL) at 4 °C. After 1 week, a dark-brown crystalline solid formed at the bottom of the Schlenk tube. Yield: 16 mg (73.4%). $^{31}P\{^1H\}$ NMR (C_6D_6/DMF, 27 °C, 161.98 MHz): $\delta = 82.3$ (br., $\omega_{1/2} = 970$ Hz) ppm. Positive-ion ESI-MS (MeN, r.t.): m/z (%) = 1611 (0.2) $[\{(FeCp''')_2(P_4)\}_2Cu_2Br]^+$, 1467 (0.5) $[\{(FeCp''')_2(P_4)\}_2Cu]^+$, 765 (7.0) $[(FeCp''')_2(P_4)Cu]^+$, 702 (100) $[(FeCp''')_2(P_4)]^+$.

$[\{(FeCp''')_2(\mu,\eta^4{:}\eta^4\text{-}P_4)\}(CuI)_2(MeCN)]_n$ (10b): A solution of CuI (18.3 mg, 0.096 mmol) in CH_2Cl_2/CH_3CN (2 mL/3 mL) solvent was layered onto a solution of $[FeCp'''(\eta^5\text{-}P_3C_2tBu_2)]$ (25 mg, 0.048 mmol) in CH_2Cl_2 (5 mL) at room temperature. After one week, a dark-brown crystalline solid was obtained on the wall of the Schlenk tube. Yield: 15 mg (33.4%). ^1H NMR (CD_2Cl_2, 27 °C, 400.13 MHz): $\delta = 4.58$ (s, 2 H), 1.11 (s, 18 H), 1.04 (s, 9 H) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6/DMF, 27 °C, 161.98 MHz): $\delta = 90.2$ (br., $\omega_{1/2} = 650$ Hz) ppm. Positive-ion ESI-MS (MeN, r.t.): m/z (%) = 953 (4.4) $[(FeCp''')_2(P_4)Cu_2I]^+$, 891 (4.0) $[(FeCp''')_2(P_4)CuI]^+$, 826 (39.0) $[(FeCp''')_2(P_4)Cu_2]^+$, 765 (5.4) $[(FeCp''')_2(P_4)Cu]^+$, 702 (100) $[(FeCp''')_2(P_4)]^+$.

$[\{FeCp(\mu,\eta^5{:}\eta^1{:}\eta^1\text{-}P_3C_2tBu_2)\}\{Ag(MeCN)\}]_2[Al\{OC(CF_3)_3\}_4]_2$ (11): A mixture of $Ag[Al\{OC(CF_3)_3\}_4]$ (30 mg, 0.028 mmol) and $[FeCp(\eta^5\text{-}P_3C_2tBu_2)]$ (20 mg, 0.028 mmol) in CH_2Cl_2 (10 mL) and MeCN (5 mL) was stirred in the dark for six hours. The reaction mixture was then filtered through diatomaceous earth and the filtrate kept at 4 °C for one week. Red-orange needle-like crystals were obtained on the walls of the Schlenk tube. Yield: 15 mg (9%). ^1H NMR ($[D_8]$THF, 27 °C, 400.13 MHz): $\delta = 3.57$ (s, 5 H), 1.43 (s, 18 H) ppm. $^{31}P\{^1H\}$ NMR ($[D_8]$THF, 27 °C, 161.98 MHz, AM_2 spin system): $\delta(P_A) = 34.3$ (t), $\delta(P_M) = 12.7$ (d) ppm [$^2J(P_A,P_M) = 44.1$ Hz]. Positive-ion ESI-MS (MeN, r.t.): m/z (%) = 811 (100) $[\{FeCp(P_3C_2tBu_2)\}_2Ag]^+$, 500 (93.5) $[FeCp(P_3C_2tBu_2)AgMeCN]^+$. Negative-ion ESI-MS (MeCN, r.t.): m/z (%) = 967 (100) $[Al\{OC(CF_3)_3\}_4]^-$.

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