*Journal of Organometallic Chemistry*, 243 (1983) 331–337
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# SYNTHESIS AND STRUCTURAL CHARACTERISATION OF PHOSPHIDO- AND CHLORO-BRIDGED DIIRON CARBONYLS

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(Received September 14th, 1982)

## Summary

Three crystalline compounds, $Fe(CO)_4PC_6H_5Cl_2$, $Fe_2(CO)_6PC_6H_5Cl_2$, and $Fe_2(CO)_6(PC_6H_5Cl)_2$ have been isolated from the reaction of phenyldichlorophosphane, $PC_6H_5Cl_2$ with diiron nonacarbonyl, $Fe_2(CO)_9$. The molecular structures of $Fe_2(CO)_6PC_6H_5Cl_2$ and $Fe_2(CO)_6(PC_6H_5Cl)_2$ have been determined by single crystal X-ray investigations.

## Introduction

It is well established that the complexes $L_nM(PRCl_2)(L_nM = (CO)_5Cr, C_5H_5(CO)_2Mn)$ undergo dehalogenation by $Fe_2(CO)_9$ to give a number of chemically interrelated mixed metal clusters [1–4]. In an investigation of the behavior of $Fe_2(CO)_9$ towards free dichlorophosphanes, the reaction of $Fe_2(CO)_9$ with $PC_6H_5Cl_2$ has been studied and the results are presented below.

## Experimental

$PC_6H_5Cl_2$ and $Fe_2(CO)_9$ were prepared by the usual methods [5,6]. Solvents were purified by standard techniques. Reactions were carried out under dry nitrogen. The IR spectra were recorded on Zeiss infrared spectrophotometer IMR-40 in $CaF_2$ cells using $CH_2Cl_2$ solutions. Bruker WP 80 FT and Varian CH 7 spectrometers were used to record the $^{31}P$ NMR and mass spectra, respectively.

### *Reaction of $PC_6H_5Cl_2$ with $Fe_2(CO)_9$*

A mixture of $Fe_2(CO)_9$ (3.64 g, 10 mmol), $PC_6H_5Cl_2$ (3.58 g, 20 mmol), and 75 ml toluene was heated slowly and stirred at 60°C for 2 h. It was then filtered to remove undissolved material, and the filtrate was chromatographed on a silica gel column.

$Fe(CO)_4PC_6H_5Cl_2$ obtained by eluting with pentane and recrystallisation from pentane, gave yellow crystals (0.95 g, 27%). Found: C, 33.96; H, 1.38; P, 9.10; Fe, 16.06. $C_{10}H_5PCl_2O_4Fe$ calcd.: C, 34.58; H, 1.44; P, 8.93; Cl, 20.46; Fe, 16.14%. IR($\nu$(CO)): 2071(s), 2004(s), 1972(vs), 1965(w) $cm^{-1}$. $^{31}P$ FT NMR: $\delta$ 211.7 ppm (Acetone-$d_6$, ext., $H_3PO_4$).

$Fe_2(CO)_6PC_6H_5Cl_2$ obtained by eluting with 10/1 pentane/toluene and recrystallisation from the same solvent mixture gave red-brown crystals (0.48 g, 11%). Found: C, 30,97; H, 1.06; P, 6.92; Cl, 15.80; Fe, 24.37. $C_{12}H_5PCl_2O_6Fe_2$ calcd.: C, 31.37; H, 1.09; P, 6.75; Cl, 15.47; Fe, 24.40%. IR($\nu$(CO)$^{-1}$): 2086(s), 2048(vs), 2020(s), 2001(s) $cm^{-1}$. $^{31}P$ FT NMR: $\delta$ 222.6 ppm (Acetone-$d_6$, ext., $H_3PO_4$).

$Fe_2(CO)_6(PC_6H_5Cl)_2$ obtained by eluting with 5/1 pentane/toluene and recrystallisation from the same solvent mixture gave orange-yellow crystals (0.3 g, 5%). Found: C, 37.85; H, 1.68; P, 11.12; Cl, 12.82; Fe, 19.71. $C_{18}H_{10}P_2Cl_2O_6Fe$ calcd.: C, 38.09; H, 1.76; P, 10.93; Cl, 12.52; Fe, 19.75%. IR($\nu$(CO)): 2073(s), 2036(vs), 2016(s), 1990(s) $cm^{-1}$. $^{31}P$ FT NMR: $\delta$ 245.2 ppm (Acetone-$d_6$, ext. $H_3PO_4$).

## Results and discussions

$Fe_2(CO)_9$ and $PC_6H_5Cl_2$ (in 1/2 molar ratio) were brought together in toluene. No significant reaction occurred at room temperature, and it was found that a temperature of 60°C * is best for formation of the compounds. The compounds $Fe(CO)_4PC_6H_5Cl_2$ (yellow), $Fe_2(CO)_6PC_6H_5Cl_2$ (red-brown) and $Fe_2(CO)_6$-$(PC_6H_5Cl)_2$ (orange-yellow) were separated by column chromatography (silica gel) and purified by recrystallisation.

Elemental analyses and (mass spectrometric) molecular weights agree well with the formulations. Fe–CO infrared stretching frequencies are found to be well within the range reported for some similar compounds [7] and does not indicate the presence of any CO group bridging two Fe atoms (see Experimental).

### *X-Ray crystallographic investigations* **

$Fe_2(CO)_6PC_6H_5Cl_2$ (A). Well-shaped dark red-brown crystals were obtained by keeping the pentane/toluene (5/1) solution of the compound at −20°C. The structure was solved by the heavy atom method [8] and refined to $R_1 = 0.049$ on 1533 significant independent reflections, $T$ 26.5°C. The crystal has the triclinic form, space group $P\bar{1}$ with $a$ 936.0, $b$ 953.8, $c$ 1084.4 pm; $\alpha$ 115.6, $\beta$ 104.2, $\gamma$ 93.9°; $Z = 2$. The structural parameters are presented in Tables 1 and 2.

$Fe_2(CO)_6(PC_6H_5Cl)_2$ (B). Suitable crystals were obtained by chilling a pentane/toluene (1/1) solution of the compound at −20°C. The structure was solved by the heavy atom method [8] and refined to $R_1 = 0.051$ on 2777 significant independent reflections, $T$ −30°C. The compound crystallises in triclinic form, space group $P\bar{1}$ with $a$ 968.7, $b$ 1283.7, $c$ 1914.5 pm; $\alpha$ 114.16, $\beta$ 100.19, $\gamma$ 92.74°; $Z = 4$. The structural parameters are shown in Tables 3 and 4.

Perspective views of the molecular structures of compounds A and B are shown in Fig. 1 and Fig. 2, respectively. The overall geometries are analogous to compounds of the general stoichiometry $Fe_2(CO)_6X_2$, where X is a bridging group [8,10]. The

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* Optimal conditions 2 h at 60°C as shown by $^{31}P$ NMR spectroscopy. The reaction producing all three compounds started around 50°C with decomposition towards 70°C. Decomposition also occurred after 3–4 h at 60°C.

** Tables of observed and calculated structure factors can be obtained from the author.

TABLE 1. FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS FOR COMPOUND A [a,b]

| Atom | $x/a$ | $y/b$ | $z/c$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Fe(1) | 0.0363(1) | 0.6663(1) | 0.3139(1) | |
| Fe(2) | 0.3016(1) | 0.6068(1) | 0.3575(1) | |
| Cl(1) | 0.1197(2) | 0.4876(2) | 0.1386(2) | |
| Cl(2) | 0.3138(2) | 1.0350(2) | 0.5026(2) | |
| P | 0.2400(2) | 0.8128(2) | 0.3308(2) | |
| C(1) | 0.2607(8) | 0.8532(8) | 0.1873(7) | 3.21(1) |
| C(2) | 0.3559(9) | 0.7857(8) | 0.1108(8) | 4.77(2) |
| C(3) | 0.3711(10) | 0.8227(10) | 0.0020(9) | 5.53(2) |
| C(4) | 0.2934(9) | 0.9257(9) | −0.0275(8) | 5.19(2) |
| C(5) | 0.1995(10) | 0.9947(10) | 0.0494(9) | 5.20(2) |
| C(6) | 0.1818(8) | 0.9585(8) | 0.1581(8) | 4.27(2) |
| C(11) | −0.0652(8) | 0.5070(9) | 0.3236(7) | 3.65(2) |
| C(12) | 0.0404(8) | 0.8026(8) | 0.4867(7) | 3.09(1) |
| C(13) | −0.1131(9) | 0.7207(9) | 0.2174(8) | 4.28(2) |
| O(11) | −0.1281(6) | 0.4068(6) | 0.3353(6) | 5.26(1) |
| O(12) | 0.0461(6) | 0.8903(6) | 0.6019(5) | 4.75(1) |
| O(13) | −0.2108(7) | 0.7581(6) | 0.1574(6) | 6.13(1) |
| C(21) | 0.3883(8) | 0.7233(8) | 0.1574(6) | 4.0(2) |
| C(22) | 0.4663(9) | 0.5757(9) | 0.3074(8) | 4.37(2) |
| C(23) | 0.2586(8) | 0.4369(8) | 0.3817(8) | 3.90(2) |
| O(21) | 0.4442(6) | 0.8000(6) | 0.6634(6) | 5.58(1) |
| O(22) | 0.5749(7) | 0.5550(7) | 0.2717(6) | 6.40(1) |
| O(23) | 0.2276(7) | 0.3314(7) | 0.4019(6) | 6.09(1) |

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 2.85(5) | 2.78(5) | 2.42(5) | 0.73(4) | 0.81(4) | 1.10(4) |
| Fe(2) | 3.05(5) | 2.81(5) | 2.66(5) | 1.03(4) | 0.81(4) | 1.23(4) |
| Cl(1) | 4.37(10) | 3.61(9) | 2.33(8) | 1.06(7) | 0.79(7) | 0.71(7) |
| Cl(2) | 4.29(9) | 2.85(9) | 3.57(8) | 0.48(7) | 1.21(7) | 1.04(7) |
| P | 3.15(9) | 2.66(8) | 2.78(8) | 0.89(7) | 1.13(7) | 1.20(7) |

[a] Estimated standard deviations (esd) of the last digit are in parentheses. [b] The anisotropic temperature factor $T = \exp[-1/4(B_{11}h^2a^{\star 2} + \ldots + 2B_{12}hka^{\star}b^{\star} + \ldots)]$; $B_{ij}$ in Å$^2$.

TABLE 2. BOND DISTANCES (Å) AND BOND ANGLES (deg.) FOR COMPOUND A [a]

| | | | |
|---|---|---|---|
| Fe(1)–Fe(2) | 2.56(0) | Fe(2)–Cl(1) | 2.29(0) |
| Fe(1)–Cl(1) | 2.29(0) | Fe(2)–P | 2.20(0) |
| Fe(1)–P | 2.20(1) | Fe(2)–C(21) | 1.73(1) |
| Fe(1)–C(11) | 1.80(1) | Fe(2)–C(22) | 1.76(0) |
| Fe(1)–C(12) | 1.75(1) | Fe(2)–C(23) | 1.79(1) |
| Fe(1)–C(13) | 1.78(1) | P–C(1) | 1.81(1) |

| | | | |
|---|---|---|---|
| Fe(1)–Fe(2)–Cl(1) | 56.0(1) | Fe(2)–Fe(1)–P | 54.4(1) |
| Fe(2)–Fe(1)–Cl(1) | 56.0(1) | Fe(1)–Fe(2)–P | 54.5(1) |
| Cl(1)–Fe(1)–P | 78.1(1) | Fe(1)–Cl(1)–Fe(2) | 68.0(1) |
| Cl(1)–Fe(2)–P | 78.2(1) | Fe(1)–P–Fe(2) | 71.1(1) |
| P–Fe(1)–C(11) | 154.8(3) | Fe(1)–P–Cl(2) | 117.4(1) |
| P–Fe(1)–C(12) | 90.8(3) | Fe(2)–P–Cl(1) | 123.3(3) |
| P–Fe(1)–C(13) | 103.6(3) | Fe(2)–P–C(1) | 124.4(3) |

[a] Esd values of the last digit are in parentheses.

TABLE 3

FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC TEMPARATURE FACTORS FOR COMPOUND B [a,b]

| Atom | $x/a$ | $y/b$ | $z/c$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Fe(1) | 0.3864(2) | 0.3994(1) | 0.6994(1) | |
| Fe(2) | 0.6211(2) | 0.3398(1) | 0.6469(1) | |
| P(1) | 0.5973(4) | 0.5011(2) | 0.7435(1) | |
| P(2) | 0.5185(4) | 0.2745(2) | 0.7175(1) | |
| Cl(1) | 0.6179(4) | 0.6527(2) | 0.7309(1) | |
| Cl(2) | 0.4392(4) | 0.1019(2) | 0.6646(1) | |
| C(11) | 0.2543(15) | 0.2857(9) | 0.6337(6) | 2.53(2) |
| C(12) | 0.3294(15) | 0.4848(9) | 0.6482(6) | 2.67(2) |
| C(13) | 0.3035(16) | 0.4534(9) | 0.7784(6) | 3.38(2) |
| O(11) | 0.1682(12) | 0.2102(7) | 0.5881(5) | 4.71(2) |
| O(12) | 0.2859(10) | 0.5387(6) | 0.6148(4) | 3.46(2) |
| O(13) | 0.2515(12) | 0.4950(7) | 0.8323(5) | 4.48(2) |
| C(21) | 0.7989(18) | 0.3155(9) | 0.6662(6) | 2.53(2) |
| C(22) | 0.6337(15) | 0.4157(8) | 0.5870(6) | 2.45(2) |
| C(23) | 0.5553(2) | 0.2079(8) | 0.5607(6) | 2.44(2) |
| O(21) | 0.9156(13) | 0.3003(7) | 0.6832(5) | 4.31(2) |
| O(22) | 0.6442(10) | 0.4620(6) | 0.5476(4) | 3.22(2) |
| O(23) | 0.5120(10) | 0.1225(6) | 0.5054(4) | 2.99(2) |
| C(51) | 0.8315(16) | 0.5246(9) | 0.8593(6) | 2.70(2) |
| C(52) | 0.9043(16) | 0.5626(9) | 0.9374(6) | 3.35(2) |
| C(53) | 0.8460(16) | 0.6301(9) | 0.9973(6) | 2.60(2) |
| C(54) | 0.7169(17) | 0.6611(9) | 0.9835(6) | 3.07(3) |
| C(55) | 0.6398(15) | 0.6250(9) | 0.9069(6) | 2.64(2) |
| C(56) | 0.6982(14) | 0.5543(8) | 0.8441(5) | 2.22(2) |
| C(61) | 0.7182(15) | 0.2249(8) | 0.8178(5) | 2.37(2) |
| C(62) | 0.7870(17) | 0.2323(9) | 0.8917(6) | 3.08(3) |
| C(63) | 0.7327(16) | 0.2916(9) | 0.9553(6) | 2.82(2) |
| C(64) | 0.6209(16) | 0.3499(9) | 0.9519(6) | 2.95(2) |
| C(65) | 0.5540(15) | 0.3447(8) | 0.8791(6) | 2.55(2) |
| C(66) | 0.6016(14) | 0.2812(8) | 0.8118(5) | 1.94(2) |

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Fe(1) | 1.1(1) | 1.6(1) | 1.6(1) | −0.2(1) | 0.0(1) | 0.7(1) |
| Fe(2) | 1.4(2) | 1.4(1) | 1.6(1) | −0.3(1) | 0.3(1) | 0.6(1) |
| P(1) | 1.5(3) | 1.5(1) | 1.8(1) | −0.2(1) | −0.0(1) | 0.6(1) |
| P(2) | 1.4(3) | 1.5(1) | 1.8(1) | −0.2(1) | 0.1(1) | 0.8(1) |
| Cl(1) | 2.8(3) | 1.4(1) | 2.8(1) | −0.3(1) | 0.2(1) | 0.9(1) |
| Cl(2) | 2.1(3) | 1.6(1) | 2.1(1) | −0.7(1) | 0.2(1) | 0.6(1) |

[a] Esd values of the last digit are in parentheses. [b] The anisotropic temperature factor $T = \exp[-1/4(B_{11}h^2a^{\star 2} + \ldots + \ldots 2B_{12}hka^{\star}b^{\star} + \ldots)]$; $B_{ij}$ in Å$^2$.

interesting feature of compound A is the presence of two different bridging groups, one of which is a chloro group.

Fe–Fe distances of 2.56(0) and 2.67(0) Å for A and B, respectively, and Fe–P distances of 2.20(0) Å for both A and B are comparable with those for similar complexes (Fe–Fe distances range from 2.40 to 2.67 Å and Fe–P distances range

TABLE 4

BOND DISTANCES (Å) AND BOND ANGLES (deg.) FOR COMPOUND B [a]

| | | | |
|---|---|---|---|
| Fe(1)-Fe(2) | 2.67(0) | P(1)-Cl(1) | 2.06(0) |
| Fe(1)-P(1) | 2.20(0) | P(2)-Cl(2) | 2.06(0) |
| Fe(1)-P(2) | 2.20(0) | P(1)-C(56) | 1.82(1) |
| Fe(2)-P(1) | 2.20(0) | P(2)-C(66) | 1.81(1) |
| Fe(2)-P(2) | 2.20(0) | C(11)-O(11) | 1.17(1) |
| Fe(1)-C(11) | 1.76(1) | C(12)-O(12) | 1.17(1) |
| Fe(1)-C(12) | 1.79(1) | C(13)-O(13) | 1.17(1) |
| Fe(1)-C(13) | 1.74(1) | C(21)-O(21) | 1.17(2) |
| Fe(2)-C(21) | 1.77(2) | C(22)-O(22) | 1.15(1) |
| Fe(2)-C(22) | 1.79(1) | C(23)-O(23) | 1.16(1) |
| Fe(2)-C(23) | 1.80(1) | | |
| Fe(2)-Fe(1)-P(1) | 52.6(1) | Fe(2)-P(1)-C(56) | 124.6(4) |
| Fe(2)-Fe(1)-P(2) | 52.7(1) | Fe(1)-P(2)-Cl(2) | 119.4(2) |
| Fe(1)-Fe(2)-P(1) | 52.6(1) | Fe(2)-P(2)-Cl(2) | 116.2(2) |
| Fe(1)-Fe(2)-P(2) | 52.5(1) | Fe(1)-P(2)-C(66) | 125.2(4) |
| P(1)-Fe(1)-P(2) | 78.7(1) | Fe(2)-P(2)-C(66) | 125.4(4) |
| P(1)-Fe(2)-P(2) | 78.6(1) | Fe(1)-C(11)-O(11) | 178.8(1) |
| Fe(1)-P(1)-Fe(2) | 74.7(1) | Fe(1)-C(12)-O(11) | 177.8(1) |
| Fe(1)-P(2)-Fe(2) | 74.7(1) | Fe(1)-C(13)-O(13) | 177.5(2) |
| Fe(1)-P(1)-Cl(1) | 117.0(2) | Fe(2)-C(21)-O(21) | 177.0(2) |
| Fe(2)-P(1)-Cl(1) | 119.0(2) | Fe(2)-C(22)-O(22) | 179.0(1) |
| Fe(1)-P(1)-C(56) | 124.7(4) | Fe(2)-C(23)-O(23) | 180.3(1) |

[a] Esd values of the last digit are in parentheses.

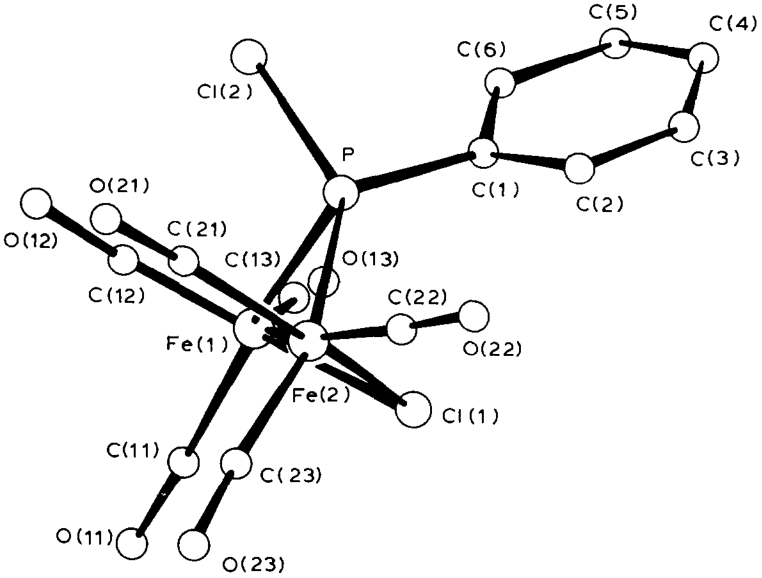

Fig. 1 Perspective drawing of the molecule, $Fe_2(CO)_6PC_6H_5Cl_2$.

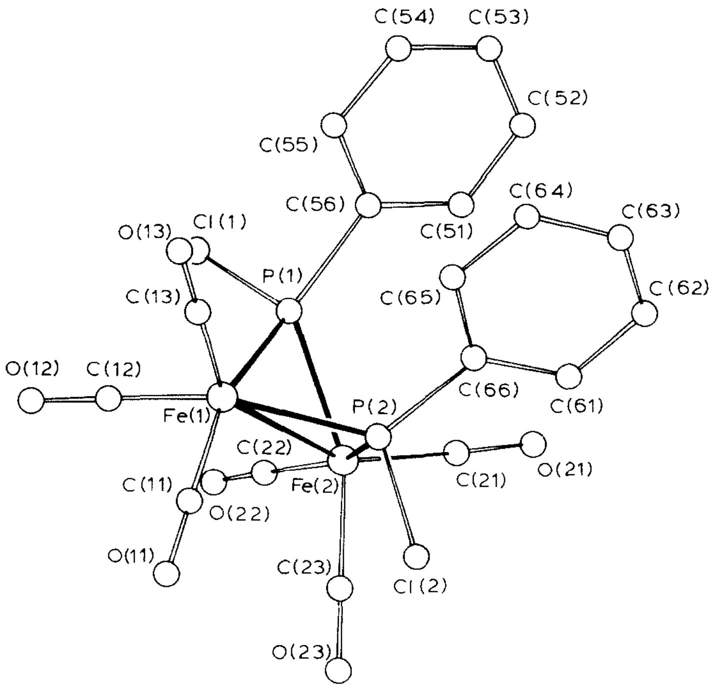

Fig. 2 Perspective drawing of the molecule, $Fe_2(CO)_6(PC_6H_5Cl)_2$.

from 2.22 to 2.30 Å) [10]. The two Fe–Cl distances for compound A are exactly the same, 2.29(0) Å, the value is a little larger than the radius sum, but this probably has little significance. Equal Fe–Cl and Fe–P distances suggest an almost $C_s$ symmetry for both the molecules A and B.

The Fe–C(carbonyl) distances are typical to other iron carbonyl complexes. But in the case of A it is noteworthy that the Fe–C(carbonyl) distances reveal a *trans*-influence such that Fe–C(carbonyl) distances *trans* to the bridging chloro group (average 1.74(0) Å) are shorter than the other Fe–C(carbonyl) distances (average 1.78(0) Å). Such effects have been observed in other cases [10,11].

The angles P–Fe(1)–Cl(1) (78.1(1)°), P–Fe(2)–Cl(1) (78.2(1)°), Fe(1)–P–Fe(2) (71.1(1)°), Fe(1)–Cl(1)–Fe(2) (68.0(1)°) (for compound A) and P(1)–Fe(1)–P(2) (78.7(1)°), P(1)–Fe(2)–P(2) (78.6(1)°), Fe(1)–P(1)–Fe(2) (74.7(1)°), Fe(1)–P(2)–Fe(2) (74.7(1)°) (for compound B) agree well with those noted in other $Fe_2(CO)_6X_2$ complexes. The fact that the smaller Fe–P/Cl–Fe angles are below the tetrahedral value may be due to the strain imposed by the Fe–Fe bond. The fact that in compound A the Fe–P–Fe angle is greater than the Fe–Cl–Fe angle can be attributed to the greater length of the Fe–Cl bond.

## Acknowledgement

The author thanks Professor Dr. G. Huttner, Lehrstuhl für Synthetische Anorganische Chemie, Universität Konstanz for encourangement, discussions and for providing all the laboratory facilities where this work had been carried out; Dr.

J. von Seyerl for structural measurements and Miss R. Naserke for elemental analyses. Thanks are also due to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support; and to Professor Dr. H. Vahrenkamp, Lehrstuhl II, Chemisches Laboratorium, Universität Freiburg for his interest.

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