SHORT COMMUNICATION

DOI: 10.1002/ejic.200800852

Unexpected Differences in the Coordination Behaviour of 1,2,4-Triphosphaferrocenes towards Cu^{I} Chloride

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

Keywords: Supramolecular chemistry / Copper / Fragmentation reactions / Triphosphaferrocenes / Tetraphosphabutadiene ligand

The coordination behaviour of 1,2,4-triphosphaferrocenes [FeCp^{R}(η^5-P$_3$C$_2$$tBu_2$)] [Cp^{R} = Cp (**1**), Cp$'''$ (**2**)] towards Cu^{I} chloride is significantly influenced by the substitution pattern of the cyclopentadienyl ring attached to iron. The dimeric copper complexes [{FeCp(η^5:η^1:η^1-P$_3$$tBu_2C_2$)}{$\mu$-CuCl(MeCN)}]$_2$ (**3**) and [{FeCp$'''$ (η^5:η^1:η^1-P$_3$$tBu_2C_2$)}($\mu$-CuCl)]$_2$ (**4**), in which two 1,2,4-triphosphaferrocenes are linked by two CuCl centres to form dimeric complexes were obtained in reactions using a 1:1 stoichiometry. Whereas in **3** a tetracoordinated Cu atom is revealed, **4** possesses a threefold-coordinated Cu atom due to the steric influence of the bulkier Cp$'''$ ligand. However, if the reaction is carried out with an excess of CuCl in a 1:2 stoichiometry for the Cp derivative **1** the same product **3** is obtained, whereas in the case of a tri-*tert*-butyl-substituted Cp$'''$ ligand complex **2** the triphospholyl ring is fragmented under mild conditions to a tetraphosphabutadiene moiety within an iron triple-decker sandwich complex [{(FeCp$'''$)$_2$(μ,η^4:η^4:η^1:η^1-P$_4$)}{μ-CuCl(MeCN)}]$_\infty$ (**5**) embedded in a CuCl polymer matrix.

Introduction

Over the last decades the chemistry of naked E$_n$ ligand complexes of the heavier group 15 elements has been developed very rapidly.[1] Major topics in research were the synthesis of novel E$_n$ rich ligands as well as the investigation of the reaction behaviour with organometallic agents. Yet, in the past the coordination chemistry towards cationic metal centres and Cu^{I} halides has so far been limited to the use of *cyclo*-P$_3$ ligand complexes like [M(η^3-P$_3$)(triphos)] [M = Co, Rh, or Ir; triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane].[2] In contrast to contemporary concepts in supramolecular chemistry using N- and O-donor ligand moieties to connect different metal centers together,[3] our approach is based on the use of E$_n$ ligand complexes of group 15 elements. The first attempts started with the use of the tetrahedral complex [{MoCp(CO)$_3$}$_2$(η^2-P$_2$)] which reacts with Cu^{I} halides to give 1D polymers.[4] Path-breaking results were obtained by using [FeCp*(η^5-P$_5$)] as starting material. In its reaction with Cu^{I} halides CuX for X = Br, I the formation of the 2D polymers [CuX{Cp*Fe(η^5:η^1:η^1:η^1-P$_5$)}]$_n$ (X = Br, I) is observed, whereas with CuCl the 1D polymer [Cu(μ-Cl){Cp*Fe(η^5:η^1:η^1-P$_5$)}]$_n$ is formed.[5] Under special conditions the formation of spherical nanostructured complexes [{FeCp*(η^5:η^1:η^1:η^1:η^1:η^1-P$_5$)}$_{12}${CuX}$_{10}${Cu$_2$X$_3$}$_5${Cu(CH$_3$CN)$_2$}$_5$] (X = Cl, Br)[6] with fullerene-like symmetry are produced.

Because in the polymers both the 1,2- (type **A**) and the 1,2,4- (type **B**) coordination mode of the *cyclo*-P$_5$ ring are observed[5] the question arises as to whether in the related 1,2,4-triphosphaferrocene derivatives [FeCp^{R}(η^5-P$_3$C$_2$$tBu_2$)] [Cp^{R} = Cp (**1**),[7] η^5-C$_5$H$_2$$tBu_3$ (Cp$'''$) (**2**)[8]] the presence of tBu groups on the neighbouring ring C atoms would influence the coordination behaviour (possible type **A**$'$ and **B**$'$ coordination) and, furthermore, if the substitution pattern on the adjacent Cp^{R} ring of the starting triphosphaferrocenes would also have an effect. To date the ligating ability of **1** was only studied towards organometallic moieties like [W(CO)$_5$] (M = Mo, W), [RhCp*(CO)], [ReCp(CO)$_3$Br], and [PtCl$_2$(PR$_3$)] (R = Me, Et, Ph).[9]

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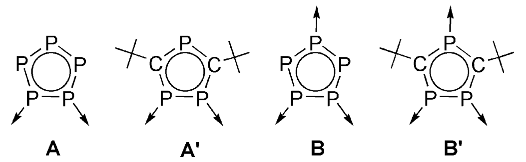
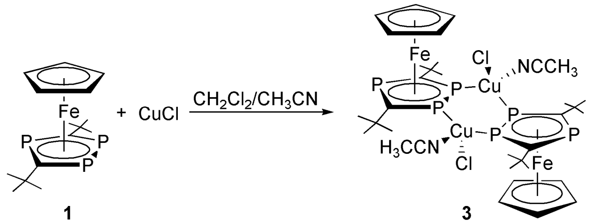


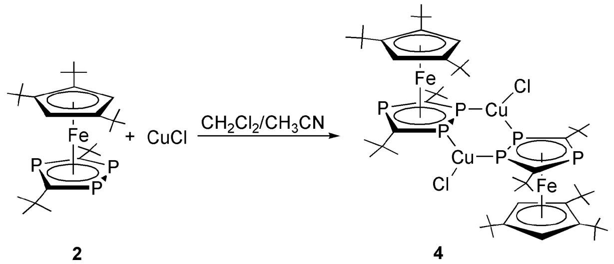
Herein we report the first results on the coordination behaviour of the 1,2,4-triphosphaferrocenes **1** and **2** towards CuCl, which depending on the substitution pattern at the Cp^R ligand results (a) in different coordination behaviour and (b) an unexpected fragmentation reaction resulting in the formation of a remarkable 1D polymeric triple-decker η^4-ligated tetraphosphabutadiene complex linked by $(CuCl)_2$ moieties.

Results and Discussion

Acetonitrile solutions of CuCl were carefully layered on a CH_2Cl_2 solutions of **1** and **2** in a stoichiometric ratio of 1:1 resulting in the formation of the dimeric copper complexes $[\{FeCp(\eta^5{:}\eta^1{:}\eta^1\text{-}P_3tBu_2C_2)\}\{\mu\text{-}CuCl(MeCN)\}]_2$ (**3**) and $[\{FeCp'''(\eta^5{:}\eta^1{:}\eta^1\text{-}P_3tBu_2C_2)\}(\mu\text{-}CuCl)]_2$ (**4**), respectively, in which two 1,2,4-triphosphaferrocenes are linked by two CuCl centres to form dimeric complexes [Equations (1) and (2)]. The only difference in the structure of both products is the coordination number of the linking Cu atoms. Whereas in **3** roughly tetrahedral Cu atoms are observed, in the more bulky Cp′′′ derivative **4** planar threefold coordinated Cu atoms are present, reflecting the steric influence of the substitution pattern of the neighbouring Cp^R ligand on iron.



1 **3** (1)



2 **4** (2)

The red crystalline and air-sensitive compounds **3** and **4** are only sparingly soluble in polar solvents such as CH_2Cl_2, CH_3CN, and THF and are insoluble in toluene and hydrocarbons. Although in the ESI-MS spectra the molecular ion peaks are not found, appropriate fragments such as $[\{FeCp^R(P_3C_2tBu_2)\}_2Cu_2Cl]^+$ and $[\{FeCp'''(P_3C_2tBu_2)\}_2Cu]^+$ (Cp^R=Cp, Cp′′′) are observed, indicating that the dimeric copper complexes also exist in solution. The $^{31}P\{^1H\}$ NMR spectra of both products reveal the expected AM_2 patterns for the P_3C_2 ring consisting of broadened triplet and doublet signals. While the chemical shift of the uncoordinated P_A-atom remains almost unchanged[10] the P_M signals are shifted upfield relative to the starting materials[7,8] resulting from the coordination to the copper atoms.

The molecular structures of **3** and **4** are determined by single-crystal X-ray diffraction as illustrated in Figures 1 and 2.

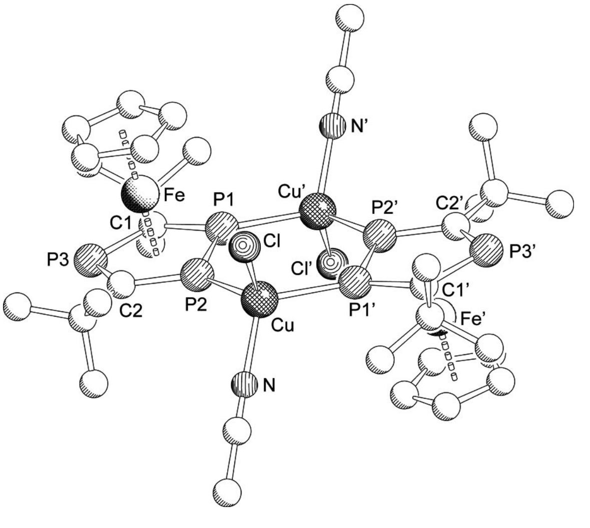


Figure 1. Molecular structure of $[\{FeCp(\eta^5{:}\eta^1{:}\eta^1\text{-}P_3tBu_2C_2)\}\{\mu\text{-}CuCl(MeCN)\}]_2$ (**3**) (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–P2 2.1163(2), P2–Cu 2.2891(3), P1–Cu′ 2.2804(4), P1–C1 1.7742(3), P2–C2 1.7740(3), P3–C1 1.7661(3), P3–C2 1.7841(3), P2–Fe 2.3405(2), P1–Fe 2.3351(2), P3–Fe 2.3026(2), Cu–Cl 2.2902(2), C1–Fe 2.1311(1), C2–Fe 2.1340(2), Cu–P2–P1 123.569(4), P2–P1–Cu′ 124.560(4), P2–Cu–P1′ 111.018(4), P1–P2–C2 99.181(5), P2–P1–C1 99.906(5), P2–Fe–P1 53.826(2), P2–P1–Fe 63.219(2), C1–P3–C2 99.249(5), P1–Cu′–Cl 113.491(3), P2–Cu–Cl 105.506(3).

Compounds **3** and **4** consist of two triphosphaferrocene units which bridge two CuCl fragments via the two adjacent phosphorus atoms in the $P_3C_2tBu_2$ ring system. The six-membered ring which is formed is not precisely planar resulting in a “stair-like” arrangement of the whole molecule (Figures 1 and 2). In **4**, the two copper atoms lie slightly above and below the plane defined by the phosphorus atoms P1, P2, P1′, and P2′ [deviation of the copper atoms from P1P2P1′P2′ plane: 0.100(1) Å], whereas in **3** the deviation of the copper atoms from the P1P2P1′P2′ plane is greater [0.189(1) Å], however, the two five-membered P_3C_2 rings are coplanar. This arrangement contrasts with that observed in a similar compound $[\{FeCp^*(\eta^5{:}\eta^1{:}\eta^1\text{-}P_3tBu_2C_2)\}\{Ni(CO)_2\}]_2$, in which the six-membered ring, consisting of four phosphorus and two nickel atoms, exhibits a clear boat configuration.[11]

The copper atoms in **3** are tetrahedrally bonded to two phosphorus atoms of two different P_3C_2 rings, one chlorine atom, and one nitrogen atom of an acetonitrile molecule [average P–Cu–Cl angle 109.50(8)°]. This differs from complex **4** where the copper atoms coordinate trigonally to two

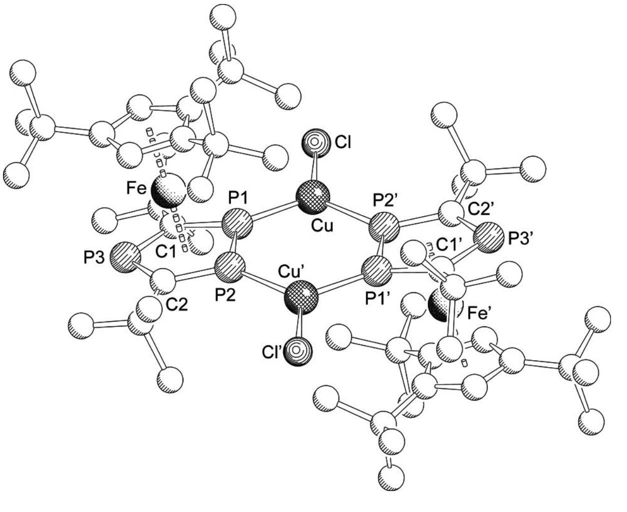
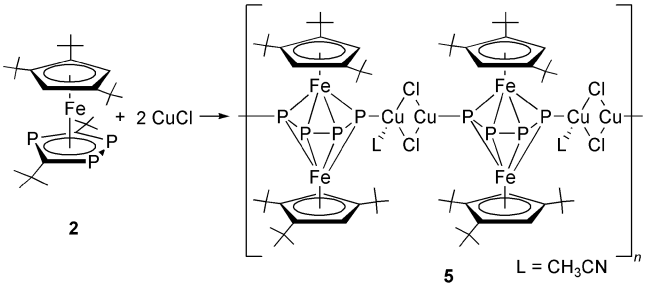


Figure 2. Molecular structure of $[\{FeCp'''(\eta^5:\eta^1:\eta^1\text{-}P_3tBu_2C_2)\}(\mu\text{-}CuCl)]_2$ (**4**) in the crystal (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–P2 2.0717(19), P1–Cu 2.1057(13), P2–Cu 2.2804(13), P1–C1 1.751(4), P2–C2 1.705(4), P3–C1 1.670(5), P3–C2 1.792(5), P1–Fe 2.3346(14), P2–Fe 2.4568(14), P3–Fe 2.3009(13), Cu–Cl 2.1539(19), C1–Fe 2.266(5), C2–Fe 2.249(4), Cu–P1–P2 121.40(6), P1–P2–Cu 124.14(6), P1–Cu–P2 114.20(6), P2–P1–C1 104.91(18), P1–P2–C2 95.72(18), P1–Fe–P2 51.16(5), P1–P2–Fe 61.37(5), C1–P3–C2 102.0(2), P2–Cu–Cl 126.60(6), P1–Cu–Cl 119.15(6).

phosphorus atoms and one chlorine atom [average P–Cu–Cl angle of 122.88(6)°]. The difference reflects the greater steric hindrance of the bulky *t*Bu groups attached to the cyclopentadienyl ring in **4** to allow only a threefold coordination of the copper atom. The Cu–P bond lengths [av. 2.2847(19) Å] in **3** are longer than those in **4** [two different P–Cu bond lengths of 2.1057(13) Å and 2.2804(13) Å; av. 2.1930(15) Å] suggesting that the Cu–P interaction is also influenced by the coordination geometry. Likewise, no variation of the P–P bond lengths is found in **3** [2.116(2) Å] and the triphosphaferrocene starting material **1** $[FeCp(\eta^5\text{-}P_3C_2tBu_2)]$ [2.114(1) Å]. In contrast, the P–P bond length in **4** [2.0707(19) Å] is shorter than that in the uncoordinated triphosphaferrocene **2** [2.121(3) Å], indicating that the two adjacent phosphorus atoms certainly participate in η^1-bonding to the Cu atoms via the phosphorus lone pairs. In contrast, the elongation of the P–P bond lengths is caused by the [RhCp*(CO)] fragment in the η^2-coordinated complex $[RhCp^*(CO)\{CpFe(\eta^5\text{-}P_3C_2tBu_2)\}]$ where bond lengthening can be attributed to significant back bonding of electrons in the Rh d-orbitals into the $\eta^5\text{-}P_3C_2tBu_2$ ring π^* orbitals.[9a]

When the reactions (1) and (2) are carried out in a 1:2 ratio with an excess of the Cu^I chloride at room temperature, **1** affords the *same* dimeric product **3**, whereas **2** undergoes an unexpected fragmentation of the triphosphacyclopentadienyl ligand with the formation of a brown crystalline polymeric product containing η^4-ligated tetraphosphabutadiene $[(FeCp''')_2(\mu,\eta^4:\eta^4\text{-}P_4)]$ moieties. These moieties coordinate through their two terminal P atoms to the CuCl dimers connecting the ligands, resulting in an infinite chain-like polymer $[\{(FeCp''')_2(\mu,\eta^4:\eta^4:\eta^1:\eta^1\text{-}P_4)\}\{\mu\text{-}CuCl(MeCN)\}]_\infty$ (**5**) [Equation (3)]. Monomeric triple-decker compounds $[(FeCp^R)_2(\eta^4\text{-}P_4)]$ [Cp^R = 1,3-$(Me_3Si)_2C_5H_3$ (**6a**) and 1,3,4-$(Me_3Si)_3C_5H_2$ (**6b**)] resulting from the reaction of $[FeCp^RBr(PPhMe_2)_2]$ and NaP_5 are described by Miluykov and co-workers[12] and Scherer et al. reported the synthesis of $[(FeCp''')_2(\eta^4\text{-}P_4)]$ (**7**) as a thermolysis



2

5

(3)

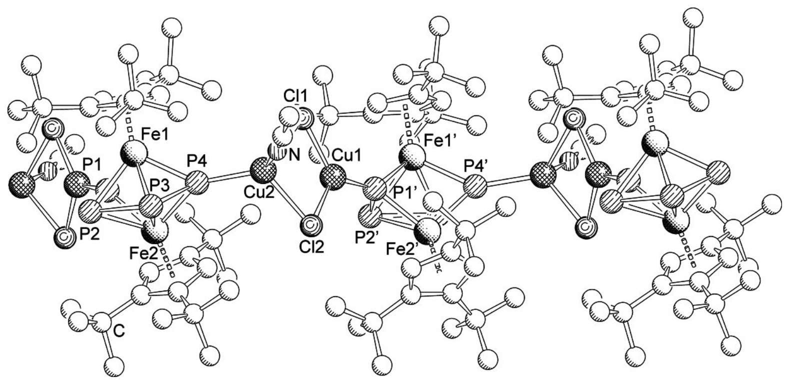


Figure 3. Section of the 1D polymeric structure of $[\{(FeCp''')_2(\mu,\eta^4:\eta^4\text{-}P_4)\}\{(CuCl)_2(MeCN)\}]$ (**5**) (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–P2 2.0956(19), P2–P3 2.3728(18), P3–P4 2.1023(17), P1–Cu1 2.1626(14), P4–Cu2 2.2285(12), P1–Fe1 2.2436(13), P2–Fe1 2.3538(13), P3–Fe1 2.3528(13), P4–Fe1 2.2657(12), P1–Fe2 2.2462(13), P2–Fe2 2.3464(14), P3–Fe2 2.3482(11), P4–Fe2 2.2591(12), Cu1–P1–P2 135.69(7), P1–P2–P3 105.44(7), P2–P3–P4 105.99(6), P3–P4–Cu2 128.46(7), Cl1–Cu1–Cl2 102.86(6), P1–Cu1–Cl2 125.17(6), Cl1–Cu1–P1 131.91(6), Cl1–Cu2–P4 121.23(6), Cl1–Cu2–Cl2 93.33(5), Cl2–Cu2–P4 116.65(5).

product of [(FeCp′′′)$_2$(CO)$_4$] and P_4 at 190 °C using decalin as solvent.[13] In these latter reactions the fragmentation of a *cyclo*-P_5 moiety at ambient temperatures and the P_4 tetrahedron under co-thermolysis conditions with transition metal units is observed. In both procedures the formation of [FeCp^R(η^5-P_5)] complexes is also noticed.

The air-sensitive polymer **5**, which dissolves sparingly in DMF and is insoluble in common solvents such as CH_2Cl_2, THF, and hexane, can be stored under an inert atmosphere at ambient temperature. The most abundant ion observed in the ESI-MS spectra of **5** in MeCN at room temperature is [(FeCp′′′)$_2$(η^4-P_4)]$^+$.[10] A peak corresponding to [{(FeCp′′′)$_2$(P_4)}Cu_2]$^{2+}$ is further present confirming the existence of the metal coordinated triple-decker unit. Due to its poor solubility, **5** was difficult to characterise by NMR spectroscopy and so the mother liquor was used for characterisation.[10]

The triple-decker structure of **5** in the solid state is established by X-ray crystallography, as shown in Figure 3. Two phosphorus atoms on the P_4 fragment in the triple-decker are bound to two copper atoms in the linking [Cu(μ-Cl)(MeCN)]$_2$ unit affording a one-dimensional polymeric structure. The coordination geometry of the copper atoms in **5** is tetrahedral with expected Cu–P bond lengths [av. 2.1956(13) Å] and Cl–Cu–P bond angles [av. 126.57(6)°]. The three P–P bonds within the P_4 skeleton are unequal, consisting of two short bonds [2.0956(1) and 2.1023(1) Å] and one long bond [2.3725(1) Å]. A similar example of the unsymmetric P_4 skeleton is also found in **7** [two short: 2.0877(13) and 2.0877(13) Å, one long: 2.3346(9) Å and P···P 3.55 Å][13] and in **6b** [two short: 2.090(2) and 2.093(2) Å, one long: 2.436(2) Å].[12]

Conclusions

In summary, we have demonstrated the influence of the *t*Bu groups on neighbouring C atoms within the [FeCp(η^5-$P_3C_2t Bu_2$)] complex hindering the coordination of the single ring P atom to Cu^I. Although both adjacent ring P atoms are able to coordinate to CuCl moieties, the coordination sphere at Cu is sensitive to the substitution pattern of the cyclopentadienyl ligand attached to iron in the 1,2,4-triphosphaferrocenes. Thus, a 1:1 reaction involving the unsubstituted Cp triphosphaferrocene ligand results in *tetrahedrally* coordinated Cu atoms, whereas using the bulky Cp′′′ analogue gives rise to *trigonal planar* Cu coordination. Furthermore, using an excess of CuCl in the coordination chemistry of the Cp-containing triphosphaferrocenes affords the *same* complex as found in the 1:1 stoichiometric reaction, whereas using the bulky Cp′′′ derivative leads to *complete fragmentation* of the triphospholyl moiety under very mild conditions with formation of an unexpected η^4-ligated tetraphosphabutadiene moiety in an iron triple-decker sandwich complex embedded within a CuCl polymer matrix. The present study reveals for the first time the important role of the substitution patterns within *both* the triphospholyl and Cp^R rings in these phosphaferrocenes in determining their coordination behaviour.

Experimental Section

General Information: Standard methods for the handling of air- and moisture-sensitive materials were utilized throughout this work. Unless otherwise indicated, all manipulations were carried out at room temperature, under an atmosphere of dry nitrogen gas, using standard Schlenk and high vacuum-line techniques. Solvent were dried, degassed and redistilled before use. The starting materials [Cp^{R}Fe(η^5-$P_3C_2t Bu_2$)] Cp^R = Cp (**1**),[7] η^5-$C_5H_2t Bu_3$ (Cp′′′) (**2**)[8] were prepared according to our published methods. Solution NMR spectra were recorded with a Bruker AVANCE 400 spectrometer. Mass spectra were performed using instrument Finnigan MAT 95. IR spectra were recorded with a VARIAN (FTS 2000) and elemental analyses were performed with an elemtar Vario EL III.

Synthesis of [{FeCp(μ,η^5:η^1:η^1-$P_3C_2t Bu_2$)}(CuCl)(MeCN)]$_2$ (3): A solution of CuCl (0.75 g, 0.075 mmol) in CH_2Cl_2/CH_3CN (5 mL/5 mL) was layered onto a solution of [FeCp(η^5-$P_3C_2t Bu_2$)] (0.27 g, 0.075 mmol) in 10 mL of CH_2Cl_2 at room temperature. After the reaction mixture diffused completely, the solution was concentrated and kept in refrigerator at about 4 °C for one week. A red crystalline compound was obtained on the wall of the Schlenk tube. Yield 0.15 g (45%). $C_{34}H_{52}Cl_2Cu_2Fe_2N_2P_6$ (984.28): calcd. C 41.49, H 5.32, N 2.84; found C 40.52, H 5.01, N 2.40. ^{1}H NMR (CD_2Cl_2, 27 °C): δ = 4.79 (s, 5 H, Cp), 1.33 (s, 18 H, *t*Bu) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 27 °C): δ = (P_A) = 33.1 (t), δ(P_M) = 15.4 (br) ($\omega_{1/2}$ = 100 Hz), J(P_A,P_M) = 45.7 Hz. MS (ESI, 25 °C): *m*/*z* (%) = 866 (92) [M – 2 CH_3CN – Cl]$^+$), 767 (96.4) [M – 2 CH_3CN – 2 Cl – Cu]$^+$.

Synthesis of [{FeCp′′′(η^5:η^1:η^1-$P_3t Bu_2C_2$)}(μ-CuCl)]$_2$ (4): A solution of CuCl (0.75 g, 0.075 mmol) in CH_2Cl_2/CH_3CN (5 mL/5 mL) was layered onto a solution of [FeCp′′′(η^5-$P_3C_2t Bu_2$)] (0.40 g, 0.075 mmol) in 10 mL of CH_2Cl_2 at room temperature. After 2 weeks, red crystals of **4** were obtained on the wall of the Schlenk tube. Yield 0.010 mmol, 0.12 g (51%). $C_{54}H_{94}Cl_2Cu_2Fe_2P_6$ (1238.87): calcd. C 52.35, H 7.65; found C 51.92, H 7.82. ^{1}H NMR (CD_2Cl_2, 27 °C): δ = 4.1 {s, 2 H, $C_5\mathbf{H_2}t Bu_3$}, 0.9 {s, 18 H, $C_5H_2\mathbf{t Bu_3}$}, 1.0 {s, 9 H, $C_5H_2\mathbf{t Bu_3}$}, 1.1 {s, 18 H, $P_3C_2\mathbf{t Bu}$-ring} ppm. ^{31}P{^{1}H} NMR {[D_8]THF/CH_3CN, 27 °C): δ = (P_A) = 52.8 (t), δ(P_M) = 27.6 (br) ppm ($\omega_{1/2}$ = 90 Hz), J(P_A,P_M) = 44.2 Hz. ESI-MS (CH_3CN, 25 °C): *m*/*z* (%) = 1203 (3.1) [M – Cl]$^+$, 1103 (21.5) [M – 2 Cl]$^+$, 624 (100) [FeCp′′′($P_3C_2t Bu$)CuMeCN]$^+$.

Synthesis of [{(FeCp′′′)$_2$(μ,η^4:η^4-P_4)}{CuCl}$_2$(MeCN)]$_\infty$ (5): CuCl (0.15 g, 0.15 mmol) in a CH_2Cl_2/CH_3CN (2 mL/3 mL) solution was layered onto a solution of [FeCp′′′(η^5-$P_3C_2t Bu_2$)] (0.39 g, 0.075 mmol) in 5 mL of CH_2Cl_2. The solution was kept at room temperature. After four weeks, dark brown crystals were obtained on the wall of the Schlenk tube. Yield 20 mg (53%). $C_{36}H_{61}Cl_2Cu_2Fe_2NP_4$ (941.46): calcd. C 45.93, H 6.53, N 1.49; found C 45.57, H 6.17, N 1.23. ^{1}H NMR (CD_2Cl_2, 27 °C): δ = 4.32 {s, 2 H, $C_5\mathbf{H_2}t Bu_3$}, 0.97 {s, 18 H, $C_5H_2\mathbf{t Bu_3}$}, 1.04 {s, 9 H, $C_5H_2\mathbf{t Bu_3}$}ppm. ^{31}P{^{1}H} ESI-MS (CH_3CN, 25 °C): *m*/*z* (%) = 826 (100) [{(FeCp′′′)$_2$(P_4)}Cu_2]$^+$, 702 (34.8) [(Cp′′′Fe)$_2$(P_4)]$^+$, 536 (9.0) [(FeCp′′′)(CpFe)(P_4)]$^+$.

X-ray Structure Determination: The crystal structure analyses were performed with a STOE IPDS diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods with the program SHELXS-97[14a] and full-matrix least-squares refinement on F^2 in SHELXL-97[14b] was performed with anisotropic displacements for non-H atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model.

3: $C_{34}H_{52}Cl_2Cu_2Fe_2N_2P_6$, M_r = 984.28, crystal dimensions 0.25 × 0.24 × 0.18 mm^3, monoclinic, space group $P2_1/n$ (No. 14), *a*

$= 11.560(1)$, $b = 7.351(1)$, $c = 24.991(4)$ Å, $\beta = 97.29(2)°$, $T = 200(1)$ K, $Z = 2$, $V = 2106.7(4)$ Å^3, $\rho_{\text{calcd.}} = 1.552$ Mg m^{-3}, $\mu = 2.052$ mm^{-1}, 9475 reflections collected, 3719 unique reflections ($R_{\text{int}} = 0.0637$, $2\theta_{\max} = 52°$), 218 parameters, $R_1 = 0.0656$, $wR_2 = 0.1656$.

4: $C_{54}H_{94}Cl_2Cu_2Fe_2P_6$, $M_r = 1238.80$, crystal dimensions $0.15 \times 0.108 \times 0.02$ mm^3, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.531(3)$, $b = 15.849(3)$, $c = 14.912(3)$ Å, $\beta = 90.00(3)°$, $T = 203(2)$ K, $Z = 2$, $V = 2961.6(10)$ Å^3, $\rho_{\text{calcd.}} = 1.389$ Mg m^{-3}, $\mu = 1.475$ mm^{-1}, 9210 reflections collected, 4667 unique reflections ($R_{\text{int}} = 0.0706$, $2\theta_{\max} = 55°$), 313 parameters, $R_1 = 0.0507$, $wR_2 = 0.1211$.

5·CH₂Cl₂: $C_{37}H_{63}Cl_4Cu_2Fe_2P_4N$, $M_r = 1097.24$, crystal dimensions $0.25 \times 0.10 \times 0.08$ mm^3, orthorhombic, space group *Pbcn* (No. 60), $a = 24.750(2)$, $b = 16.969(1)$, $c = 23.977(2)$ Å, $T = 173(1)$ K, $Z = 8$, $V = 10069.6(11)$ Å^3, $\rho_{\text{calcd.}} = 1.448$ Mg m^{-3}, $\mu = 1.87$ mm^{-1}, 70439 reflections collected, 9107 unique reflections ($R_{\text{int}} = 0.0892$, $2\theta_{\max} = 50.5°$), 424 parameters, $R_1 = 0.0438$, $wR_2 = 0.0991$.

CCDC-691158 (for **3**), -691159 (for **4**) and -691160 (for **5**) 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.

Supporting Information (see also the footnote on the first page of this article): Further experimental details of the ^{31}P NMR characterisation of the crude reaction mixture of reaction (3).

Acknowledgments

This work is comprehensively supported by the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie. The Alexander von Humboldt Foundation is gratefully acknowledged for the Humboldt Research Prize awarded to J. F. N. We also thank the Engineering and Physical Sciences Research Council (EPSRC) for financial support and Dr. M. M. Al-Ktaifani for providing some of the triphosphaferrocenes used in this study.

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Received: August 25, 2008
Published Online: September 25, 2008