New Organometalated Phosphinato-*O*,*O*′ Ligands in the Planar Eight-Membered Ring [{Cp(CO)$_2$Fe}*t*BuPO$_2$FeCl$_2$]$_2$

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By simple oxidation of the diferriophosphonium salt [Fp$_2$P(H)*t*Bu]$_2$FeCl$_4$ (**1′d**) with air the planar eight-membered heterocycle {Fp*t*BuPO$_2$FeCl$_2$}$_2$ (**2**) was generated. Compound **2** contains two organometalated phosphinato-*O*,*O*′ ligands bridging two tetrahedrally configured iron(III) centres [Fp = CpFe(CO)$_2$ = ferrio]. The new ferrio phosphinato ligand Fp*t*BuPO$_2^-$ was synthesized in a controlled manner for the first time. Compound **1′d** was obtained by the so-called insertion reaction of Fp$_2$ and *t*BuPCl$_2$, or by the silyl method using CpFe(CO)$_2$Cl and *t*BuP(SiMe$_3$)$_2$, both in toluene with traces of water present.

Introduction

The phosphinato ligand R$_2$PO$_2^-$ has a significant position among the classical ligands. Their syntheses, stability, and complex chemical behaviour towards the main group and transition elements (mono-, bidentate and bridging ligands), as well as their applications, especially as coordination polymers, has been the subject of numerous publications.[1] Within the scope of our investigations on organometalated phosphorus compounds,[2] which follow the isolobal theory, we succeeded in the synthesis and structural characterisation of the cage-like molecule [{CpFe(CO)$_2$(Mes)PO$_2$}$_4${MesPO$_3$Fe$_2$(OH)Cl}$_2$].[3] Besides the phosphonato ligand RPO$_3^{2-}$, it contains for the first time the organometalated phosphinato ligand FpRPO$_2^-$ (Fp = CpFe(CO)$_2$; R = Mes). The very complex framework of 4 iron(III) and 6 phosphorus centres connected by oxygen atoms, was formed unexpectedly by simple oxidation of the ferriophosphonium salt [Fp$_2$P(H)Mes]Cl with air.[3] Our attempts to separate the novel ferriophosphinato ligand from this cage compound have not been hitherto successful.

Mono-, di- and triferriophosphanes Fp$_n$PR$_{3-n}$ ($n = 1-3$) can be easily oxidised to the corresponding organometallated (chalcogeno)phosphoranes Fp$_n$PR$_{3-n}$(E) (E = O, S, Se), as well as the organic derivatives PR$_3$.[4] While the organic phosphonium salts [PR$_4$]X are normally air-stable, the diferriophosphonium salts [Fp$_2$P(H)R]X (X = any anion) turned out to be very reactive towards oxidising reagents, especially air oxygen.[3]

In the following, we report on the simple and selective transformation of a dimetalated phosphonium salt into an eight-membered planar ring molecule containing two Fe^{III} centres as well as two bidentate bridging ferriophosphinato-*O*,*O*′ ligands.

Results and Discussion

Our aim was to prove the surprising result of the oxidation of the PH-functionalized diferrio(mesityl)phosphonium salt [Fp$_2$P(H)Mes]Cl with air, leading to the cage molecule.[3] Therefore, we first synthesized a series of PH- and PCl-functionalized diferrio(organyl)phosphonium salts of the type [Fp$_2$P(X)R]$_2$FeCl$_4$ (X = H, Cl; R = Me, Et, *i*Pr, *t*Bu, Ph, *p*Tol, Xyl, Mes), which could then be oxidized. We used the so-called insertion method, which is the reaction of RPCl$_2$ with the dimer {CpFe(CO)$_2$}$_2$ (Scheme 1).

Depending on the substituent R and the solvent, we were able to obtain both the corresponding PCl- and PH-functionalized diferriophosphonium salts. In toluene at 80 °C both derivatives were obtained concurrently, whereby traces of H$_2$O played a role. Whereas in the case of R = Me, Et, Ph, and Tol, only the PCl phosphonium salts [Fp$_2$P(Cl)R]$_2$FeCl$_4$ (**1a**, **b**, **e**, and **f**) were formed, for R = *i*Pr, *t*Bu, Xyl, and Mes; however, the PH derivatives [Fp$_2$P(H)R]$_2$FeCl$_4$ (**1′c**, **d**, **g**, and **h**) were also obtained in considerable amounts, besides the PCl compounds. The best yields for **1a−h** and **1′a−h** were achieved when the starting materials Fp$_2$ and RPCl$_2$ were used in a 3:2 ratio. When dichloromethane was used as the solvent, only the PCl derivatives **1b−d** were formed at room temp. As NMR experiments with the combinations H$_2$O/toluene, D$_2$O/toluene, and H$_2$O/C$_6$D$_6$ and absolutely dry toluene as the solvent have shown, the hydrogen atom is derived from traces of water in the toluene. It is surprising that the P−Cl moiety, once formed could not be transformed into the PH entity. Further experiments showed that P−Cl could be changed into P−OH or P−OR by reaction with H$_2$O or ROH, respectively.[5]

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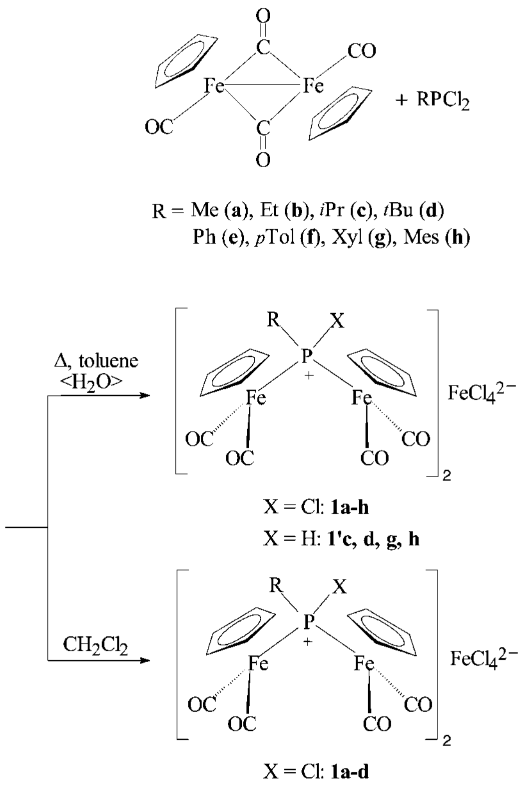
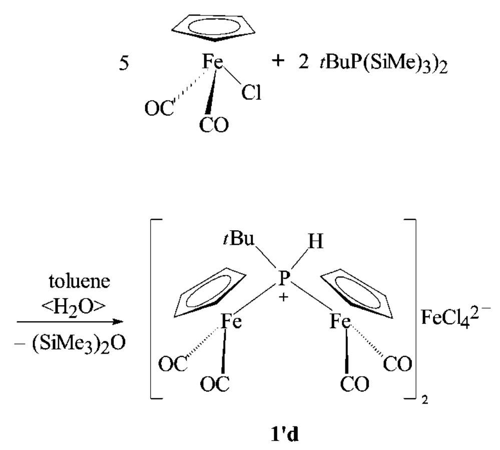


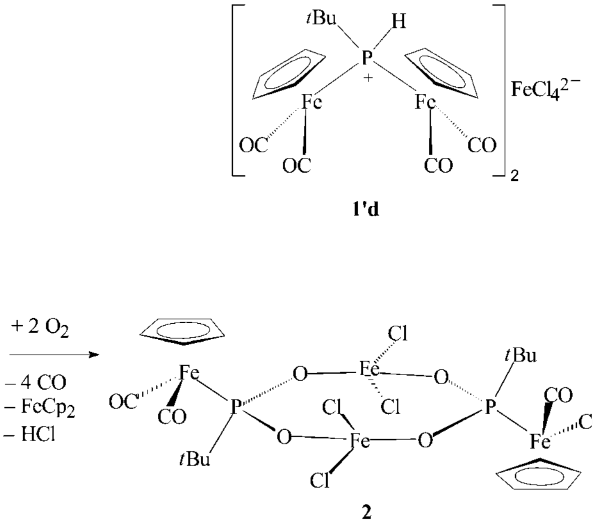
Scheme 1

We were not able to successfully obtain single crystals of any PH derivative, $[Fp_2P(H)R]_2FeCl_4$, but we succeeded in obtaining single crystals of the PCl compounds, $[Fp_2P(Cl)R]_2FeCl_4$ (R = Me, Et, *i*Pr, *t*Bu) **1a−d**. In this context, however, we only report on the molecular structure of the *tert*-butyl derivative **1d**, instead of the analogous **1′d**, which is the starting material for the formation of the novel ring molecule **2**. Compound **1′d** was obtained by using the silyl method, where $CpFe(CO)_2Cl$ was treated with *t*BuP-$(SiMe_3)_2$ in toluene at room temperature in the presence of traces of water (Scheme 2).



Scheme 2

The phosphonium salts **1a−h** and **1′c**, **d**, **e**, **g**, and **h** were treated with air oxygen for periods ranging from a few days to weeks. Only the mixed PH/Cl-functionalized salt with R = *t*Bu (**1d/1′d**) yielded a homogeneous product with **2**, besides the by-product ferrocene. Related experiments showed that the pure, rather stable PCl derivative **1d** could not be oxidized to give **2**. On the other hand, the oxidation of the pure PH compound **1′d** gave a greater yield of **2** than using the mixed salt **1d/1′d**. A plausible reaction mechanism is shown in Scheme 3, in which the balance of electrons and stoichiometry is correct. In the first step, the phosphonium cation is oxidised by oxygen under elimination of one ferrio group. In the next step, the resulting unstable monoferriophosphinic acid reacts with the $FeCl_4^-$ counter anion, which is derived by oxidation from the $FeCl_4^{2-}$ present in the starting material **1′d**. The resulting eight-membered ring of **2** seems to be the consequence of self assembling under thermodynamic control.



Scheme 3

The IR spectra (solid, KBr) of the mixed compound **1d/1′d** and the pure **1d** and **1′d** show the characteristic vibrations $\nu(CO_t)$ at 2055, 2031, and 1989 cm^{-1}. The ^{31}P NMR spectrum of **1d** shows a singlet at $\delta = 289$ and that of **1′d** shows a doublet at $\delta = 31$ ($^1J_{PH} = 303$ Hz), which are in the expected regions. The ^1H NMR spectra of both compounds **1d** and **1′d** show two signals at $\delta = 5.36$ (s, Cp) and 1.29 (s, Me), **1′d** additionally a doublet at $\delta = 3.40$ ($^1J_{PH} = 303$ Hz). In the FAB$^+$ (*m*NBA) mass spectra the parent signals are found at *m*/*z* = 477 [M(*PCl*)]$^+$ (**1d**) and 443 [M(*PH*)]$^+$ (**1′d**), respectively. In the case of the mixed salt **1d/1′d**, both signals appear in a 1:1 ratio. The elemental analysis does not indicate any exact product distribution in the mixed salt, the Cl value, however, points to an excess of the PCl-functionalised derivative **1d** in the mixed salt.

All attempts to obtain single crystals of **1′d** failed. The PCl-functionalised derivative **1d**, however, could be obtained as single crystals suitable for an X-ray structure analysis. In **1d**[6] both the Fe atoms and the central P atom are

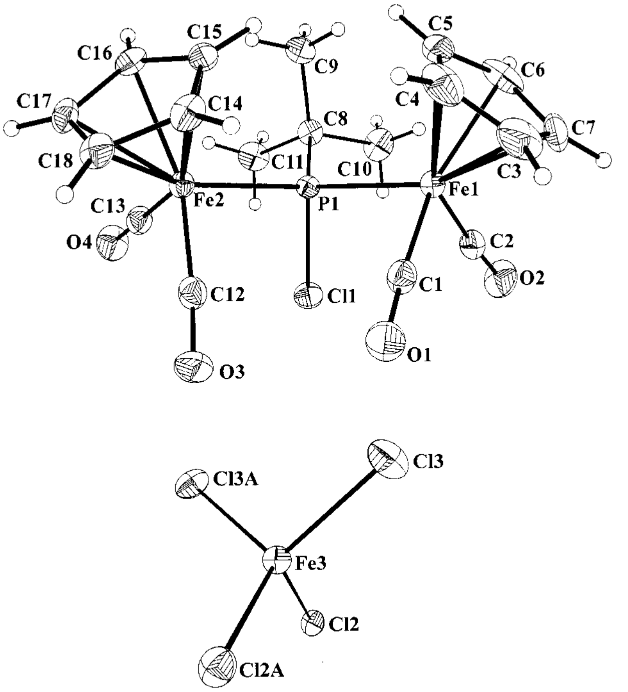


Figure 1. Molecular structure of **1d** (only 1 cation and the anion) in the crystal; selected bond lengths [Å] and angles [°]: Fe1−P1 2.3070(9), Fe2−P1 2.2930(10), P1−Cl1 2.0989(11), P1−C8 1.900(3), Fe3−Cln 2.3159(11), 2.3231(10); Fe1−P1−Fe2 119.78(4), Fe1−P1−Cl1 102.46(4), Fe1−P1−C8 114.47(11), Fe2−P1−Cl1 102.46(4), Fe2−P1−C8 114.66(11), Cl1−P1−C8 98.57(11), Clx−Fe3−Cly 103.67(6), 115.52(4), 107.96(4), 106.52(6)

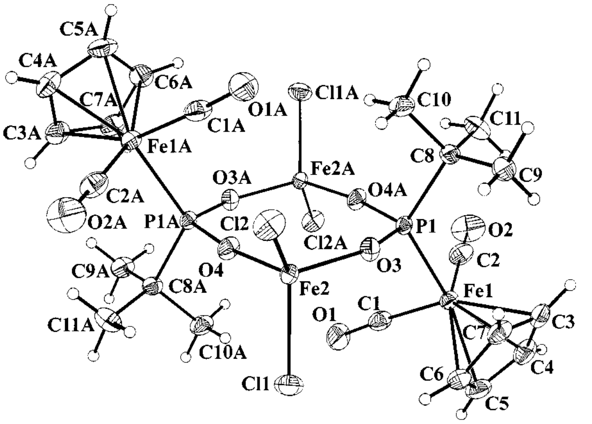


Figure 2. Molecular structure of **2** (only 1 cation and the anion) in the crystal; selected bond lengths [Å] and angles [°]: P1−Fe1 2.2190(11), P1−C8 1.860(4), P1−O3 1.552(3), P1−O4A 1.555(2), Fe2−O3 1.845(3), Fe2−O4 1.825(3), Fe2−Cl1 2.2029(12), Fe2−Cl2 2.1910(12); O3−P1−O4A 108.6(2), Fe2−O3−P1 146.5(2), P1−O4A−Fe2A 171.5(2), O3−P1−C8 103.7(2), O3−P1−Fe1 109.82(11), O3−Fe2−O4 110.80(12), O3−Fe2−Cl1 107.04(9), O3−Fe2−Cl2 109.43(9), Cl1−Fe2−Cl2 110.60(5)

pseudo-tetrahedrally coordinated (Figure 1). The two Fe−P distances have the same size and fit very well within the range of symmetric diferriophosphonium salts.[2] There is no bonding interaction between the two Fe centres (Fe−Fe 3.979 Å). Because of the steric effect of the two ferrio groups, the tetrahedron of the P atom is strongly distorted [Fe1−P1−Fe2 119.78(4)°; Cl1−P−C8 98.57(11)°].

Compound **2** is slightly soluble and paramagnetic (μ_B = 6.04 B.M.).[7] Therefore, NMR measurements were not possible, and the spectroscopic characterization was restricted. The IR spectrum of **2** shows, besides the absorptions of the Cp and *t*Bu groups, those of the corresponding ν(CO) at 2044 and 1999 cm^{-1} and ν(PO_2) at 1070 and 971 cm^{-1}. In the EI (*m*NBA) mass spectrum the signal of highest mass appears at m/z = 791 as the fragment $[M - 2\ CO]^+$; the further fragmentation includes Cl and CO eliminations with signals at m/z = 719, 692, and 664 $[M - 2\ CO - 2Cl - n\text{CO}]^+$ (n = 0−2).

The solution of the composition and the structure of **2** could only be achieved by a single-crystal X-ray diffraction analysis[6] (Figure 2). Accordingly, **2** consists of a nearly planar centrosymmetric eight-membered ring with alternating O−P−O−Fe positions and C_i symmetry. The four tetrahedra at both P and Fe centres are linked by four common O atoms. The maximum deviation of the least-squares plane over all atoms is 0.067 Å. The heterocycle of **2** has a diameter of about 4.7 Å (Fe2−Fe2A 4.576 Å, P1−P1A 4.792 Å). The tetrahedra are completed at the Fe atoms by two Cl atoms, and at the P atoms by a ferrio and a *t*Bu group. The P−O and Fe−O distances are in pairs nearly in the same range [P1−O3 1.552(3), P1−O4A 1.555(2) Å, Fe2−O3 1.845(3), Fe2−O4 1.825(2) Å]. The exocyclic distances P1−Fe1, P1−C8 and Fe2−Cl1 are 2.219(0), 1.860(4) and 2.203(0) Å. The corresponding ring angles of the Fe and P atoms are quite similar [O3−Fe2−O4A 110.80(12), O3−P1−O4A 108.6(2)°], the angles including the substituents, however, differ more noticeably [Cl1−Fe2−Cl2 110.60(5), Fe1−P1−C8 120.44(13)°]. The angles at the ring O atoms are surprisingly different [P1−O3−Fe2 146.5(2)° and P1A−O4−Fe2 171.5(2)°].

The structural constitution of **2** is very similar to that of cyclic tetrametaphosphates[7] and dimeric diorganophosphinato complexes of transition metals,[1] which in contrast are not planar. Formally, **2** can be regarded as the dimeric compound of a (*tert*-butyl)(ferrio)phosphinato-*O*,*O′* complex of tetrahedrally configured Fe^{III}, where the phosphinato ligand is not behaving as a chelating ligand towards *one* Fe^{III} atom, but as a bridging ligand between *two* Fe^{III} centres. Theoretical calculations (B3LYP, hybrid density functional theory) indicate a planar ring skeleton with island-like π-electron delocalisation.[9]

Our experimental results are a first step towards the synthesis of novel organometalated phosphinato ligands, for which a similar manifold coordination chemistry and field of application is expected as for the organic phosphinato ligands. Because of the simultaneous coupling to two metal centres − perhaps two different ones − they seem to be more interesting.

Experimental Section

1d/1′d: A solution of $\{CpFe(CO)_2\}_2$ (2.0 g, 5.64 mmol) and $t\text{BuPCl}_2$ (0.3 mL, 3.7 mmol) in 80 mL of toluene was stirred at 80 °C for 12 h. A yellow solid precipitated that was filtered off, washed with 50 mL of dry toluene, and dried in vacuo. Yield: 1.4 g (75%) of **1d/′d** as a bright yellow powder, no correct elemental analysis was obtained because of the existence of a mixture of PCl- and PH-functionalised product.

1d: A solution of $\{CpFe(CO)_2\}_2$ (2 g, 5.64 mmol) and *t*BuPCl$_2$ (0.3 mL, 3.7 mmol) in 20 mL of dichloromethane was kept at room temperature for up to 1 week. The product **1d** separated as very thin plates at the surface of the glass. Yield: 0.2 g (10%). FAB$^+$ MS (*m*NBA): m/z = 477 [M]$^+$. IR (KBr): ν(CO) = 1987, 2003, 2030, 2050 cm^{-1}. ^{31}P NMR (CD_3CN, 109.4 MHz): δ = 289. ^{13}C NMR (CD_3CN, 67.9 MHz): δ = 211 (CO), 90 (Cp), 50 [$C(CH_3)_3$], 30 (CH_3). ^{1}H NMR (CD_3CN, 270.2 MHz): δ = 5.55 (Cp), 1.45 (CH_3). $C_{36}H_{38}Cl_6Fe_5O_8P_2$ (1152.6): calcd. C 37.5, H 3.3, Cl 18.4; found C 36.7, H 3.1, Cl 18.4.

1′d: A solution of $CpFe(CO)_2Cl$ (5.0 g, 23.54 mmol) and 1 mL (4.70 mmol) of *t*BuP(SiMe$_3$)$_2$ in 100 mL of toluene was stirred at 25 °C for 12 h. A yellow solid precipitated, which was filtered off, washed with 80 mL of dry toluene, and dried in vacuo. Yield: 4.2 g (82%). FAB$^+$ MS (*m*-NBA): m/z = 443 [M]$^+$. IR (KBr): ν(CO) = 1987, 2024, 2034 cm^{-1}. ^{31}P NMR (CD_3CN, 109.4 MHz): δ = 27 (d, $^{1}J_{PH}$ = 303 Hz). ^{13}C NMR (CD_3CN, 67.9 MHz): δ = 91 (Cp), 50 [$C(CH_3)_3$], 30 (CH_3). ^{1}H NMR (CD_3CN, 270.2 MHz): δ = 5.41 (Cp), 3.4 (d, $^{1}J_{PH}$ = 303 Hz, PH), 1.27 (d, $^{3}J_{PH}$ = 18 Hz, CH_3). $C_{36}H_{40}Cl_4Fe_5O_8P_2$ (1083.7): calcd. C 39.9, H 3.7, Cl 13.1; found C 38.7, H 3.5, Cl 16.2.

2: A solution of **1′d** (140 mg, 0.12 mmol) in 12 mL of acetonitrile was kept for about 2 weeks in an air atmosphere. After this time, small prismatic, deep purple-red single crystals of **2** separated at the bottom of the vessel. They were isolated by decantation of the solution. In the mother liquor some of product **2** still remained, which could not, however, be separated as a pure product. Yield: 33 mg (33%). EI MS (*m*NBA): m/z = 791 [M − 2 CO]$^+$, 692, 664 [M − 2 CO − 2 Cl − *n*CO (*n* = 0, 2)]$^+$. IR (KBr): ν(PO_2) = 971, 1070 cm^{-1}, ν(CO) = 1999, 2044 cm^{-1}. $C_{22}H_{28}Cl_4Fe_4O_8P_2\cdot 2CH_3CN$ (929.7): calcd. C 33.6, H 3.7, Cl 15.1; found C 33.1, H 3.9, Cl 14.3.

Acknowledgments

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[1] Selected examples: [1a] E. Lindner, S. Trad, S. Hoehne, H.-H. Oetjen, *Z. Naturforsch., Teil B* **1979**, *34*, 1203−1212 (and cit. ref.). [1b] W. V. Cicha, J. S. Haynes, K. W. Oliver, S. J. Rettig, R. C. Thompson, J. Trotter, *Can. J. Chem.* **1985**, *63*, 1055−1062. [1c] A. Bino, L. Sissman, *Inorg. Chim. Acta* **1987**, *128*, L21−L22. [1d] P. Betz, A. Bino, *Inorg. Chim. Acta* **1988**, *147*, 109−113. [1e] D. S. Bohle, H. Vahrenkamp, *Inorg. Chem.* **1990**, *29*, 1097−1099. [1f] S.-J. Liu, R. J. Staples, J. P. Fackler, Jr., *Polyhedron* **1992**, *11*, 2427−2430. [1g] M. McCann, E. Murphy, C. Cardin, M. Covery, *Polyhedron* **1993**, *12*, 1725−1731. [1h] C. M. Barnes, D. S. Bohle, S. K. Madsen, *Inorg. Chem.* **1994**, *33*, 6411−6414. [1i] N. S. Dean, L. M. Mokry, M. R. Bond, C. J. O'Connor, C. J. Carrano, *Inorg. Chem.* **1996**, *35*, 2818−2825. [1j] N. S. Dean, M. R. Bond, C. J. O'Connor, C. J. Carrano, *Inorg. Chem.* **1996**, *35*, 7643−7648.

[2] [2a] G. Effinger, W. Hiller, I.-P. Lorenz, *Z. Naturforsch., Teil B* **1987**, *42*, 1315−1327. [2b] I.-P. Lorenz, C. Klasen, S. Schmid, G. Beuter, *J. Organomet. Chem.* **1992**, *428*, 363−378. [2c] I.-P. Lorenz, C. Klasen, S. Schmid, *Z. Naturforsch., Teil B* **1993**, *48*, 705−712. [2d] I.-P. Lorenz, W. Pohl, H. Nöth, M. Schmid, *J. Organomet. Chem.* **1994**, *475*, 211−221. [2e] I.-P. Lorenz, W. Pohl, H. Nöth, M. Schmid, *Z. Naturforsch., Teil B* **1995**, *50*, 1485−1493. [2f] I.-P. Lorenz, W. Pohl, K. Polborn, *Chem. Ber.* **1996**, *129*, 11−13.

[3] I.-P. Lorenz, W. Pohl, H. Nöth, *Angew. Chem.* **1997**, *109*, 55−56; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 55−56.

[4] I.-P. Lorenz, P. Mürschel, W. Pohl, K. Polborn, *Chem. Ber.* **1995**, *128*, 413−416.

[5] M. Maier, PhD Thesis, University of Munich, **2001**.

[6] X-ray structure analyses: **1d:** $C_{38}H_{41}Cl_6Fe_5NO_8P_2$, M_r = 1193.6, purple crystals, 0.43 × 0.37 × 0.13 mm, monoclinic, space group $P2/c$, a = 14.501(2) Å, b = 8.938(2) Å, c = 18.017(3) Å, β = 92.999(14)°, Z = 2, V = 2332.0(7) Å^3, $\rho_{calcd.}$ = 1.700 Mg/m^3, μ = 1.979 mm^{-1}, $F(000)$ = 1204, diffractometer: Enraf−Nonius CAD4, Mo-K_α (λ = 0.71073 Å), T = 293(2) K, θ =2.26−23.96°, reflections collected 3804, independent reflections 3645 [R(int) = 0.0174], 2995 observed reflections [$I > 2\sigma(I)$], final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0294, $wR2$ = 0.0640, R indices (all data): $R1$ = 0.0426, $wR2$ = 0.0724, goodness-of-fit on F^2: 1.086, largest diff. peak and hole: 0.336 and −0.247 e·A^{-3}, absorption correction: semi-empirical from ψ-scans, max./min. transmission: 0.9991/0.8336, refinement method: full-matrix least squares on F^2, data/restraints/parameters: 3645/0/276. **2:** $C_{26}H_{34}Cl_4Fe_4N_2O_8P_2$, M_r = 929.69, deep purple crystals, 0.53 × 0.4 × 0.13 mm, triclinic, space group $P\bar{1}$, a = 9.592(2) Å, b = 9.622(2) Å, c = 11.944(3) Å, α = 82.29(2), β = 72.50(2), γ = 64.06(2)°, Z = 1, V = 945.4(4) Å^3, $\rho_{calcd.}$ =1.633 Mg/cm^{-3}, μ = 1.916 mm^{-1}, $F(000)$ = 470, diffractometer: Enraf−Nonius CAD4, Mo-K_α (λ = 0.71073 Å), T = 293(2) K, θ = 2.59−23.97°, reflections collected: 3150, independent reflections 2952 [R(int) = 0.0146], 2517 observed reflections [$I > 2\sigma(I)$], final R indices [$I > 2\sigma(I)$] $R1$ = 0.0343, $wR2$ = 0.0864, R indices (all data): $R1$ = 0.0439, $wR2$ = 0.0937, goodness-of-fit on F^2: 1.091, largest diff. peak and hole: 0.269 and −0.296 e·A^{-3}, absorption correction: semi-empirical from ψ-scans, max./min. transmission: 0.9995/0.7440, refinement method: full-matrix least squares on F^2, data/restraints/parameters: 2952/0/211. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112648 (**1d**) and -112647 (**2**). Copies of the data can be obtained free of charge on applicaton to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[7] Magnetic measurement of **2:** $C_{26}H_{34}Cl_4Fe_4N_2O_8P_2$: μ_B = 6.04; Θ = −58.44 K; we thank Dr. R. Hoffmann for the measurement.

[8] A. Durif in *The Chemistry of Inorganic Homo- and Heterocycles*, vol 2 (Eds.: I. Haiduc, D. B. Sowerby), Academic Press, London, **1987**, p. 659−679.

[9] I.-P. Lorenz, M. Maier, A. Schulz, paper in preparation.

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