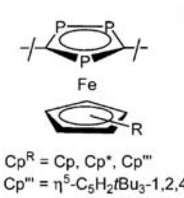
Synthesis and unprecedented coordination behaviour of a novel 1,2,3-triphosphaferrocene complex†‡

Shining Deng,[a] Christoph Schwarzmaier,[a] Christiane Eichhorn,[b] Otto Scherer,[b] Gotthelf Wolmershäuser,[b] Manfred Zabel[a] and Manfred Scheer*[a]

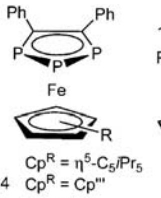
Received (in Cambridge, UK) 6th May 2008, Accepted 30th May 2008
First published as an Advance Article on the web 3rd July 2008
DOI: 10.1039/b807658h

A novel 1,2,3-triphosphaferrocene has been synthesised, which reacts with CuBr to give a 2D polymer, revealing an unprecedented π-stacking of the triphospholyl moieties.

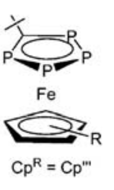
Phosphaferrocenes are an interesting class of compounds because they combine aspects of fundamental, as well as applied research.[1] Within this class of compounds, triphosphaferrocenes exist as two different isomers: the longer known 1,2,4-triphosphaferrocene derivatives, **I**,[2] and the only recently synthesised 1,2,3-substituted derivatives, **II**.[3] The coordination ability of type **I** compounds has been explored by reacting $[Cp^RFe(\eta^5\text{-}P_3C_2tBu_2)]$ (Cp^R = Cp, Cp*) with metal carbonyl fragments, as well as with Pt(II) chloride complexes.[4] We have recently been able to add the tri-*tert*-butyl substituted derivative $[Cp'''Fe(\eta^5\text{-}P_3C_2tBu_2)]$ ($Cp''' = \eta^5\text{-}C_5H_2tBu_3$) to this series of type **I** compounds when we synthesised the 1,2,3,4-tetraphosphaferrocene, $[Cp'''Fe(\eta^5\text{-}P_4CtBu)]$, **III**.[5]



I



II

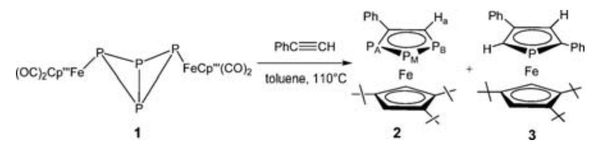


III

We are particularly interested in extending the number of examples involving type **II** compounds and introducing them into the coordination chemistry of Cu(I) halides. The latter aspect is in line with the current general research interests of the Scheer group, using P_n ligand complexes in coordination chemistry. Thus, compounds like $[CpMo(CO)_2(\mu,\eta^2\text{-}P_2)]$,[6] $[Cp''Ta(\eta^4\text{-}P_4)]$ ($Cp'' = \eta^5\text{-}C_5H_3tBu_2\text{-}1,3$)[7] or $[Cp^*Fe(\eta^5\text{-}P_5)]$[8] react with Cu(I) halides to form 1D and 2D polymers, and under special conditions, spherical nano-sized aggregates[9] are formed.

Herein, we report the synthesis of both a novel class **II** derivative and a related coordination polymer. The 1D polymer based on this P_n ligand complex consists of a doubly-layered structure, revealing an unprecedented example of π-stacking between triphosphaferrocene moieties.

Following the synthetic procedure that was applied to the synthesis of the type **II** compounds by the Scherer group,[3] a mixture of $[\{Cp'''(CO)_2Fe\}_2(\mu,\eta^1{:}\eta^1\text{-}P_4)]$ (**1**) and PhC≡CH, in a ratio of 1 : 4, was refluxed in toluene for 18 h. The reaction mixture was separated by column chromatography, which yielded a red and a green fraction, from which the novel complexes **2** and **3** could be isolated (eqn (1)).



(1)

The red oily $[Cp'''Fe(\eta^5\text{-}P_3C_2PhH)]$ (**2**) and green crystalline $[Cp'''Fe(\eta^5\text{-}PC_4H_2Ph_2)]$ (**3**) compounds dissolve readily in CH_2Cl_2, THF and in hydrocarbons. In the EI mass spectra of **2** and **3**, their corresponding molecular ion peaks, and those of characteristic fragments, were found.

In the ^1H NMR spectrum of **2**, a doublet of doublet of doublets at 6.24 ppm was assigned to proton H_a on the P_3C_2-ring (eqn (1)). From the ^1H-coupled ^{31}P NMR spectrum, coupling constants of J_{H_a,P_B} = 40.1, J_{H_a,P_M} = 10.8 and J_{H_a,P_A} = 4.5 Hz were determined. In the $^{31}P\{^1H\}$ NMR spectrum of **2**, three groups of signals representing an ABM spin system were detected. The signal at 51.7 ppm was attributable to the P_A atom, with coupling constants of J_{P_A,P_M} = 427.4 and J_{P_A,P_B} = 4.4 Hz. The signal at 15.2 ppm represents the P_M atom and that at 48.9 ppm, with J_{P_M,P_B} = 399.6 Hz, belongs to the P_B atom in the P_3C_2-ring. The latter shows the largest coupling to the neighbouring H_a proton in the ^{31}P NMR spectrum.

The ^{31}P NMR spectrum of complex **3** displays a doublet of doublets at −64.1 ppm (J_{P,H_a} = 35.6 and J_{P,H_b} = 4.9 Hz), inferring that complex **3** adopts the structure shown in eqn (1).

---

[a] *Institute of Inorganic Chemistry, University of Regensburg, D-93040 Regensburg, Germany. E-mail: manfred.scheer@chemie.uni-regensburg.de; Fax: +49 941-943-4439*
[b] *Institute of Inorganic Chemistry, University of Kaiserslautern, D-67663 Kaiserslautern, Germany*

† Electronic supplementary information (ESI) available: Experimental, analytical and crystallographic details. See DOI: 10.1039/b807658h

‡ Crystal data for **3**: $C_{33}H_{41}FeP$, M = 524.48, orthorhombic, space group *Pbca*, a = 10.5821(7), b = 16.6027(8), c = 33.0952(18) Å, V = 5814.5(6) Å^3, T = 293(2) K, Z = 8, μ(Mo-K$_\alpha$) = 0.592 mm^{-1}, 64 880 reflections measured, 5529 unique (R_{int} = 0.1183) which were used in all calculations. The final R_1 and wR_2 [$I > 2\sigma(I)$] were 0.0400 and 0.0802, respectively. CCDC 687163.
Crystal data for **5**: $C_{54}H_{76}Br_4Cu_4Fe_2N_2P_6\cdot1.5CH_2Cl_2$, M = 1751.88, triclinic, space group $P\bar{1}$, a = 15.1002(10), b = 15.5709(11), c = 16.3950(12) Å, α = 110.545(7), β = 94.432(6), γ = 104.171(6)°, V = 3442.8(5) Å^3, T = 123(1) K, Z = 2, μ(Cu-K$_\alpha$) = 10.019 mm^{-1}, 25 040 reflections measured, 10 799 unique (R_{int} = 0.0389) which were used in all calculations. The final R_1 and wR_2 [$I > 2\sigma(I)$] were 0.0366 and 0.0744, respectively. CCDC 687164.
For crystallographic data in CIF or other electronic format see DOI: 10.1039/b807658h

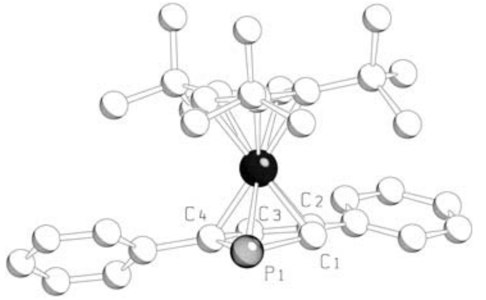


Fig. 1 Molecular structure of **3** (H atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): P–C(1) 1.755(15), P–C(4) 1.80(2), C(1)–C(2) 1.42(3), C(2)–C(3) 1.44(3), C(3)–C(4) 1.39(3), Fe···C_4P_{cent} 1.722, Fe···Cp'''_{cent} 1.682; C(4)–P(1)–C(1) 85.6 (9), C(2)–C(1)–P 119.4(13), C(3)–C(4)–P 113.6(15), C_4P_{cent}–Fe–Cp'''_{cent} 176.6.

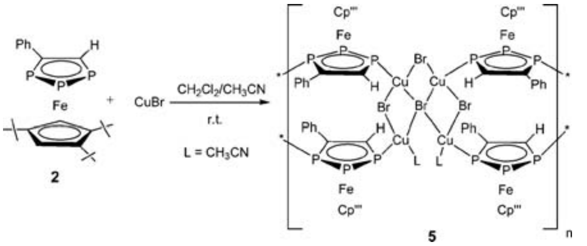
The arrangement of the phenyl groups in the PC_4-ring of **3** (2 and 4 positions) is in contrast to that of the methyl groups in the PC_4 ring of a similar phosphaferrocene, [Cp*Fe(η^5-$PC_4Me_2H_2$)] (**4**) (3 and 4 positions), prepared by Mathey and co-workers.[10,11] The reason for this may be due to the steric demand of the more bulky phenyl groups in **3**.

Additionally, an X-ray structural analysis of **3** was determined to confirm the presence of the proposed isomer (Fig. 1).‡

In the molecular structure of **3**, positional disorder of the phosphorus atom P(1) with respect to atom C(1) at a probability ratio of 57% : 43% was observed. The arrangement of the slightly higher site occupation factor for P(1) and C(1) is shown in Fig. 1.

The phosphorus atom is 0.17 Å out of the plane, as defined by the four carbon atoms of the phospholyl ligand (the maximum deviation of the C atoms from this plane is 0.02 Å). The average C–C bond length of 1.42 Å is comparable to the C–C bond length of 1.39 Å in aromatic hydrocarbons like benzene. The P–C bond lengths of 1.75 and 1.80 Å are consistent with the P–C bond lengths of 1.76 and 1.77 Å in Mathey's compound, **4**.[10,11] Between the five-membered rings, a staggered conformation is observed, whereby the phenyl groups on carbon atoms C(2) and C(4) are located in the cavities of the *tert*-butyl groups of the Cp''' ligand. The angle between the planes of the four carbon atoms in the phospholyl ligand and the five carbon atoms in the cyclopentadienyl derivative is 3.6°; this is very small and is comparable to the angle of 3.18° found by Mathey[10,11] in compound **4**.

Whereas reactions of **2** with CuCl and CuI only yield amorphous products, which cannot be adequately characterised, a layering reaction involving CuBr/MeCN and **2**/CH_2Cl_2 produces red crystals of polymer **5** (eqn (2)).



(2)

Polymer **5** dissolves very sparingly in CH_2Cl_2 and MeCN, but is not soluble in THF or toluene. Because of the limited solubility of **5**, the mother liquor of the reaction mixture was used for NMR investigations. Three slightly broadened doublets of doublets (40.5, 37.7 and 0.2 ppm), representing an ABM spin system, are present in the $^{31}P\{^1H\}$ NMR spectrum. In comparison to the signals of the uncoordinated compound, **2** (51.7, 48.9 and 15.2 ppm), a 10–15 ppm upfield shift is observed. The coupling constants (J_{P_A,P_M} = 436.4 and J_{P_M,P_B} = 419.6 Hz) are somewhat larger than those of the starting material (J_{P_A,P_M} = 427.4 and J_{P_M,P_B} = 399.6 Hz). In the ESI mass spectrum of **5** in MeCN, peaks corresponding to the cations $[\{Cp'''Fe(P_3C_2PhH)\}_2Cu_3Br_2]^+$, $[\{Cp'''Fe(P_3C_2PhH)\}_2Cu_2Br]^+$ and $[\{Cp'''Fe(P_3C_2PhH)\}_2Cu]^+$ were detected, revealing that in solutions of **5**, oligomeric fragments of corresponding $(CuBr)_n$ aggregates of **2** are present. This is supported by the NMR spectrum of the mother liquor of **5**.

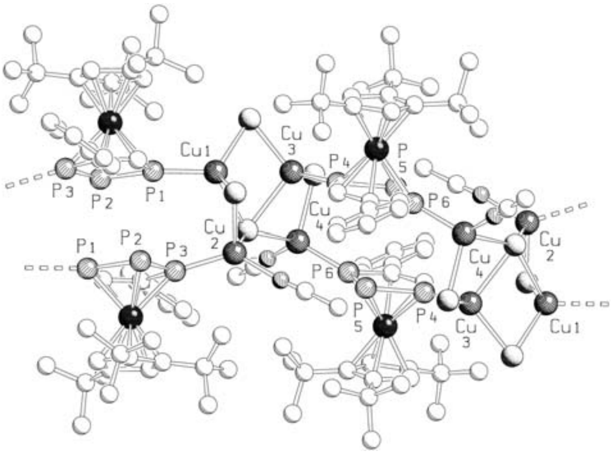


Fig. 2 Section of the 1D polymeric structure of polymer **5** (H atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): P(1)–P(2) 2.1272(18), P(2)–P(3) 2.1242(18), P(1)–C(18) 1.745(5), P(3)–C(37) 1.775(5), P(1)–Cu(1) 2.2391(15), P(3)–Cu(2) 2.2180(14), P(4)–P(5) 2.1226(18), P(5)–P(6) 2.1171(18), P(4)–C(36) 1.750(5), P(6)–C(44) 1.783(5), P(6)–Cu(4) 2.2220(14), P(4)–Cu(3) 2.2006(14), Cu(1)–Br(1) 2.4704(9), Cu(1)–Br(2) 2.7359(8), Cu(1)–Br(3) 2.4158(8), Cu(2)–Br(1) 2.4792(8), Cu(2)–Br(2) 2.5247(8), Cu(3)–Br(2) 2.6205(8), Cu(3)–Br(3) 2.4348(8), Cu(3)–Br(4) 2.4762(8), Cu(4)–Br(2) 2.6241(9), Cu(4)–Br(4) 2.4694(8); P(1)–Cu(1)–Br(3) 121.66(4), P(4)–Cu(3)–Br(3) 119.26(4), P(3)–Cu(2)–Br(1) 102.64(4), P(6)–Cu(4)–Br(2) 114.38(5).

The solid-state structure of complex **5** was established by X-ray crystallography and is shown in Fig. 2. It consists of a polymeric chain, in which a $[(CuBr)_4(CH_3CN)_2]$ unit is doubly-bridged by the [Cp'''Fe(η^5-P_3C_2PhH)] moieties, which represent a 1,3 coordination mode at the triphospholyl ring. Each copper atom of this unit (Fig. 3) consists of three annulated

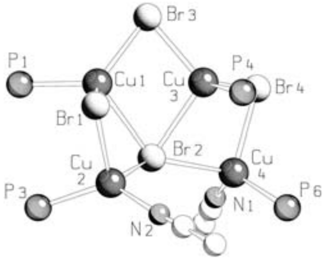


Fig. 3 Cage structure of the $[(CuBr)_4(CH_3CN)_2]$ unit in **5**.

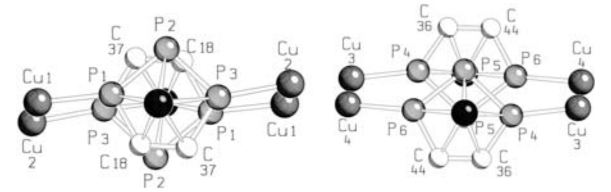


Fig. 4 Top view of the double layered triphospholyl units of **5** (Cp′′′ ligand, phenyl groups and H atoms are omitted for clarity).

four-membered $(CuBr)_2$ rings, coordinated in a distorted tetrahedral fashion to one phosphorus atom from four different $[Cp'''Fe(\eta^5\text{-}P_3C_2PhH)]$ units, with an average P–Cu–Br angle of 114.5° and a P–Cu bond length of 2.2199 Å (Fig. 2). The P–P bond lengths in the cyclo-P_3C_2 rings (P1–P2 2.128(2) and P2–P3 2.124(2) Å) of **5** are comparable to that in $[Cp'''Fe(\eta^5\text{-}P_3C_2Ph_2)]^3$ (P1–P2 2.129(1) and P2–P3 2.119(2) Å).

The most remarkable feature of the structure of **5** is the double-layered structure, in which two of the triphosphacyclopentadiene rings approach each other in a π-stacking fashion (Fig. 4).[12]

In the first case (Fig. 4, left), the rings lie directly on the top of each other, the phosphorus atoms are on opposite sides of the rings and the atoms are in a nearly eclipsed conformation (16.1° deviation). The five-membered rings are co-planar (0° deviation), with a distance of 3.69 Å between them. In the second case (Fig. 4, right), the five-membered ring-centres are shifted 1.27 Å with respect to each other. As in the first case, the phosphorus atoms are on opposite sides of the rings and are perfectly co-planar (0° deviation). The distance between the planes is 3.61 Å and therefore slightly smaller than in the first case.

These results show that the reaction of bicyclo-tetraphosphane complex **1** with alkynes is an efficient method for obtaining novel triphosphaferrocene complexes, in which the P atoms are attached to each other. Besides the formation of the title compound, **2**, formation of the novel monophosphaferrocene, **3**, is observed in high yields. The nature of the main products provides evidence for a P_3/P_1 fragmentation[13] of complex **1**, which is followed by further reaction with one or two equivalents of the alkyne, to give products **2** and **3**, respectively. A possible intermediate, with the formula $[Cp'''(CO)Fe{\equiv}P]$,[14] could play a decisive role in the formation of phosphaferrocene **3**. In a subsequent reaction, triphosphaferrocene **2** is reacted with CuBr to give a double-layered 1D polymer, in which, for the first time, π-stacking of the triphospholyl moieties is observed that is almost perfectly co-planar, with van der Waals distances of 3.61 and 3.64 Å.

The authors thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Notes and references

1 F. Mathey, in *Phosphorus–Carbon Heterocyclic Chemistry: The Rise of a New Domain*, ed. F. Mathey, Elsevier, Oxford, UK, 2001, pp. 767; *Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996, vol. **1** and **2**; K. B. Dillon, F. Mathey and J. F. Nixon, in *Phosphorus: The Carbon Copy*, Wiley, Chichester, UK, 1998F. Mathey, *Angew. Chem.*, 2003, **115**, 1617 (*Angew. Chem., Int. Ed.*, 2003, **42**, 1578); F. Mathey, *Coord. Chem. Rev.*, 1994, **137**, 1.

2 C. Müller, R. Bartsch, A. Fischer, P. G. Jones and R. Schmutzler, *J. Organomet. Chem.*, 1996, **512**, 141; R. Bartsch, P. B. Hitchcock and J. F. Nixon, *J. Organomet. Chem.*, 1988, **340**, C37; R. Bartsch, P. B. Hitchcock and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1987, 1146; C. Müller, R. Bartsch, A. Fischer and P. G. Jones, *J. Organomet. Chem.*, 1993, **435**, C16.

3 O. J. Scherer, T. Hilt and G. Wolmershäuser, *Angew. Chem.*, 2000, **112**, 1484 (*Angew. Chem., Int. Ed.*, 2000, **39**, 1425).

4 C. S. J. Callaghan, P. B. Hitchcock and J. F. Nixon, *J. Organomet. Chem.*, 1999, **584**, 87; R. Bartsch, A. Gelessus, J. F. Nixon and P. B. Hitchcock, *J. Organomet. Chem.*, 1992, **430**, C10; C. Müller, R. Bartsch, A. Fischer and P. G. Jones, *J. Organomet. Chem.*, 1993, **453**, C16.

5 M. Scheer, S. Deng, O. J. Scherer and M. Sierka, *Angew. Chem.*, 2005, **117**, 3821 (*Angew. Chem., Int. Ed.*, 2005, **44**, 3755).

6 J. Bai, E. Leiner and M. Scheer, *Angew. Chem.*, 2002, **114**, 820 (*Angew. Chem., Int. Ed.*, 2002, **41**, 783); M. Scheer, L. Gregoriades, J. Bai, M. Sierka, G. Brunklaus and H. Eckert, *Chem.–Eur. J.*, 2005, **11**, 2163; M. Scheer, L. J. Gregoriades, M. Zabel, M. Sierka, L. Zhang and H. Eckert, *Eur. J. Inorg. Chem.*, 2007, 2775; S. Welsch, L. J. Gregoriades, M. Sierka, M. Zabel, A. Virovets and M. Scheer, *Angew. Chem.*, 2007, **119**, 9483 (*Angew. Chem., Int. Ed.*, 2007, **46**, 9323).

7 B. P. Johnson, F. Dielmann, G. Balázs, M. Sierka and M. Scheer, *Angew. Chem.*, 2006, **118**, 2533 (*Angew. Chem., Int. Ed.*, 2006, **45**, 2473).

8 J. Bai, A. V. Virovets and M. Scheer, *Angew. Chem.*, 2002, **114**, 1808 (*Angew. Chem., Int. Ed.*, 2002, **41**, 1737).

9 J. Bai, A. V. Virovets and M. Scheer, *Science*, 2003, **300**, 781; M. Scheer, J. Bai, B. P. Johnson, R. Merkle, A. V. Virovets and C. E. Anson, *Eur. J. Inorg. Chem.*, 2005, 4023; M. Scheer, A. Schindler, R. Merkle, B. P. Johnson, M. Linseis, R. Winter, C. E. Anson and A. Virovets, *J. Am. Chem. Soc.*, 2007, **129**, 13386.

10 F. Mathey, A. Mitschler and P. Weiss, *J. Am. Chem. Soc.*, 1977, **99**, 3537.

11 F. Mathey, *New J. Chem.*, 1987, **11**, 585.

12 For the importance of π-stacked assemblies *cf.*: Y. Morisakim and Y. Chujo, *Angew. Chem.*, 2006, **118**, 6580 (*Angew. Chem., Int. Ed.*, 2006, **45**, 6430); *Modern Cyclophane Chemistry*, ed. R. Gleiter and H. Hopf, Wiley-VCH, Weinheim, 2004; E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem.*, 2003, **115**, 1244 (*Angew. Chem., Int. Ed.*, 2003, **42**, 1210); G. P. Bartholomew and G. C. Bazan, *Acc. Chem. Res.*, 2001, **34**, 30; F. J. M. Hoeben, P. Jonkheijm, P. W. Meijer and A. P. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491.

13 For P3/P1 fragmentation of P_4 phosphorus *cf.*: M. Scheer, K. Schuster and U. Becker, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1996, **109–110**, 141; M. Scheer and U. Becker, *Chem. Ber.*, 1996, **129**, 1307; M. Scheer, U. Becker and J. Magull, *Polyhedron*, 1998, **17**, 1983.

14 For reviews *cf.*: M. Scheer, *Coord. Chem. Rev.*, 1997, **163**, 271; B. P. Johnson, G. Balazs and M. Scheer, *Top. Curr. Chem.*, 2004, **232**, 1; B. P. Johnson, G. Balázs and M. Scheer, *Coord. Chem. Rev.*, 2006, **250**, 1178.